Integrated Approach to Chemical Process Flowsheet Synthesis

By

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CERTIFICATE OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this thesis, that the original work is my own except as specified in acknowledgements or in footnotes, and that neither the thesis nor the original work contained therein has been submitted to this or any other institution for a degree.

………………………………………….… (Signed)

23rd June 2008

To my Parents and Family

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Abstract

Chemical process synthesis is an open ended step of process design as it deals with the problem of how to develop and integrate the chemical process flowsheet. Over the past four decades, very few systematic procedures have been proposed for the rigorous synthesis of complete chemical process flowsheets. Mathematical design and heuristics from experience of past processes are the two main methods usually employed in process synthesis. Most approaches for new designs use heuristics based on studying reaction and separation systems in isolation. This thesis discusses the development of a new process synthesis systematic procedure and software that integrates a knowledge based system with Aspen HYSYS process simulator, HYSYS optimizer, Aspen Icarus economic evaluator, and databases, utilising knowledge from existing industrial processes to obtain design rules. The proposed generic superstructure for the synthesis and optimization of reaction-separation-recycle systems has been validated. To account for the non-ideal behaviour of reactors, modular simulation is used and an example of the approach is illustrated for a fluidized bed reactor. Preliminary work in customizing Aspen HYSYS to simulate new unit operation has been illustrated. A Visual Basic for Application (VBA) programming code has been developed to link the integrated knowledge based system (IKBS) to Aspen HYSYS.

The prototype IKBS has been applied for the selection of reactor-separator-recycle systems for ethylene oxide, ethylene glycol, acetic acid and cumene manufacturing processes as case studies. A wide range of chemical reactors and separators were considered during the selection process and then elimination occurs at different levels leading to the best alternatives being selected for simulation, optimization and economic evaluation in the second phase of the IKBS for future development. The suggested alternative reactor-separator-recycle systems by the IKBS include currently used processes in addition to novel and recommended reactors/separators in industrial research. The proposed integrated knowledge based approach to chemical process flowsheet synthesis is expected to yield a cost effective design methodology for the petrochemical industry.

Nomenclature

$\mathbf{A}$	cross-sectional area (m^2)
$\mathbf{A_b}$	bubble phase cross sectional area (m^2)
$\mathbf{A_e}$	emulsion phase cross sectional area (m^2)
$\mathbf{A_f}$	constant of dynamic two-phase model
$\mathbf{a_i}$	interphase area per unit volume (m^{-1})
$\mathbf{A_o}$	pre-exponential factor (variable)
$\mathbf{As}$	particle surface area (m^2)
$\mathbf{A_{void\text{-}b}}$	constant of dynamic two-phase model
$\mathbf{A_{void\text{-}e}}$	constant of dynamic two-phase model
$\mathbf{C_{Ab}}$	concentration of reactant A in stage i bubble phase ($kmol/m^3$)
$\mathbf{C_{Ae}}$	concentration of reactant A in stage i emulsion phase ($kmol/m^3$)
$\mathbf{C_p}$	heat capacity (kJ/kmol K)
$\mathbf{D_{AB}}$	diffusion coefficient (m^2/s)
$\mathbf{D_b}$	bubble mean diameter (m)
$\mathbf{D_{bm}}$	bubble maximum diameter (m)
$\mathbf{D_{bo}}$	bubble initial diameter (m)
$\mathbf{d_p}$	particle diameter (m)
$\mathbf{D_r}$	reactor diameter (m)
$\mathbf{\Delta Hc}$	net heat of combustion (kJ/kmol)
ΔH_R	heat of reaction (kJ/kmol)
$\mathbf{E}$	activation energy (J/mol)
$\mathbf{f}$	emulsion phase fraction
$\mathbf{F}$	reactor feed stream flowrate (kmol/hr)
$\mathbf{F_{FT}}$	fresh feed rate (kmol/hr)
$\mathbf{g}$	gravity acceleration (m/s^2)
$\mathbf{h}$	bed height (m)
$\mathbf{H}$	reactor height (m)
$\mathbf{Ha}$	Hatta number (-)
$\mathbf{h_{mf}}$	bed height at minimum fluidization condition (m)
$\mathbf{J}$	dimensionless number (-)
$\mathbf{k}$	reaction constant (variable)
$\mathbf{K_A}$	adsorption coefficient of A
$\mathbf{K_{eq}}$	equilibrium constant
$\mathbf{K_{bc}}$	bubble to cloud mass transfer coefficient (s^{-1})

K_{be}	bubble to emulsion mass transfer coefficient (s^{-1})
K_{ce}	cloud to emulsion mass transfer coefficient (s^{-1})
LFL	Lower Flammability Limits
N	total number of stages
N_D	number of orifices in unit area of grid
N_h	number of grid holes
P	total pressure (k Pa)
p	partial pressure (k Pa)
Q	volumetric flowrate (m^3/s)
Q_R	reactor heat load (kJ/hr)
R	ideal gas law constant (J/mol K)
r_A	reaction rate based on component A (variable)
Re	Reynolds number
T	temperature (K)
$T_{R,in}$	reactor inlet temperature (K)
$T_{R,out}$	reactor outlet temperature (K)
U_b	rise bubble velocity in a bubbling bed (m/s)
u_{br}	single bubble rise velocity (m/s)
U_e	emulsion gas velocity (m/s)
U_{mf}	minimum fluidization velocity (m/s)
U_o	superficial gas velocity (m/s)
U_t	terminal velocity (m/s)
UFL	Upper Flammability Limits
y_i	mole fraction of species i in the vapour
V	volume of reactant/product mixture contained in the reactor (m^3)
$V_{(i)}$	volume of the i^{th} stage (m^3)
$V_{b(i)}$	bubble phase volume (m^3)
$V_{CSTR(i)}$	CSTR volume (m^3)
$V_{e(i)}$	emulsion phase volume (m^3)
$V_{PFR(i)}$	PFR volume (m^3)
V_t	total volume of stages (m^3)
W	catalyst mass (kg)
X	conversion
x_i	mole fraction of species i in the liquid

Greek Symbols

α	reaction partial order with respect to A
ε_b	bubble phase voidage
ε_e	emulsion phase voidage
ε_g	average void fraction of the bed during fluidization
ε_{mf}	minimum fluidization voidage
γ	solids dispersed in the emulsion
η	effectiveness factor
δ	bubble phase fraction
μ	gas viscosity (Pa s)
ρ	density (kg/m^3)
σ	number of active sites
ϕ	Thiele modulus
ψ	particle Sphericity

Subscripts

b	bubble
c	cloud
e	emulsion
g	gas
p	particle

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Chapter 1

Introduction

Innovation in chemical process design is a key issue in today's petrochemical business environment. Process synthesis is an important part of the overall chemical innovation process which starts with the identification of the process needs prior to construction and operation of the process plant. Conceptual design is the initial stage of chemical process design where the conceptual synthesis of a process flowsheet is developed. Chemical process synthesis is a highly important field of activity in industry and academia as it deals with the problem of how to develop and integrate flowsheets for chemical product manufacturing processes.

There are three basic tasks in process synthesis, the representation of the problem, which generates all possible alternatives, the evaluation of all investigated alternatives and the development of a strategy to search for the best design alternative (Arva and Csukas 1988; Westerberg 1989; Grossmann, 1996). The initial stage of process synthesis comes from the discovery of a sequence of chemical reactions linking available raw materials to more valuable products, and it ends with the development of alternative flowsheets for the commercial processes.

Douglas (1988) indicated that for new process, the chances of commercialization at research stage are only about 1%, whereas at the development stage they are about 10 to 25%, and at the pilot plant stage they are about 40 to 60%. Figure 1.1, illustrates the economic incentives of a plant project, starting from conceptual design and ending with the construction and commissioning. According to Dimian and Bildea (2008), conceptual design takes about 2% of the total project cost, but it may contribute with more than 30% in cost reduction opportunities. In the detailed design phase, the cost of engineering rises to 12%, but saving opportunities goes down to 15%. In contrast, the cost of procurement and construction are more than 80%, but the savings are below 10%. At the commissioning stage the total project cost is fixed. Therefore, establishing a hierarchy of design with short cut calculations to screen the alternatives can be useful at the early stages of process design.

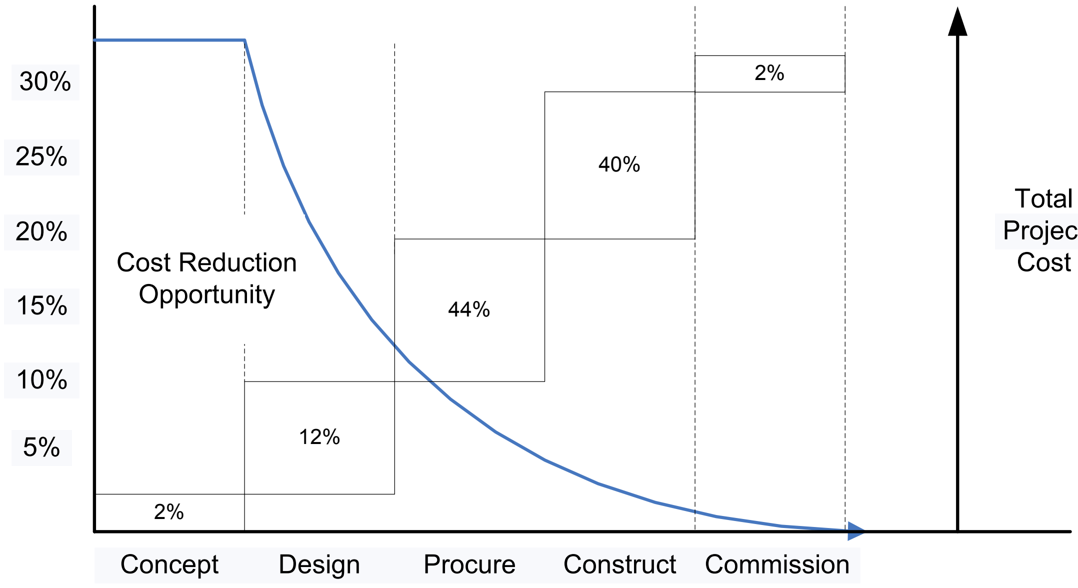


Figure 1.1: Economic incentives in a project. (adapted from Dimian and Bildea, 2008)

Total process flowsheet synthesis is an open ended problem as it takes into account a large number of alternatives and constraints of technical, economical, chemistry, safety and environmental nature which are often contradictory. According to Douglas (1988), in chemical flowsheet synthesis problems there are 10^4-10^9 alternative flowsheets which include choices of the process equipment configuration and the interactions between this equipment. Another challenge is the interaction between the reaction and separation systems. Ideally, the assessment of a separation system should be done in the context of the total system (Smith, 2005). The goal of process engineers it to find among the large number of alternative flowsheets, the least expensive one and to evaluate whether or not this alternative is profitable. A synthesis approach can utilise the availability of effective design methods aided by powerful simulation tools and other third party software for flowsheet optimization, sizing and cost estimation (Dimian and Bildea, 2008).

Since the early work on the synthesis of heat exchanger networks by Rudd (1968), much research has been conducted based on the systematic generation of a flowsheet such as the work by Kirkwood (1987) and Han (1994), evolutionary modification such as the work by Lu and Motard (1985), and superstructure optimization such as the work by Linke (2001); Montolio-Rodriguez et al. (2007). Conceptual design methods are currently used for retrofit design of existing processes and in the innovation process. Due to the fact that process synthesis problems are by nature combinatorial and open ended, a number of different approaches have been proposed.

The two main approaches for process synthesis are heuristic methods, which consist of a series of heuristic rules to screen process alternatives, and the mathematical methods which rely on optimization techniques. When only heuristics are used, optimal design is not guaranteed and the method is limited to the current state of knowledge. The mathematical programming methods restrict design considerations to the proposed superstructure and only limited size problems can be handled. Based on the previous research efforts in process synthesis, existing approaches mostly use heuristics based on the study of reactors and separation systems in isolation. Therefore, the synthesis of a total process flowsheet using a practical method has not yet been fully investigated.

This research work has been structured around two themes,

1- The development of a systematic procedure that can analyse a wide range of petrochemical manufacturing processes using basic or detailed input information to generate several good alternative process flowsheets corresponding to different design decisions.

2- The development of prototype software that can provide automation of the synthesis procedure to exploit interactions between reaction and separation systems utilising third-party software.

The aim of this research is to develop an Integrated Knowledge Based System (IKBS) for the synthesis of a chemical process flowsheet. The developed integrated system should be able to synthesise reactor-separator-recycle systems, generate and simulate different alternative process flowsheets at several levels of complexity. The proposed flowsheets can ultimately be evaluated in future work to determine the near-optimal design conditions, size process unit operations and, perform economic evaluation.

The objectives of this research are to:

- Propose a systematic approach that integrates knowledge based systems with third-party process simulators, flowsheet optimizers and economic evaluators.
- Develop a generic superstructure for the synthesis and optimization of reaction-separation-recycle systems.
- Develop software that implements the proposed systematic procedure to synthesise multiple and novel reactor-separator-recycle systems for petrochemical processes.
- Incorporate databases to obtain information about the species involved in the process such as physical properties, azeotropes, dissociation constants, solvents, adsorbing agents, prices, and safety and environmental impacts.
- Conduct modular simulation of technical reactors to account for non-ideal behaviour.
- Validate software synthesis results by using existing commercial processes and industrial research.

1.1 Structure of the Thesis

The thesis extends over eight chapters. The first two chapters introduce the research problem and the previous efforts to tackle it. The third and forth chapters present the structure and the framework for the integrated knowledge based system for chemical process flowsheet synthesis. The fifth and sixth chapters discuss the reactor and separator-recycle systems synthesis detailed procedures. The seventh chapter demonstrates the application of the proposed systematic procedure. The work is concluded in chapter eight. A brief summary on the subsequent chapters is given here.

Chapter 2 reviews the previous work in the area of chemical process synthesis as one of the most important areas within chemical process design. The two main methods of process synthesis, the heuristics and mathematical programming are discussed with an extensive review of the literature. In the chapter, the previous systematic procedures for the synthesis of a total process flowsheet are discussed. It also discusses the main previous research contributions towards chemical reactor selection and the main previous work in the area of separation systems synthesis.

Chapter 3 discusses the structure of the proposed integrated knowledge based system. The developed software integrates a knowledge based system with third party software and databases. The integrated system utilizes a database at an early stage of the synthesis to provide the required physical properties, prices, and safety and environmental impacts of the chemicals used in the process. It uses the Aspen HYSYS process simulator to calculate the mass and energy balances, which are required for the flowsheet optimization by HYSYS Optimizer, sizing and economic evaluation. A Visual Basic for Application (VBA) program has been written to link Aspen HYSYS simulator with the knowledge based system in Excel.

Chapter 4 discusses the proposed generic representation framework for chemical process flowsheet synthesis. The decision hierarchy generates design alternatives for process synthesis using a combination of qualitative and quantitative knowledge. The systematic procedure represents the levels of synthesis, such as collecting the input/output information, the economic potential determination, safety and environmental evaluation, the synthesis of the reactor-separator-recycle systems, and flowsheet simulation, optimization, sizing and economic evaluation to propose alternative process flowsheets. The optimization of chemical process flowsheets using HYSYS Optimizer is also discussed. The optimized flowsheet sizing and preliminary economic evaluation using the Aspen Icarus process evaluator is discussed as a final step of the overall synthesis of a chemical process flowsheet. A generic superstructure of reaction-separation-recycle systems is developed to create a unified representation of a generic flowsheet which includes conventional and novel combinations of system units and design configurations.

Chapter 5 focuses on the detailed synthesis of the chemical reactor system strategy presented in Chapter 4. The work covers the levels of reactor system synthesis and the development of decision-making criteria for the exploration and comparative evaluation of different reactor systems and process alternative options. The procedure describes the interaction with separation systems at different synthesis levels. In this technique, decision-making criteria are examined for validity and applicability in the case studies reported in Chapter 7. Chapter 5 also illustrates the modular simulation of key technical reactors such as the fluidized bed reactor using the proposed generic superstructure.

Chapter 6 addresses the synthesis of separation-recycle systems in a systematic procedure. Output from the reactor system and general information provided by the user are used as input information to analyse the separation processes. Databases are used to provide the key physical properties and select the mass separation agents. A database also lists all possible azeotropes of mixtures. The procedure demonstrates the integration between reactor system synthesis level and separation-recycle systems synthesis. It also shows the interaction with flowsheet optimization, sizing and economic evaluation which eventually leads to the proposal of a process flowsheet. It also shows how the simulation of the generic flowsheet is used during the synthesis of the separation-recycle systems.

Chapter 7 illustrates and validates the use of the proposed synthesis framework. The work presents the implementation of the total flowsheet synthesis using a number of case studies from a wide range of petrochemical applications. The selection of processes was constrained by the problem of availability of sufficient design and technology data, and the diversity of reaction and separation conditions. Case studies include ethylene oxide, ethylene glycol, cumene and acetic acid manufacturing processes. These case studies can be useful to identify any new heuristics, and to investigate if reasonable base case flowsheets can be generated.

Chapter 8 concludes the work and discusses the merits and limitation of the developed chemical process synthesis software and suggests ideas for future research, and further development.

Chapter 2

Chemical Process Synthesis Approaches

2.1 Introduction

Chemical process design is a complex activity carried out by a team of professionals from different disciplines. The design decisions are based on a combination of synthesis, analysis, and evaluation of process alternatives. The conceptual design of a chemical process is an early stage of process design, where the conceptual synthesis of alternative process flowsheets is developed. Process synthesis is the step in process design where the alternative process units and their interconnections are determined. Synthesis is a generation step of process design and act of selecting the best alternatives.

As noted by Arva and Csukas (1988); Westerberg (1989); Grossmann, (1996), there are three basic tasks in process synthesis, the first step is the representation of the problem which generates all possible alternatives. In this step, all process structures including all the acceptable unit operations and connections are considered. This is usually done by constructing flowsheets that include all the major alternative process equipment. The second step is the evaluation of all investigated alternatives. In this step the assignment of all variables representing the possible states of the processes take place. An algebraic system, representing a process model, and consisting of equality and inequality constraints acting on the process variables together with some objective function to be optimized are constructed. The third step is the development of a strategy to search for the best design alternative. In this step, the optimization task is accomplished, and the results are analyzed. Some difficulties may accompany these problems, such as the great number of possible variants, formalisation of contradictory constraints and human knowledge considerations.

Over the past four decades, chemical process synthesis has been a highly important field of activity in industry and academia as it is used for retrofit design of existing processes as well as in the innovation process (Harmsen, 2004). Furthermore, conceptual design takes up to 20% of the total cost of developing a new commercial process (Douglas, 1988).

Early work in process synthesis research dealt with the synthesis of heat exchanger networks as in Rudd (1968) and Masso and Rudd (1969). They described a heuristic approach for building a heat exchange network fixing one exchanger at a time. In the late sixties, Rudd and co-workers were the first team to create a computer programme that used a systematic approach for process synthesis. The developed program was called Adaptive Initial DEsign Synthesiser (AIDES) (Rudd 1968; Siirola and Rudd 1971; Siirola et al. 1971; Powers 1972; Rudd et al. 1973). Their programme was able to develop a structure of a preliminary process flowsheet using limited information. This early work and other subsequent contributions are discussed below.

Extensive reviews on a large number of publications in the area of process synthesis can be found in Hendry et al. (1973); Hlavacek (1978); Westerberg (1980); Nishida et al. (1981); Umeda (1983); Westerberg (1987); Liu (1987); Floquet (1988); Westerberg (1989); Stephanopoulos and Han (1996a); Johns (2001), Westerberg (2004).

The first published book on process synthesis was by Rudd et al. (1973). The first three chapters cover a historical perspective, reaction path synthesis, material balance and species allocation. Chapter four and five introduced the idea of separation and separation task selection. Chapter six dealt with energy integration and the last two chapters covered the applications to synthesis processes, such as fresh water by freezing, detergents from petroleum, food processing, waste treatment and minerals processing.

Several books on artificial intelligence in chemical and process engineering have been published to provide background information, such as Mavrovouniotis (1990); Quantrille and Liu (1991); Baughman and Liu (1995); Stephanopoulos and Han (1996b).

In addition, several books addressing design by systematic methods from different professional backgrounds and perspectives have been published, such as Westerberg et al. (1979); Resnick (1981); Kumar (1981); Wells and Rose (1986); Douglas (1988); Hartmann and Kaplick (1990); Biegler et al. (1997); Seider et al. (1999); Koolen (2001); Barnicki and Siirola (2001); Turton et al. (2003); Seider et al. (2003); Smith (2005); Vogel (2005); Woods (2007).

A new, and latest, book on process design was written by Dimian and Bildea (2008). This book gives information on the design of sustainable chemical processes by means of systematic methods aided by computer simulation. The book also gives detailed discussion on process synthesis by a hierarchical approach and the synthesis of separation and reactor-separation-recycle systems. The systematic methods were applied to eleven case studies. The case studies include phenol hydrogenation to cyclohexanone, alkylation of benzene by propylene to cumene, vinyl chloride monomer process, fatty-ester synthesis by catalytic distillation, isobutane alkylation, vinyl acetate monomer process, acrylonitrile by propene ammoxidation, biochemcial process for NO*x* removal, PVC manufacturing by suspension polymerization, biodiesel and bioethanol manufacturing processes.

2.2 Process Synthesis Methods

Since Rudd (1968) proposed the first method for process synthesis, several works have been published based on the systematic generation of flowsheets, evolutionary modification, and process flowsheet optimization. Due to the fact that process synthesis problems are in nature combinatorial and open ended, a number of different approaches have been proposed.

The two main approaches for process synthesis include heuristic methods which consist of a series of heuristic rules to screen process alternatives and mathematical methods which rely on optimization techniques to mainly solve a mixed integer nonlinear programming (MINLP) problem. In general, systematic techniques for the synthesis of complete process flowsheets can also be classified into two approaches, synthesis without an initial structure (heuristics) and structural parameter or integrated approach (mathematical). An overview, including the advantages and disadvantages of each method are discussed here.

2.2.1 Mathematical Programming Methods

The main idea of the mathematical programming approach is to formulate a synthesis of a flowsheet in the form of an optimisation problem. The mathematical programming approach addresses both nonlinear and non-ideal behaviour, and can provide optimal designs. These mathematical programs may consist of thousands of linear and nonlinear equations containing both discrete and continuous variables.

In the mathematical programming methods, the entire design space is considered, and then the optimal design is selected. The major advantage of mathematical programming strategies for process synthesis is that they perform simultaneous optimization of the configuration and operating conditions. Among the advantages of process synthesis using mathematical methods are that it provides a common mathematical framework to solve a variety of process synthesis problems, provides a natural way of accounting explicitly for the interaction between flowsheet units, and the handling of rigorous analysis of features such as capital costs. In addition, mathematical programming can be implemented as an automatic tool for process synthesis.

2.2.2 Process Optimization

Over the last two decades, the chemical process industry has undergone significant changes due to the increased cost of energy and increasingly stringent environmental regulations. To reduce the cost of chemical processes, modification of plant design procedures and operating conditions are required to meet the constraints. This can be achieved by employing optimization. Process optimization is one of the major quantitative tools in industrial decision making. Optimization is the use of specific methods to determine the most cost effective and efficient solution to process design. It deals with finding the optimum design parameters for maximizing the profit or minimizing the total investment on process plant with a trade-off between capital and operating costs.

The three key components of an optimization problem are: the objective function, process model and variables, and constraints. The objective function is mathematical function that, for best value of the design variables, reaches a minimum or maximum. Constraints are limitations on the values of process variables. These can be linear or nonlinear, and may involve more than one variable. A constraint is called an equality constraint when it is written as an equality involving two or more variables. For example, an oxidation reaction may require a specific amount of oxygen in the combined feed to the reactor and the mole balance on the oxygen in the reactor feed is an equality constraint. When a constraint is written in an inequality involving one or more variable, it is called an inequality constraint such as in a process where the catalyst operates effectively at temperature below 300 ^{o}C, or a pressure below 25 bar.

Typical problems in chemical process design or plant operation have many solutions. Optimization is concerned with selecting the best solution using efficient quantitative methods. The method chosen for any optimization problem depends primarily on: the character of the objective function and whether it is known explicitly, the nature of the constraints, and the number of independent and dependent variables.

Optimization methods take advantage of the mathematical structure of the economic and the process models to locate the optimum. Models should be developed to use these capabilities to locate optima. Optimization problems can be generally classified as Linear Programming (LP) and Non-Linear Programming (NLP) problems. The word "programming" does not refer to computer programming, but it means optimization. For optimization problems involving both discrete and continues variables, the adjective mixed-integer is used. When a linear programming problem is extended to include integer variables, it becomes a Mixed Integer Linear Programming problem (MILP). Correspondingly, when a nonlinear programming problem is extended to include integer variables it becomes a Mixed Integer Nonlinear Programming problem (MINLP) (Smith, 2005). Another method for solving nonlinear programming problems is based on Quadratic Programming (QP). The nonlinear optimization method is called Quadratic Programming if the objective function is second order in the variables and the constraints are linear (Turton et al., 2003). Optimization problems involve many variables, equations and inequalities. Optimization solutions must not only satisfy all of the constraints, but also must achieve the objective function.

Edgar et al. (2001) compared the linear versus the nonlinear models. Linear models exhibit the important properties of superposition whereas the nonlinear models do not. The ability to use linear models is of great significance because they are much easier to manipulate and solve than nonlinear models. If linear equations can provide satisfactory representation of the economic and processes of the plant, Linear Programming (LP) can be used to locate the global optimum. However, if the models are nonlinear, optimization methods can only guarantee a better point than the starting point or a local optimum (Pike, 2006). The global optimum is a point at which the objective function is the best for all allowable values of the variables. The local optimum is a point from which no small allowable change in the variable in any direction will improve the objective function (Turton et al., 2003).

Figure 2.1, illustrates the classification of global optimization methods. The exact methods are guaranteed to find an arbitrarily close approximation to a global optimum and it is possible to prove it. The exact methods include Branch and bound (BB), interval arithmetic and multistart methods. Branch and bound is a class of methods for linear and nonlinear mixed-integer programming. If carried to completion, it is guaranteed to find an optimal solution to linear and convex nonlinear problems. It is the most popular approach in all commercial MILP (Edgar et al., 2001). The multistart methods attempt to find a global optimum by starting the search from many starting points.

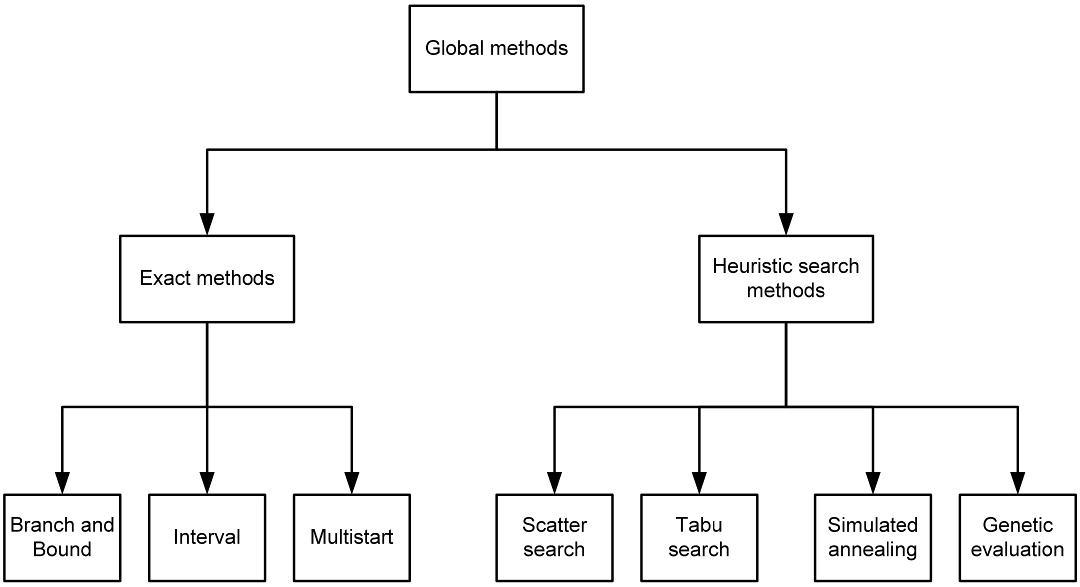


Figure 2.1: Classification of global optimization methods. (adapted from Edgar et al., 2001)

The heuristic search methods starts with some current solution, then explores all solutions in the neighbourhood of the point to look for the best one. This is followed by repeats if an improved point is found. Methaheuristics algorithms such as Tabu Search (TS), Scatter Search (SS), Simulated Annealing (SA) and Genetic Algorithm (GA) can guide and improve the heuristic algorithm. These Methaheuristics algorithms methods use a heuristic procedure for the problem class, which itself may not be able to find a global optimum and guide the procedure by changing its logic based search to prevent the method from becoming trapped in a local optimum (Edgar et al., 2001). The genetic and evolutionary, and scatter search are population based methods that combine a set of solutions in an effort to find improved solutions and then update the population when the better solution is found.

Babu (2004) classified the optimization algorithms into two types. The first is the traditional optimization techniques based on algorithms that are deterministic with specific rules for moving from one solution to the other. The second is the non-traditional optimization techniques based on algorithms that stochastic in nature with probabilistic transition rules. Figure 2.2, illustrates the traditional optimization methods.

1. Analytical methods:
- a) Direct search without constraints
- b) Lagrangain multipliers with constraints
- c) Calculus of variable
- d) Pontryagin's maximum principle

2. Mathematical programming:
- a) Geometric programming
- b) Linear programming
- c) Dynamic programming

3. Gradient methods:
- a) Methods of steepest descent linear programming
- b) Sequential simplex method

4. Computer control and model adaptation:

5. Statistical optimization:
- a) Regression analysis
- b) Correlation analysis

1. Other methods:
- a) Golden section search
- b) Brent's methods
- c) Quasi-Newton methods
- d) Direction set methods

Figure 2.2: Methods of traditional optimization. (adapted from Babu, 2004)

Depending upon the degree of non-linearity and the initial guess, most of the traditional optimization techniques based on gradient methods can possibly become trapped at local optima. Hence, these traditional optimization techniques do not guarantee the global optimum and can also limit the applications. To overcome this problem the non-traditional optimization techniques can be used. The non-traditional optimization techniques include (Babu, 2004): Simulated Annealing (SA), Genetic Algorithms (GA), Evolutionary Programming (EP) such as Evolution Strategy (ES), Evolution Programming (EP) and Genetic Programming (GP), and population-based search algorithms such as Memetic Algorithms (MA), Scatter Search (SS), Ant Colony (AC) optimization and Self-organizing Migrating Algorithms (SMA).

Figure 2.3, illustrates the three main areas of optimization in industry. These are management, process design and equipment specification, and plant operation. The management makes decisions concerning project evaluation, product selection, and corporate budget, investment in sales versus research and development, and plant construction. Allocation and scheduling is concerned with the overall picture of shipping, transportation, and distribution of products to engender minimal costs. To maintain low–cost operation, it is important to study the frequency of ordering, the method of scheduling production, and scheduling delivery. Plant operation is concerned with operating controls for process units at the best temperature, pressure, or flowrate.

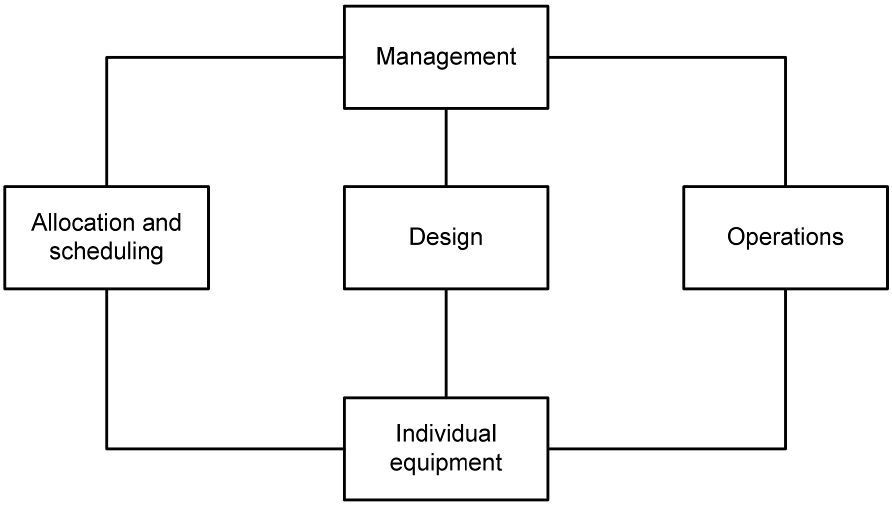


Figure 2.3: Hierarchy of levels of optimization. (adapted from Edgar et al., 2001)

Process design and equipment specification are concerned with the choice of processes and nominal operating conditions such as the required number of reactors ,or separators, the configurations of the plant, the arrangement of the processes so that the plant operating efficiency is at a maximum, and the optimum size of process units. The process design and equipment specification is usually performed prior to the implementation of the process, and management decisions to implement designs are usually made far in advance of the process design step.

A wide range of problems in chemical plants design, operation and analysis can be resolved by optimization. Optimization can be applied to chemical processes and plants in several types of project such as:

1. determination of the best site location for the plant
2. routing tankers of crude and refined products distribution
3. pipeline sizing and layout
4. design of individual process equipment and entire plant
5. scheduling maintenance and equipment replacement
6. operating equipment
7. evaluating plant data to construct a process model
8. minimizing inventory charges
9. resources and services allocation
10. planning and scheduling construction.

Edgar et al. (2001) demonstrated the applications of optimization with twenty four examples in the area of heat transfer and energy conservation, separation processes, fluid flow systems, chemical reactor design and operation, optimization of large scale plant design and operations, and integrated planning, scheduling and control in process industries.

Spreadsheet optimization to solve linear and nonlinear programming, and mixed integer programming problems can be achieved by using either the Excel solver, Quattro Pro Solver, or LOTUS123. Examples of software systems for global optimization include: Premium Excel Solver, OPTQUEST® and LOG® (Edgar et al., 2001). The Premium Excel Solver includes an involuntary algorithm which finds the nearest local solution to its starting point. The solver stops when either the time or iterations limit is reached, or when 99% of the population members have fitness values such that the fractional deviation between largest and smallest is less than the convergence tolerance. OPTQUEST® is an optimization software system developed by OptTek Systems, Inc. OPTQUEST® consists of a set of the function that: input the problem size and data, set options and tolerances, perform the initial Scatter search steps to create an initial reference set, retrieve a trial solution from OPTQUEST® to be inputted to the improvement method, and input to the solution resulting from the improvement method back to OPTQUEST®. LOG® is intended for smooth problems with continues variables. LOG® operates in two phases. The first is the global phase to find a point which is a good approximation to a global optimum. It uses a random sampling technique and an adaptive deterministic, with an option to apply these within a Branch and Bound procedure. From this point, the ensuing local phase starts to find an improved point which is the nearest local point.

2.2.3 Superstructure Optimization

Superstructure optimization is one of the important mathematical process synthesis approaches. In the superstructure optimization technique, the structure of a process design, i.e. the equipment identity and connectivity in all possible ways, as well as the design and operating parameters for equipment can all be determined optimally and simultaneously (Barnicki and Siirola, 2001). Therefore, superstructure optimization allows complex interactions between all possible process flowsheet pieces of equipment and then chooses the combination that minimizes, or maximizes, the objective functions. As noted by Li and Kraslawski (2004), process synthesis using this method may encounter some difficulties in optimisation of under defined design problems and uncertainties that result from the multi objective requirements of the design problem.

Harmsen (2004) has listed five steps that superstructure optimisation by MINLP contains:

1- Generation of all conceivable unit operations

2- Connection of all individual units in all possible ways into a superstructure

3- Development of a superstructure mathematical model, containing component mass and enthalpy flows, feed stock cost expressions and, capital expenditure and fixed cost for equipment sizing

4- Defining the cost optimisation function along with all constraints of the variables

5- Determination of optimum unit selection and conditions using MINLP numerical optimisation methods

The preliminarily work on selecting the optimal configuration from a given superstructure using mathematical methods through the use of branch and bound search, was conducted by Lee et al. (1970) and direct search methods for continuous variables by Umeda et al. (1972); Ichikawa and Fan (1973). Grossmann and his co-workers (Grossmann, 1985; Lee et al., 2003) used a mathematical programming approach utilising optimization techniques to select the parameters and configuration of the processing system.

Kravanja and Grossmann, 1997, proposed a multilevel-hierarchical MINLP synthesis of flowsheet. Their strategy can enable the designer to postulate the superstructure at different levels of representation of flowsheet alternative. The framework follows the hierarchical strategy of process synthesis by Douglas, (1988) and Siirola, (1998). The hierarchical strategy of process synthesis and MINLP superstructure approach starts with reactor network synthesis (MINLP1), separation synthesis (MINLP2) and heat exchanger network synthesis (MINLP3).

The approach address different process operations such as reactions, connectivity and species allocation, separation, energy and heat integration, and heat exchanger network through simultaneous superstructure optimization. As algorithmic approach to the N-level MINLPs is complex, one of the two-level approaches can be outlined as follows:

the first step involves solution of MINLP1 to obtain an upper bound on the profit and binary variables for substructure selection. This can be individual units or groups of units. In the second step, the MINLP2 is solved for fixed binary variables. This could be NLP if individual units are chosen binary variable, or MINLP if is a group of units. The solution gives the lower bound. The third step involves adding an integer cut and perhaps other bounding information such as profit ≥ lower bound. This is followed by resolving MINLP1 and iteration until bounds are within specific tolerance. This approach does not evaluate alternative type of reactors or separators. The work does not consider simulation, or sizing and economic evaluations of alternative configurations.

Linke (2001); Linke and Kokossis (2003) have developed a general framework for selecting process designs through simultaneous exploitation of reaction and separation options. They implemented successfully two stochastic algorithms, Simulated Annealing (SA) and Tabu Search (TS) for reaction and separation process integration. TS search incorporates concepts of artificial intelligence to guide the optimal search. It makes use of the adaptive memory to escape local minima. The adaptive memory is also called tabu list which makes some attributes fixed for a certain period. The length of the tabu list is called tabu length. Once an attribute enters into the tabu list, the oldest attribute is released from the tabu list (Mori and Ogita, 2000). The SA search strategy randomly modifies an initial solution and accepts downhill moves when encountered. It also accepts other moves if they satisfy a condition that depends on the advancement of the algorithm. This means, the SA method has the ability to accept moves that can escape from a local optimum. In his thesis, Linke (2001) presented a number of numerical examples to illustrate the performance of the search strategies for performance targeting. Examples illustrate the performance characteristics of the optimization framework through a gas-liquid reactor system.

These superstructure optimization approaches discussed above have the disadvantage of not evaluating alternative type of reactors and separators. They are focusing in finding the optimal design conditions and configurations of a specific reactor-separator-recycle system. Other disadvantage is that only conventional reactors and separators are optimized.

Grossmann (1985) highlighted the arguments against the use of mathematical programming methods that are based on optimisation for process synthesis. He summarised the arguments against mathematical methods for optimization as following: the mathematical programming methods remove the design engineer from the decision-making process. It provides less explanation on how the decisions are made and the reasons behind the decisions. The methods are computationally expensive. Finally, the fact that many of the mathematical methods cannot guarantee “true” optimality as some good alternatives may not have been included in the problem representation. As noted by Kaibel and Schoenmakers (2002), due to the large size of the numerical optimisation problems and, the complexity and time required for setting up the models, industry does not always apply mathematical methods for generating completely new process designs.

In the proposed systematic procedure presented in Chapter 4, a generic superstructure is developed to account for different configuration and design decisions by the Integrated Knowledge Based system IKBS. The proposed generic superstructure is applied as a generic flowsheet in Aspen HYSYS for mass and energy balances calculation, and unit operations sizing and economic evaluation.

2.2.4 Heuristics Method

At the preliminary level of process design, heuristic methods can be very useful to analyze the process and suggest alternatives that can be further considered for design decisions and optimization. The word heuristics is Greek which means ‘’to discover’’ (Giarratano and Riley, 2005). The term “heuristic” is generally used to refer to knowledge that is used to control the search. Heuristics can also be used to suggest alternatives that might lead to correct, or satisfactory solutions. In the heuristics method the design space is reduced until an acceptable design remains. Although an optimal solution may not be guaranteed, Heuristics can remove non-sensible optimal solutions. Therefore, heuristics does not solve the optimization problem, but it can be used to suggest good solutions by following a set of rules from industrial experience.

The heuristics method can be regarded as knowledge based method, which concentrates on the representation and knowledge organisation of the design problem. The main idea of the heuristics method is to apply design rules based on specific process knowledge and experience. The heuristics method can be useful in the early stages of process synthesis especially when only limited amount of experimental data are available.

Hartmann and Kaplick (1990) have divided process synthesis heuristic rules into five groups:

1. Preparation and modification of rules for formulated tasks in the process synthesis
2. Structuring rules for the determination of system structure
3. Parameter rules for system and process unit operation parameters selection
4. Evaluation rules for generated system modification
5. Evaluation rules for generated systems evaluation

By using heuristic rules a design problem can be analyzed to reduce the discrete variables prior to reducing the size of the search space. Without heuristics, industrial problems may be too difficult to converge and too large to search. Heuristics can use a nonlinear solver to help decide which approach to use to solve a problem. Furthermore, heuristics can aid process engineers to make decisions. Hierarchical decomposition is essential for the conceptual design phase, to create good initial flowsheets.

2.3 Total flowsheet Synthesis

Previous effort at the systematic generation of alternative flowsheets using heuristic methods have been based on paradigms derived from artificial intelligence planning, as in the means-ends analysis of AIDES, resolution theorem-proving as in BALTAZAR, expert design practice as in Process Invention Procedure (PIP) and ConceptDesigner and, the expert systems approaches based on documented experience supported by numerical methods using a number of different programs from different experience fields as in PROSYN.

The AIDES system of Siirola and Rudd (1971), and the BALTAZAR system of Mahalec and Motard, (1977a,b), were among the earliest efforts in the development of computer aided programs for process flowsheet synthesis without an initial structure. AIDES decomposed the process synthesis problems into three levels: raw material selection and chemical reaction, product selection, and mixing, splitting and separation selection (Siirola et al. 1971). AIDES implements only nine out of the twelve alternating synthesis and analysis steps proposed by Siirola and Rudd (1971) which are reproduced in Figure 2.4

Step 1 : Chemical reaction path synthesis
Step 2 : Stoichiometric material balance
Step 3 : Component matching
Step 4 : Match evaluations
Step 5 : Information difference detection
Step 6 : Species allocations
Step 7 : Non-separation task identification
Step 8 : Physical property evaluations
Step 9 : Separation task identification
Step 10: Separation task feasibility
Step 11: Task integration
Step 12: Final evaluation

Figure 2.4: AIDES synthesis steps. (Adapted from Siirola et al., 1971)

BALTAZAR used a depth-first sequential search for a feasible process structure based on three structural rules, the use of compositionally most similar sources to generate products, giving preference to by-products instead of raw materials and reducing mass load on separation tasks.

AIDES performs the stream source/destination matching for the entire flowsheet based on a general problem solver in one step whereas BALTAZAR starts with a set of goals and attempts to solve the problem by eliminating of contradictions between a set of facts and goals. Most of the synthesis steps in AIDES and BALTAZAR are considered in the proposed integrated systematic procedure presented in Chapter 4. None of these programs calculate equipment sizes or use process simulation.

Lu and Motard (1985) extended the previous work of Nath and Motard (1981) to develop a heuristic-evolutionary approach for the synthesis of a total flowsheet. The synthesis procedure starts with the creation of two stream matrices, representing goals and sources, followed by the application of a linear programming to solve the stream matching problem and to create a preliminary flowsheet. The separation tasks in the preliminary flowsheet are then synthesized and cost estimated by using seven heuristic rules and six evolutionary rules. This work only suggests conventional reactors and separators and it does not use process simulation, or databases.

Douglas (1985, 1988, 1992) produced a design procedure based on the hierarchical decomposition approach to process synthesis as illustrated in Figure 2.5. Douglas' process synthesis hierarchical method relies on sets of rules at different stages during process development. His decision ordering was initially in five levels: choosing between continuous and batch processing, selecting the raw materials and products, selecting the reactor based on reaction selectivity, designing the vapour and liquid separation systems and designing the heat recovery system. The sixth level added to the procedure was the evaluation of alternatives (Rajagopal et al. 1988).

Douglas has further developed his method by introducing two additional decision levels, flexibility and control, and safety (Douglas, 1992). This technique has been used for the synthesis of single product processes to multi-step reaction processes (Douglas, 1988), the design of solid processes (Rossiter and Douglas, 1986 a,b; Rajagopal et al.,1988; Rajagopal et al., 1992), the design of polymer processes (McKenna and Malone, 1990), process synthesis for waste minimization (Douglas, 1992) and metallurgical process design (Linninger, 2002).

Level 1: Batch versus continuous
Level 2: Input-output structure of the flowsheet
Level 3: Recycle structure
Level 4: Separations system synthesis
  Level 4a: general structure: phase splits
  Level 4b: vapour recovery system
  Level 4c: liquid recovery system
  Level 4d: solid recovery system
Level 5: Energy integration
Level 6: Evaluation of alternatives
Level 7: Flexibility and control
Level 8: Safety

Figure 2.5: Douglas' Hierarchy of decision levels procedure for process design.

The hheuristics used in Douglas work to select reactor type are very simple: if the reaction phase is liquid, use Plug Flow Reactor (PFR) or Continuous Stirred Tank Reactor (CSTR), and if the reaction phase is vapour, use Plug Flow Reactor (PFR). This heuristic ignores all other types of reactors and the wide range of criteria that can affect the selection of reactors type such as the use of catalyst, the reaction exotherm etc.

An example of a heuristic used is that distillation is a recommended separation technique when the relative volatility (α) is ≥ 1.5. Separation using distillation is competitive for $1.1 \geq \alpha \leq 1.5$ and not recommended if $\alpha \leq 1.1$. General heuristic rules for column sequencing include, removing corrosive and reactive components as soon as possible, removing liquid products as distillates, and removing the recycle streams as distillates. Other important simple column sequencing heuristics include:

1. separation of the most plentiful first,
2. removal lightest components first,
3. high recovery and save difficult separation until last,
4. favour equimolar splits,

Some of these heuristics depend on feed compositions and relative volatilities. Furthermore, some of these heuristics might contradict each other, such as the second and third heuristics as they are dependent on relative volatility. These sequencing heuristics are limited to sequences of a simple column having a single feed stream that were isolated from the remainder of the process. The sequencing heuristics from Douglas' procedure and other additional heuristics are considered in the sequencing procedure of the proposed integrated approaches.

The first system implementing Douglas' hierarchical decomposition method using an expert system and short cut models was the Process Invention Procedure (PIP) presented by Kirkwood (1987) and Kirkwood et al. (1988). In PIP, the reaction path is first constructed considering only the molecular identity properties. This was followed by species allocation to construct the plant connections and recycles. In the next step, PIP resolves composition differences for each reactor effluent by a rule based decision procedure to specify the phase separation systems followed by vapour and liquid separation systems. PIP ends the synthesis of the flowsheet by energy integration.

Douglas' systematic procedure and its implementation in PIP do not consider the separation operation between intermediate and primary products reactor systems. It uses only distillation to separate liquid mixtures and absorption for vapour mixture, and does not handle non-ideal mixtures. PIP only employs continuous stirred tank reactors (CSTR) for liquids, or mixed phase reactions and a Plug Flow Reactor (PFR) for vapour phase reactions. PIP also does not study the effect of the reactor configurations on product distribution. In the proposed integrated systematic procedure presented in Chapter 4, some heuristics used in Douglas's systematic procedure levels: 2,3,4(a,b,c),6 and 8 are considered. Level 1 is not considered as only continuous processes are synthesised. Energy and control are also not covered as they are beyond the objectives of this research. However they are suggested for future work.

Other implementations of Douglas's hierarchical synthesis of a process flowsheet are in ConceptDesigner and the computational model by Han (1994) and Han et al. 1996a,b. Han (1994), developed a Hierarchical Design Language (HDL) which is a framework for the development of a computational process that emulates the Douglas conceptual process design methodology. HDL has been designed to meet two classes of modelling needs, the multifaceted modelling of the various states of the evolved process design and the modelling of the procedural design tasks which are described by the goal structure.

Figure 2.6 shows the computational process for the various design tasks contained in HDL (Han et al. 1996a,b). The position of the hierarchy defines the role and the scope of the task during the design process. In HDL, there is a design manager which is an abstract task that can be used to create a specific design manager. The classes that are descendants of the design manager can refine a process flowsheet from less detailed levels to complex levels. The project manager is a task that coordinates and organizes the activities of design managers for the design project. The design agent is an abstract task that has a domain-specific knowledge. Specific design knowledge is represented as a design plan for each design agent. The subclasses of each design agent are: StructureAgent, CoordAgent, DrawAgent, ModelAgent and EvalAgent.

The StructureAgent decomposes a given system into a set of subsystems and coordinates subsystems for interactions identification. The CoordAgent establishes the connections among generic units that do not have connections. A generic unit is used to represent an isolated system by defining the boundary that separates it from the surroundings. Thus, this agent supplements the StructureAgent in terms of coordination. The DrawAgent transforms a generic unit into an icon associated with the given generic unit. It also draws the streams that connect the ports between generic units based on the connection information of each port.

The ModelAgent is in charge of the flowsheet analysis by solving the material and energy balances. The EvalAgent computes the economic potential of the flowsheet. Therefore, the StructureAgent, CoordAgent, and DrawAgent are sufficient to synthesise a structure and present it to the user whereas, the ModelAgent and EvalAgent, set up the material and energy balance and compute the economic potential of the flowsheet.

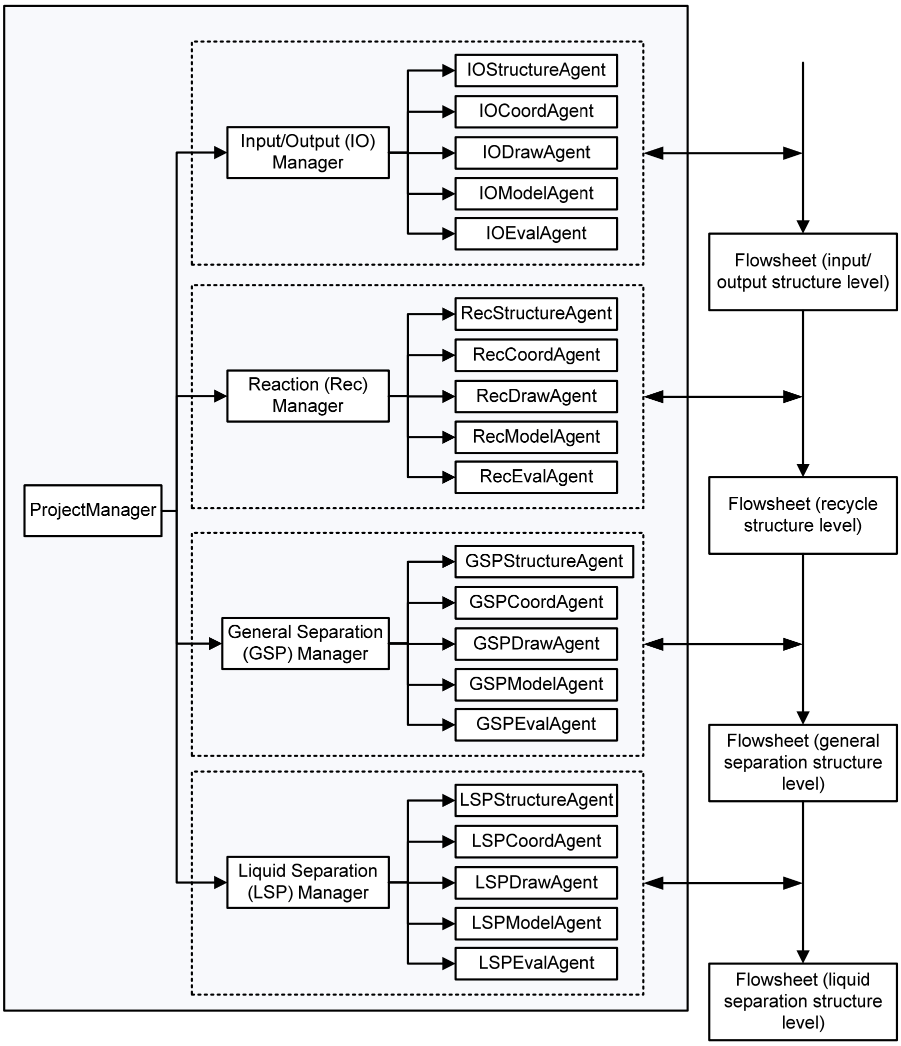


Figure 2.6: HDL's object model for design and design agents. (Adapted from Han et al. 1996a,b)

ConceptDesigner is a software that implements the computational model of HDL (Han et al. 1996a,b), as another implementation of Douglas's hierarchical synthesis of a process flowsheet. Figure 2.7 illustrates the functional modules of ConceptDesigner.

ConceptDesigner provides an intelligent user interface, quick process design and generation/screening of alternatives, together with a process analysis tool for material and energy balance and cost analysis.

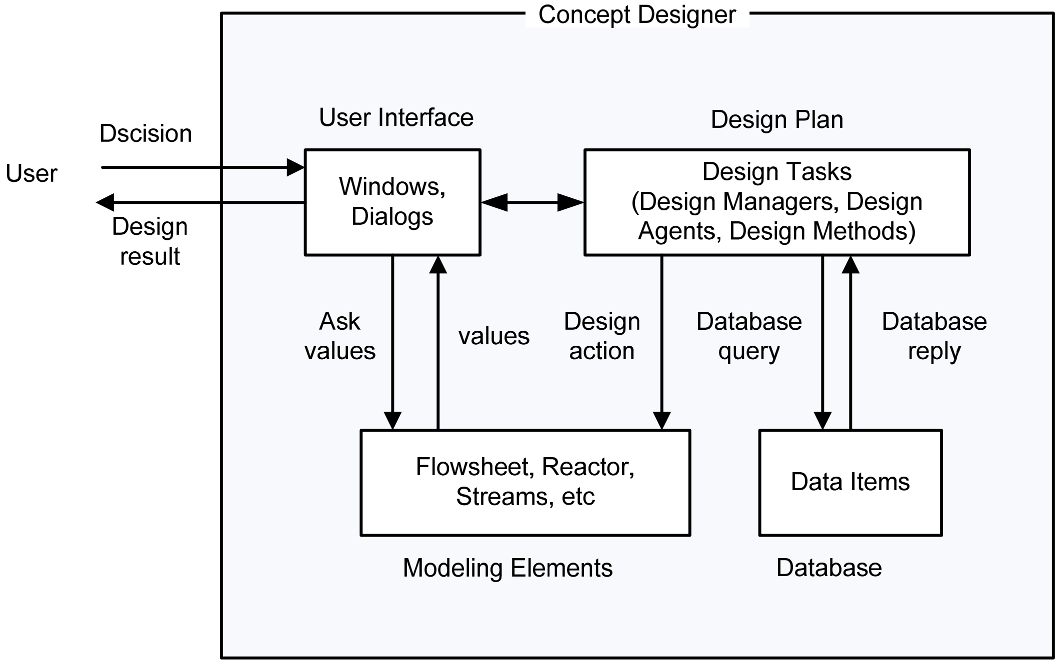
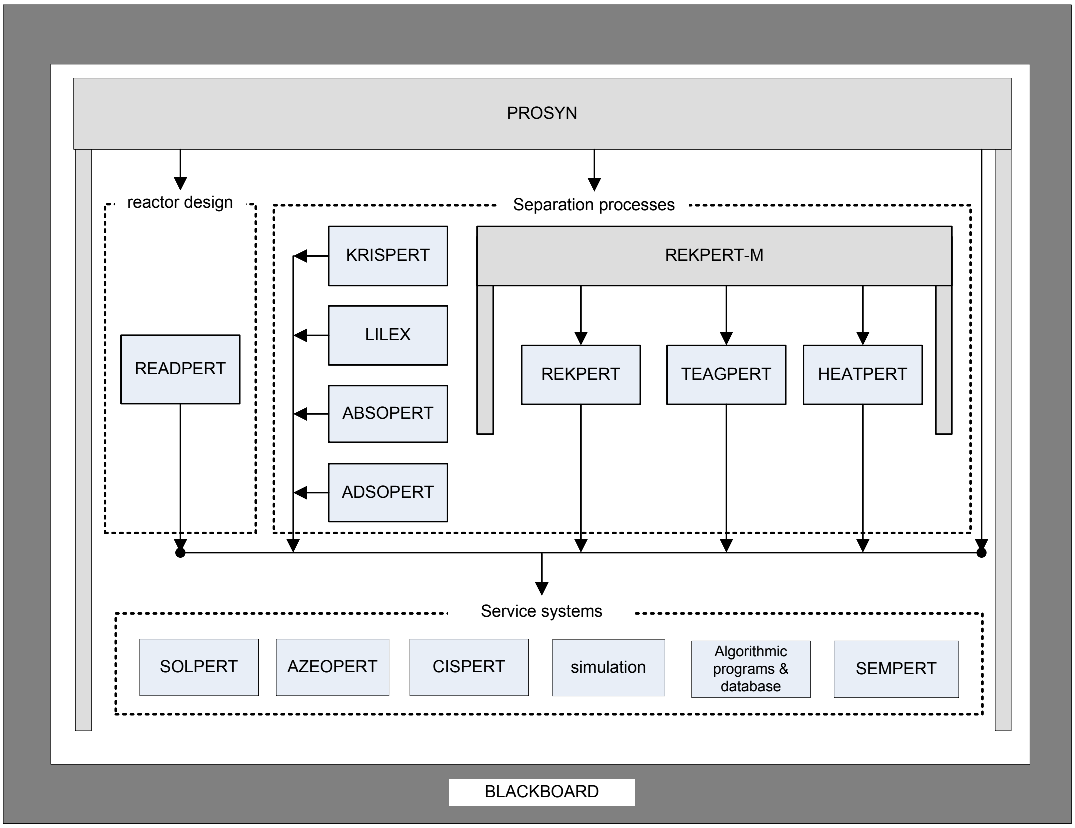


Figure 2.7: Functional modules of ConceptDesigner. (adapted from Han et al. 1996a,b)

ConceptDesigner and HDL are limited to conventional reactor-separator techniques. It does not use process simulators, or handle non-ideal mixtures. It also does not size the developed flowsheets. The demonstrated styrene case study using ConceptDesigner by Han in his thesis (Han, 1994), shows alternative flowsheets that contain the same reactor and separator units. The only differences are in recycle system configuration. The three steps of ConceptDesigner and HDL which include input/output, reactor and separator design tasks are considered in the proposed systematic procedure presented in Chapter 4.

Schembecker and co-workers have developed a comprehensive expert software system for supporting conceptual process design. The software package is called "PROSYN". A summary of the results of their research and overview description of software is given by Schembecker et al. (1994) and Schembecker and Simmrock (1996). PROSYN applies a heuristic branch and bound method to administrate and evaluate process synthesis alternatives. As illustrated in Figure 2.8, PROSYN contains a number of separate expert systems.



READPERT	Reactor Selection and Design Expert System
KRISPERT	Crystallization Expert System
LILEX	Liquid-Liquid Extraction Expert System
ABSOPERT	Absorption Expert System
ADSOPERT	Adsorption Expert System
REKPERT	Rectification Knowledge Based System
TEAGPERT	Separation of Close-Boiling and Azeotropic Mixtures Expert System
HEATPERT	Heat Integrating Expert System
SOLPERT	Solvent selection Expert System
AZEOPERT	Azeotrope Predicting Expert System
CISPERT	Columns Internals Selection Expert System
SEMPERT	Selection of Methods Expert System

Figure 2.8: Structure of PROSYN. (Adapted from Schembecker et al. (1994))

The first expert system is “READPERT” for the selection of reactors and reactor design. The READPERT expert system for reactor selection is discussed in detail in the subsequent sections. The separation process expert systems includes the selection of crystallization (KRISPERT), liquid-liquid extraction (LILEX), absorption

(ABSOPERT), adsorption (ADSOPERT), rectification (REKPERT), heat integration (HEATPERT) and, separation of close-boiling and azeotropic mixtures (TEAGPERT). The service systems contain solvent selection (SOLPERT), azeotrope prediction (AZEOPERT) and columns internals selection (CISPERT) expert systems.

It is claimed that PROSYN can be used as an interface to process simulators, algorithmic programs and databases, but there is no published implementation of this. PROSYN is used by BASF, Shell and other companies (Seider et al., 1999; Harmset, 2004). PROSYN does not size process units nor does it evaluate process alternatives economically. Each expert system in PROSYN works in isolation from the other expert systems, algorithmic programs and database. This means PROSYN tackles the synthesis problem in one-way approach without feedback from later synthesis expert systems to the earlier ones. Unlike PROSYN, the proposed integrated systematic procedure presented in Chapter 4, all alternative separation techniques are evaluated in one integrated knowledge based system.

Mizsey and Fonyo (1990 a,b) have developed another combined approach of mathematical and hierarchical methods for the synthesis of chemical process flowsheets. They used the hierarchical design strategy to create and screen process alternatives. To account for additional implicit knowledge during the conceptual design, they applied a user-driven synthesis technique. Mathematical methods were used for the final tuning of the superstructure by optimisation.

Grossmann and co-workers have also developed a combined approach of hierarchical decomposition and mathematical programming methods for the synthesis of a process flowsheet that exploits the advantages of each of the two methods (Kravanja and Grossmann, 1997; Daichendt and Grossmann, 1998). They followed the hierarchical strategy of process synthesis by Douglas (1998) and Siirola (1996), starting from reaction path to plant connection to phase separation and, heat and energy integration. The mathematical programming method they used was the MINLP superstructure approach, starting with reactor network synthesis, then separation synthesis and ending with heat exchanger network synthesis. One of the limitations of their approach is that it does not take into account interactions of the upstream subsystems with the detailed MINLP models.

The combined approach of hierarchical decomposition and mathematical programming by Grossmann and his team differs from Mizsey and Fonyo's approach in that it employs the use of hierarchical decomposition and mathematical programming at the first step of the design. Therefore, alternatives generated using the Mizsey and Fonyo approach can be incorporated into the superstructure and then subjected to screening prior to rigorous simulation and optimisation. Both approaches by Grossmann and his team and Mizsey and Fonyo do not use databases or process simulators. Furthermore, only conventional reactors and separators are used. Alternative flowsheets do not include different reactor and separation types. The only difference between the alternative flowsheets is in the process configuration and the number of distillation columns used. In Chapter 4, a generic superstructure is proposed to examine and optimize different alternative flowsheets as a part of the integrated systematic approach.

Recently, Montolio-Rodriguez and co-workers (Montolio-Rodriguez et al., 2007) have proposed a systematic identification of optimal design for the acetic acid process. Their case study involves only conventional reactors and separators such as CSTRs, a series of fixed bed reactors, a simple two phase separator and single distillation column. Their work accounts for the internal recycle around the reactor and the distribution of the reactants between reactor zones to improve the process performance and maximise the economic potential. The separation performance assumes the recovery of all unreacted materials, and complete purification of the product from the by-products. It also assumes complete removal of combustion gases. The work does not incorporate process simulation for mass and energy balances. A generic Superstructure optimization of alternative flowsheet configurations is considered in the subsequent chapters. In Chapter 7, one of the case studies is related to the acetic acid manufacturing process. Results form the proposed integrated approach and its implementation in the IKBS, will be compared with the work by Montolio-Rodriguez and co-workers.

2.4 Reactor System Synthesis

Reactor system synthesis is the problem of deciding the optimal types, configurations and sizes of the reactors for a given reaction mechanism and kinetics. The difficulty in reactor system synthesis comes from the complexity and the nonlinear characteristics of chemical reactions.

Important information on different types of reactor design and selection are available in different textbooks such as Ullmann's Encyclopaedia of Industrial Chemistry by Elvers et al. (1996) and, Trambouze and Euzen (2004). Other important textbooks in chemical reaction engineering and reactor design are by Walas (1989); Froment and Bischoff (1990); Schmidt (1998); Levenspiel (1999); Missen et al. (1999); Silla (2003); Fogler (2005); Nauman (2008).

One of the early and important synthesis problems in reactor system synthesis is the generation of alternative reaction paths by which a desired target product might be made. As a big number of reaction paths can be generated, simple evaluation functions are required to allow for the screening and elimination of alternatives with little computational effort. This can be, for example, by analyzing the thermodynamics of the reactions and then eliminating any severely limited equilibrium reactions.

A comprehensive set of literature and heuristics have been reported by Hartmann and Kaplick (1990). They covered different methods for reaction paths selection and analysis and, the synthesis of a reactor system using heuristic and mathematical methods. About thirty heuristic rules were discussed. Examples of the heuristic rules include:

1. simple homogeneous reactions should be performed in a reactor with ideal plug flow.
2. non- reacting raw materials should be recycled, if possible
3. exothermic reactions should be performed adiabatically, if reaction enthalpy is supposed to be higher than the heat required for preheating the raw materials.

4. a reaction with volume decrease should be realized at higher pressure, and volume increase should be realize at lower pressure
5. for homogonous reactions use CSTR for high backmixing and PFR for low backmixing.

It is possible to implement most of Hartmann and Kaplick heuristic rules in this research to select reactors types and configuration. However, some of these rules may not be applicable for non-ideal and advanced reactors such as fluidized bed reactors.

Fujiwara et al. (1995) developed an expert system called EXPRES for reaction cycles synthesis. With the help of reaction databases and various kinds of knowledge bases, EXPRES can generate two kinds of reaction cycles systematically, chemical reaction cycles and chemical reaction clusters. This expert system can be used for saving thermal energy of recycling resources.

Li et al. (2000) have proposed a hierarchical optimization method for reaction path synthesis as illustrated in Figure 2.9.

Level 1: Determination of overall reactions
Level 2: Evaluation of reactions
  Level 2a: economic potential
  Level 2b: thermodynamics
  Level 2c: mechanism
Level 3: Decomposition of infeasible overall reactions

Figure 2.9: Hierarchy of decision levels procedure for reaction paths.
(Adapted from Li et al., 2000)

Their procedure starts with the determination of overall reactions to identify and evaluate all of the meaningful overall reactions by enumerating the full rank matrix. Once overall reactions are generated, evaluation can be made using several criteria such as economic potential, thermodynamics, and mechanism of reaction. If an overall reaction is not achievable thermodynamically, or is undesirable with respect to the mechanism of reaction but it has a large economic potential, it can be decomposed at the second level by introducing intermediate chemicals. Potential safety and environment effects are not considered in their process of selecting the reaction paths.

Palaniappan et al. (2002), developed another expert system for the reaction route by focussing the design on inherently safer processes. They developed a systematic methodology for identifying hazards. Their design selection was based on the safety criteria. In the proposed integrated approach, safety and environmental impacts based on information from the internal databases are considered at the early stage of the process synthesis.

The two main previous works in chemical reactor system synthesis using heuristics methods were carried out by Schembecker and co-workers (Schembecker et al. 1995a,b) and Jacobs and co-workers (Jacobs, 1998 and Jacobs et al., 2000a,b). Both works synthesise reactor systems in isolation from the separation system.

READPERT was developed by Schembecker and co-workers (Schembecker et al. 1995a,b) as a heuristic-numerical consulting system containing different modules as illustrated in Figure 2.10.

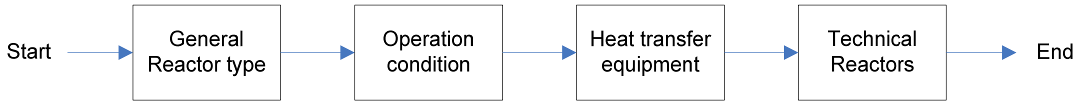


Figure 2.10: The main modules of READPERT. (Adapted from Schembecker et al. 1995a,b)

The general reactor type module involved defining the reactor schemes in terms of combinations of multiple reactor steps. Five reaction kinetic models are provided, irreversible, reversible, catalytic, autocatalytic and inhibited reaction. The operating conditions module provides recommendations of the most important reactor operating conditions based on the results from the previous module. Most important parameters involve reactor temperature profile, the need for recycle streams, qualitative temperature levels at the beginning and end of the reactor, qualitative concentration levels for the reactant, need for inerts, degree of conversion, rates of reactions, the location or manner of reactant input and product separation and, finally the pressure.

The heat transfer equipment module addresses the problem of choosing between a wide range of different type of heat transfer equipment in three steps. The first step is to check the kind of equipment suitable for the particular problem. The second step is the calculation of the heat flow. The third step is the selection of the best element among the remaining heat transfer possibilities with the consideration of equipment cost to obtain a proper choice. The technical reactor module determines the appropriate technical reactors that satisfy the proposal developed in the previous three modules and any further criteria of technical relevance. The fifth module is treated as additional functions which allow the determination of reaction data for several basic reactor types. Results from this calculation module can be plotted in various forms such as concentration versus time or selectivity versus conversion plots.

READPERT does not consider the separation system and does not use precise kinetic information. It also does not use databases to import the facts required during the synthesis such as physical properties. Furthermore, READPERT does not size the reactor or perform an economic evaluation. READPERT systematic procedure is a one-way process as there is no reassessment of reactor selection decisions.

The other work in reactor synthesis is the Knowledge Based System KBS for reactor selection which was developed by Jacobs and co-workers (Jacobs et al., 1996; Jacobs, 1998; Jacobs et al., 2000a,b). As illustrated in Figure 2.11, KBS for reactor selection contains seven steps of synthesis.

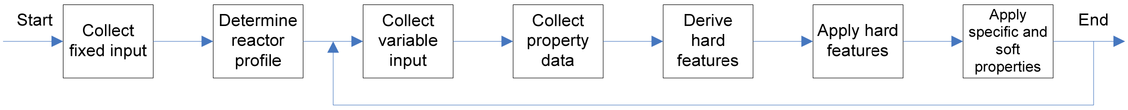


Figure 2.11: KBS for reactor selection synthesis decomposition levels. (Adapted from Jacobs, 1998)

The first step is “collect fixed input”, where basic information about the process which is needed for reactor selection is provided by the user. This includes the problem class i.e. the phase of reaction and the use of catalyst, the chemical components involved in the process, the objectives of the process and reactions and their rates. The key factors that determine the phase in which reaction is conducted include the reactant volatility, thermal stability of the reactants and products, specific reaction rate, space time yield, process safety, and process economics (Mills and Lambert, 2006). In the determination of reactor profile step, a set of strategic notations is derived based on the fixed input. An example of reactor profile is the qualitative notation of the desired operating temperature and concentration. In the third step, the user will provide some information as a variable input about the feed streams to the reactor such as the phase, mole fraction and flowrate of each feed stream.

At this stage the system has enough information to start the reactor selection process. Unsuitable reactor choices will be eliminated based on deriving and applying hard features of the process which are the properties of reactor and the process that have to be met by necessity. Examples of hard features of a chemical process include: reactor scale, heat transfer, and catalyst replacement. This will be followed by applying specific and soft properties.

Specific properties can not be compromised as they are strictly required. Furthermore they do not apply to every reactor in a problem class as they are specific to few particular reactors. Examples of specific properties include: sensitively to dust, catalyst attrition resistance, and force in packed bed, thermal recycle catalyst.

The soft properties describe reactor properties that do not have the character of a constraint that should be met. Examples of soft properties include: pressure drop, residence time, catalyst sizes and shapes, catalyst volume fraction, and catalyst residence time distribution.

The problem with KBS selection criteria is that it does not allocate scores to each criterion. On other word, reactors can be either suitable or not suitable for a specific criterion. In the IKBS, each criterion is given a score from 1 to 4, and not suitable ones are given “#”. Some of the selection criteria used in the KBS is considered in the IKBS.

The KBS reactor selection method works by using a choice matrix which represents the reactors that are available and the reactor properties that can be used for the selection. A new choice matrix represents the selection process progress after the rejection of some reactors. This selection process is described as a sequential construction of new reduced choice matrices. These new reduced choice matrices are constructed by matching reactor properties suitable for the desired chemical process.

KBS synthesises reactor systems in isolation from the separation system. It also relies heavily on the user to provide many facts during the synthesis steps instead of utilising a database for this purpose. KBS does not include reactor sizing or economic evaluation. Furthermore, synthesised reactor systems are not simulated. Another drawback is that KBS does not suggest different alternative configurations of reactor systems.

2.5 Separator System Synthesis

Separation is used in chemical manufacturing processes to process and purify raw materials, intermediates and products. The separation of reactor effluents is of critical importance to the chemical industry. Separation system synthesis strategy is a more complex problem than the reactor system synthesis. It involves the selection of the methods and sequences of separating component mixtures into desired products.

Several books addressing separation systems design, and principles, as well as the synthesis of systematic methods from different professional backgrounds and perspectives have been published, such as Holland (1975); King (1980); Henley and Seader (1981); Lo et al. (1983); Mumphrey and Keller (1997); Petlyuk (2004); Wankat (2004); Mujtaba (2004); Seader and Henley (2006).

One of the early expert systems for separation systems synthesis was developed by Wahnschafft et al. (1991). They developed a systematic procedure and expert system called SPLIT, for separation system synthesis. Figure 2.12, illustrates the specification of the overall approach being realized in SPLIT which combines multiple knowledge bases into an integrated system with process simulation and mathematical optimization software for azeotropic separation.

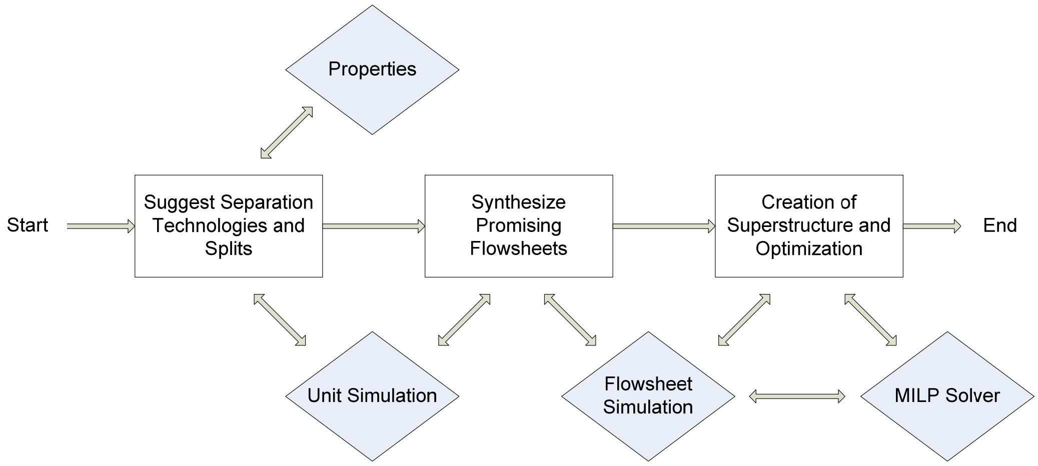


Figure 2.12: Specification of the integrated system for the synthesis of separation processes. (adapted from Wahnschafft et al., 1991)

SPLIT combines data-driven and goal-oriented strategies. The representations of the problem and the current state of the solution are embedded in the blackboard as several semantic hierarchies. This framework is used within several domain knowledge sources to invoke such external programs such as Aspen Plus and a mixed-integer nonlinear programming package for the analysis and optimization of partial and complete flowsheets. The system is designed to handle problem formulations on different levels of abstraction. SPLIT starts with decomposing separation problems into explicitly represented binary split tasks. A classification of the components according to a criterion such as molecular structure is used to identify abstract tasks. Once the species to be separated are specified in SPLIT, differences in their physical properties are determined and applicable separation technologies are proposed.

Drawbacks of SPLIT include the lack of sizing and economic evaluation of alternatives. Furthermore, the alternative separation does not include advanced separation techniques, or hybrid separation systems.

Another expert system for separation systems synthesis was developed by Brunet and Liu (1993). The expert system is called EXSEP. EXSEP applies the plan-generate-test approach to heuristically synthesise a separation system. The separation units considered in EXSEP are distillation, absorption, extraction and stripping. Therefore, only conventional separations are considered and no simulation, sizing or economic evaluation of alternative separations is included in their work.

One of the most important knowledge based approaches to separation system synthesis was proposed by Barnicki and Fair for liquid mixture separation (Barnicki and Fair, 1990) and gas-vapour mixture separation (Barnicki and Fair, 1992). Figure 2.13, illustrates the complete selection and hierarchy steps for their Separation Synthesis Hierarchy (SSH). SSH contains three types of task, separation sequencing manager, separation methods and MSA selector, and separation equipment designer. Their approach starts with dividing components based on their boiling points then selecting the separation technique based on the relative volatility, chemical family, thermal sensitivity, product purity, difference in freezing points, difference in polarities, and existence of an azeotrope. Most of these selecting criteria are considered in the proposed IKBS. The scoring system used in this work is only limited to suitable or not suitable separation technique. Therefore, no range of suitability is considered in evaluating each separator based on different criteria. In the proposed IKBS suitable separator are given 4 levels in the scoring system.

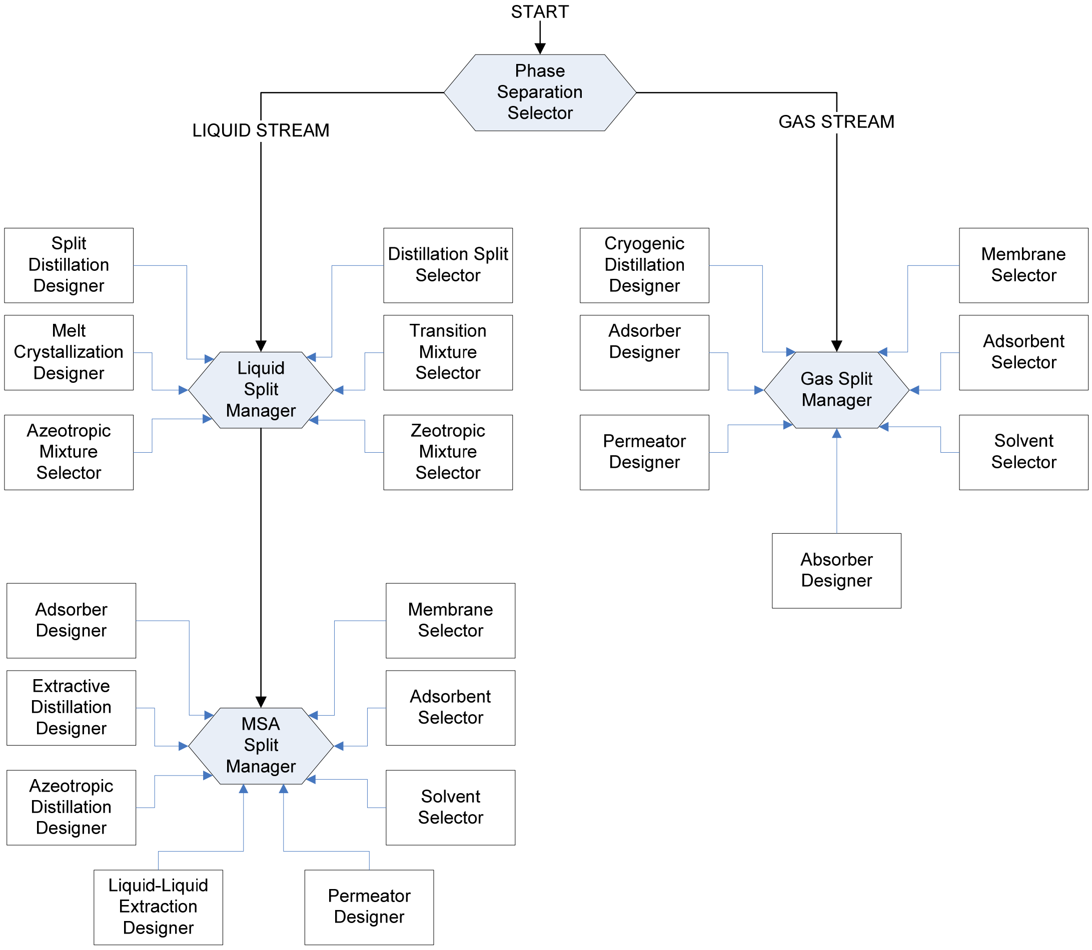


Figure 2.13: Separation synthesis hierarch by Barnicki and Fair. (Adapted from Barnicki and Fair, 1990)

Douglas (1995) has developed a hierarchical decomposition systematic procedure for the synthesis of separation system flowsheets. Only conventional separation techniques are considered. The separation system starts with phase separation followed by liquid and vapour separation.

A systematic procedure for environmentally benign separation process synthesis has been proposed by Kheawhom and Hirao (2004). As illustrated in Figure 2.14, the method combines the use of algorithmic and heuristic processing of symbolic and numeric data. The heuristic approach which applies experience-based rules and thermodynamic insights for selection of separation operations is used to reduce the complexity and the size of synthesis search space. The algorithmic approach is used to formulate and solve the remaining problems.

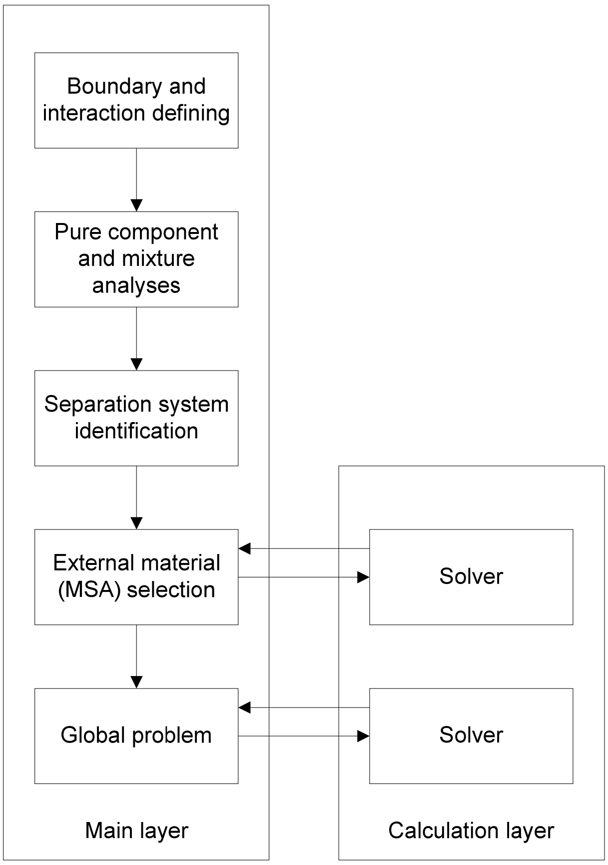


Figure 2.14: The diagram of the framework for environment benign separation process synthesis. (Adapted from Kheawhom and Hirao, 2004)

Other work involves the synthesis of separation processes using case-based reasoning was proposed by Seuranen et al. (2005). Their method is based on screening feasible separation process sequence alternatives by reusing the existing design cases. These approaches above do not simulate the separation process or size and evaluate economically the alternatives.

2.6 Conclusion

From the discussion of the previous research in chemical process flowsheet synthesis, it is clear that there are different types of approach:

1- Studying either reactor or separation systems in isolation such as Barnicki and Fair, (1992); Schembecker et al. (1995a,b); Jacobs et al. (2000a,b),
2- Superstructure optimization without proposing alternative type of reactors and separators such as Montolio-Rodriguez et al.(2007),
3- Synthesis of reactor-separator-recycle systems based only on heuristics such as Douglas (1988),
4- Synthesis with out using databases, or process simulation such as Lu and Motard (1985); Daichendt and Grossmann (1998),
5- Synthesis without flowsheet sizing, or economic evaluation such as Schembecker and Simmrock (1996),
6- Synthesis without process optimization such as Kirkwood (1987)
7- Synthesis without considering process safety and environmental impacts such as Linke and Kokossis (2003), and
8- Synthesis of reactor-separator-recycle systems using only conventional reactors and separators such as Han (1994).

It is important in any synthesis to account for the interaction between the reaction and separation systems instead of synthesising the reaction and separation systems in isolation. The power of mathematical process simulators and optimizers can help process engineers in analysing, evaluating and synthesising a total process flowsheet in a reliable and effective way. The sizing and economic evaluation of the simulated and optimized flowsheets can lead to proposing the best alternative which can be considered for further analysis.

The synthesis of reactor-separator-recycle systems using heuristics and mathematical methods has not yet been fully investigated. This could be achieved by using heuristics based on industrial experience and by using third-party software such as process simulation, process optimizer, flowsheet sizing and economic evaluation in addition to databases of safety and environmental information, physical properties, azeotropes, mass separating agents and chemical prices. This proposed integrated approach and the software developed are discussed in the subsequent chapters.

Chapter 3

Structure of the Integrated Knowledge Based System

3.1 Introduction

The technology of Artificial Intelligence (AI) provides an efficient approach to the implementation of process synthesis. Artificial Intelligence is needed in process design as the process synthesis deals with many diverse knowledge representations, and integrates software packages for different functions. Expert systems are probably the most practical application in the field of artificial intelligence. Because of the emphasis on knowledge rather than on numerical computation, expert systems are often known more appropriately as knowledge based systems (KBS). KBS is a computer program that encodes symbolic knowledge about domains and tasks, and then solves problems by manipulating this knowledge using qualitative techniques (Howe-Grant and Kroschwitz, 1999). The proposed Integrated Knowledge Based System (IKBS) can also solve design problems using quantitative techniques as explained in the subsequent chapters. A knowledge based system can also be essentially defined as a computer program that has a specialised knowledge about a specific area and solves a specific class of problems using the knowledge (Han et al. 1996a).

Knowledge based systems support human decision-making, learning and action. Human experience can be scarce, expensive, fallible and inconsistent. The knowledge base can be constructed in such way that it maps the systematic procedure for process flowsheet synthesis. The human usually interacts with the knowledge based system by monitoring the design process, providing decisions and values which the program requests.

The five roles of the knowledge based approach, as suggested by Stephanopoulos and Han (1996b), are to:

1. represent and preserve knowledge using various knowledge schemes
2. clone represented knowledge
3. identify inconsistencies and conflicts and, test represented knowledge
4. incorporate various forms of knowledge into a single system
5. export knowledge by copying and sending a KBS to other places

The development of knowledge based expert systems has been progressing over the last four decades. There have been six main application areas of knowledge based systems in chemical engineering (Quantrille and Liu, 1991): fault diagnosis, process control, process design, planning and operations, modelling and simulation and, product design, development and selection. Process design is much more complicated than the other engineering application in the following aspects (Wang et al., 1994):

1. multiplicity of design results and uncertainty of objectives
2. multiple levels and objectives of design tasks
3. integrated AI environment for alternately performing computation and inferences
4. multiplicity of knowledge representation and problem solving strategy

A knowledge based system can be considered for a particular application when development is possible, appropriate and justified. The previous effort over the past four decades led to computer aided design (CAD) environments that support various tasks during the synthesis development of a chemical process flowsheet. Figure 3.1 shows the typical computer aided design environment.

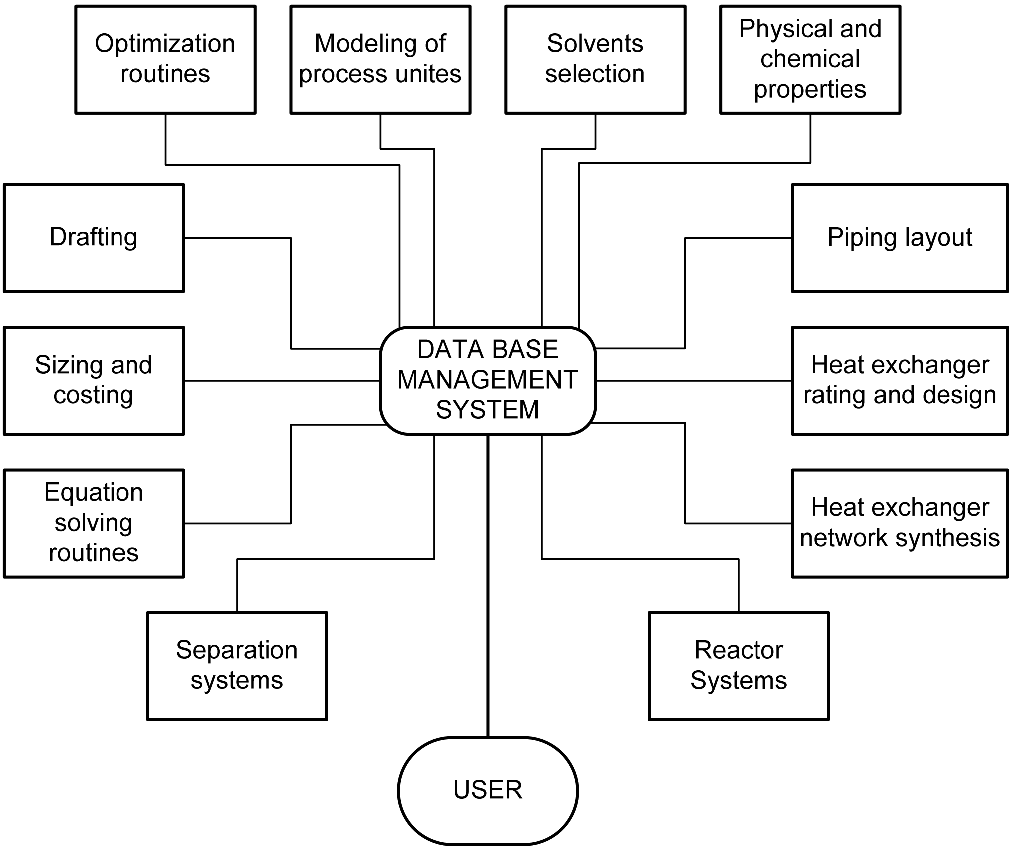


Figure 3.1: Typical computer-aided design environment. (modified from Stephanopoulos and Han, 1996b)

In a knowledge based system for process design applications, heuristic rules can be used to identify units required in the process and connections between them. Then calculations provide a quantitative analysis of the flowsheet. The design engineer can execute various design tasks by invoking a series of tools such as equation solvers, optimization routines, physical property estimation techniques and a list of solvents. The design tasks can be reactor and separator selection, heat exchangers design, and the design of individual process units, sizing, and costing. The computer structure of tasks during the synthesis of a process flowsheet can be very large and complex for design engineers to document and undertake. By using the proposed integrated knowledge based system, the process can be mechanized to perform the design procedure and emulate the design methodology.

3.2 The Integrated Knowledge Based System Structure

The proposed Integrated Knowledge Based System (IKBS) contains the following main parts: a knowledge base, an inference engine, a user interface, process simulator, flowsheet optimizer and process economic evaluator. In this study Excel and Excel Visual Basic for Application (VBA), and Aspen HYSYS process simulation package are used to synthesise reactor-separator-recycle systems.

The HYSYS Optimizer, Aspen Open Simulation Environment (OSE) and Aspen Icarus Process Evaluator (IPE) are suggested for the second phase of the software development to obtain a rigorous design and sizing of flowsheet units, and to estimate the cost of alternative flowsheets. The developed system can be used as tool to obtain a first estimate of the design condition and to perform a rapid screening of different alternatives. This structured method allows systematic identification of the most economical process flowsheet.

The structure of IKBS for chemical process flowsheet synthesis is illustrated in Figure 3.2. Microsoft Excel and Excel programming language, Visual Basic for Application, are used as the backbone of the developed integrated knowledge based system. Excel VBA expert system is being used as a decision support system and to develop the process flowsheet.

In the IKBS, the user communicates with the system using the user interface in Excel. An example user interface using Excel is shown in Figure 3.3, where the user can select from a drop-down list of the species involved in the reaction equation and provide other required input information to synthesise chemical processes.

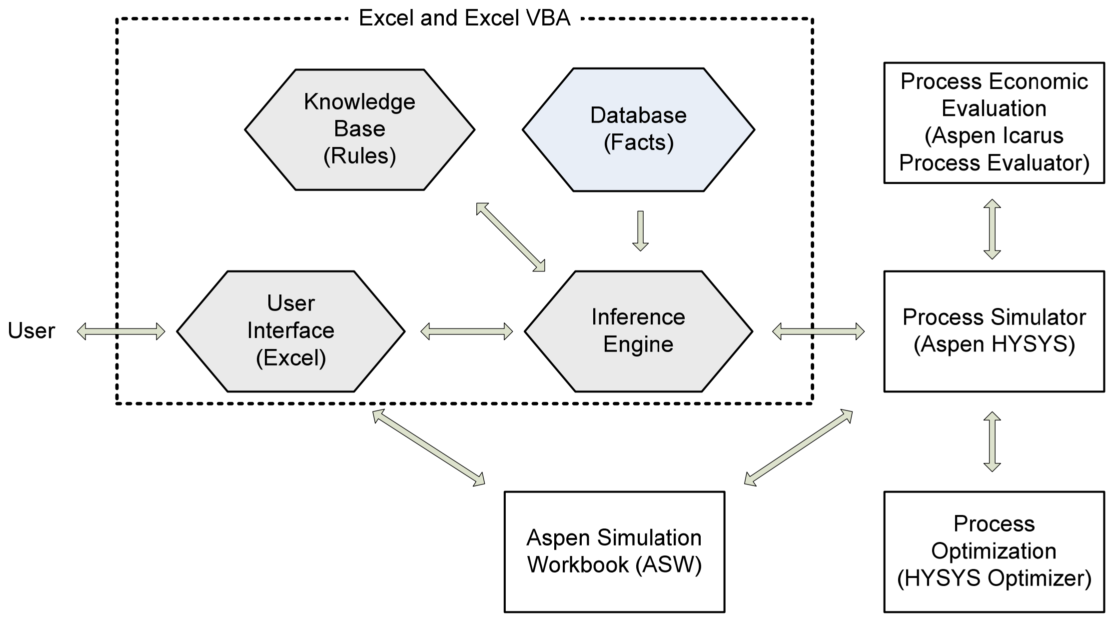
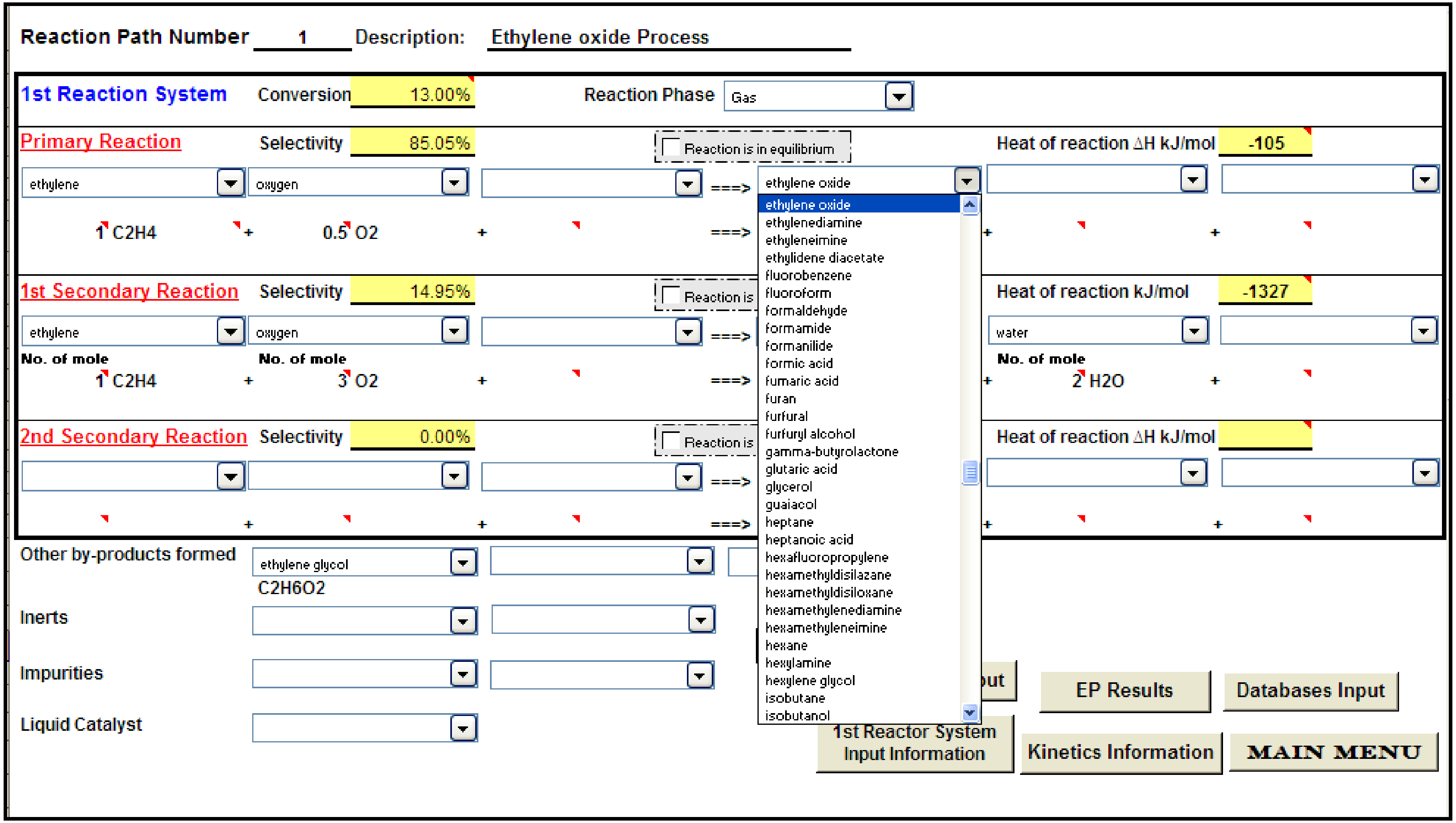


Figure 3.2: Structure of the Integrated Knowledge Based System (IKBS).

General heuristic rules can be gathered from chemical process engineering experience, textbooks, process evaluation reports, existing plant information, published papers and patents. Knowledge-based rules are used to interpret the physical and chemical nature of species used in the process and rules to generate potential reactor-separator-recycle system options and eliminate the less adequate options. Other rules are used to determine the heuristic ranking of the chemical process unit operation options and provide an estimate of their efficiency.

The database of facts invoked by the rules includes the fact list, which contains the data from which inferences are derived. The knowledge-base contains all the rules used by the expert system. The inference engine infers by deciding which rules are satisfied by facts, prioritises the satisfied rules, and executes the rule with the highest priority. In each level of the synthesis, the user is guided in a step by step manner to generate process alternatives.



Reaction Path Number 1 Description: Ethylene oxide Process

1st Reaction System Conversion 13.00% Reaction Phase Gas

Primary Reaction Selectivity 85.05% ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol -105

ethylene | oxygen | ===> ethylene oxide

1 C2H4 + 0.5 O2 + ===> + +

1st Secondary Reaction Selectivity 14.95% ☐ Reaction is Heat of reaction kJ/mol -1327

ethylene | oxygen | ===> water

No. of mole 1 C2H4 + No. of mole 3 O2 + ===> + No. of mole 2 H2O +

2nd Secondary Reaction Selectivity 0.00% ☐ Reaction is Heat of reaction ΔH kJ/mol

+ + ===> + +

Other by-products formed: ethylene glycol C2H6O2

Inerts

Impurities

Liquid Catalyst

Figure 3.3: Example of user interface in Excel.

Aspen HYSYS chemical process simulator is used in this IKBS as a design tool in the development of chemical flowsheets and is considered as a means to evaluate different design options and to calculate the mass and energy balances. Aspen Simulation Workbook (ASW) can be used as another tool for interfacing Aspen HYSYS with Excel worksheets. HYSYS Optimizer is being used as a flowsheet optimizer to determine the near optimal operating conditions of a presented flowsheet.

Aspen Icarus Process Evaluator (IPE) is a tool to extend the results of Aspen HYSYS to generate rigorous unit operation sizing and estimates the capital and operating costs for more detailed costing analysis. This structured method allows systematic identification of the most economical process flowsheet. Detailed discussion of the integrated knowledge based system components are here.

3.3 Excel Visual Basic for Application (VBA)

An expert system is a computer program that uses expert knowledge to reach a level of performance in a particular domain. This computer program is intended to model human expertise or knowledge. The design rules used in expert systems are based on experience and judgment. Expert system tool is a language plus associated utility programs to facilitate the development, debugging and delivery of application programs (Giarratano and Riley, 2005).

In the research, two Expert system tools, CLIPS (C Language Integrated Production System) and Excel VBA, were evaluated to provide the basic elements of the integrated knowledge based system.

CLIPS is an expert system tool that provides a complete environment for developing expert systems which includes features such as a debugging tool and an integrated editor. CLIPS was developed by NASA at the Johnson Space Centre. Since its first release in 1986, CLIPS has undergone continual improvement and refinement (Giarratano, 2002). CLIPS is essentially a forward chaining system where the left hand side of the rules is matched against the facts. Figure 3.4, illustrates a general form of a CLIPS rule. There are three ways to represent knowledge in CLIPS by using: rules, generic functions and object-oriented programming. Rules are primarily intended for heuristic knowledge based on experience where the object-oriented programming and generic functions are primarily intended for procedural knowledge. The CLIPS tool provides the basic elements of an expert system. These elements are the database which contains the fact list where the knowledge base contains all rules. The inference engine controls overall execution of rules.

```
(defrule     Rule-Name
    "Optional Documentation String"
   (condition-I)    ;The left-hand side is composed of
   (condition-2)    ;zero or more conditions
   (condition-D)    ;each enc1osedinparentheses
=>
   (action-1)     ;The right-hand side is composed of
   (action-2)     ;zero or more actions
   (action-n)  )
```

Figure 3.4: General form of a CLIPS rule.

Due to the difficulties in conducting a substantial amount of design calculations which are required for the design decision making as well as the problem of linking CLIPS with the process simulation software, CLIPS was found to be less suitable than the MS Excel and Excel VBA.

Visual Basic for Applications (VBA) is an implementation of Microsoft's Visual Basic which is built into all Microsoft Office applications. VBA can be used for rapidly customising and integrating other software package applications with existing data and systems. It provides a complete integrated development environment (IDE) that features the same elements familiar to developers using Microsoft Visual Basic, including project and properties windows, and, debugging tools. VBA also includes support for Microsoft Forms, for creating custom dialog boxes, and ActiveX Controls, for rapidly building user interfaces. VBA can be used to create a user defined function (UDF) for use in a Microsoft Excel workbook. VBA also provide the technology for tailoring applications, and adding features and functionality specific to the requirements (Walkenbach, 2004).

VBA provides a way to invoke a large number of built-in procedures as well as writing add-in procedures. Spreadsheets can be used to integrate ordinary differential equations and partial differential equations. Excel also adds important features to these capabilities through its Goal Seek command for algebraic equation root finding and Excel Solver procedure for nonlinear equation set solution and optimization (Rosen and Partin, 2000).

A program written in Excel VBA may consist of rules, facts, and objects. The inference engine decides which rules should be executed and which rules are satisfied by facts. A rule-based expert system written in Excel VBA is a data-driven program where the inference engine stimulates execution of facts and objects. Excel VBA inference engine uses inference mechanisms to process the knowledge and arrive at a conclusion.

There are three major components of the expert system: dialog structure, inference engine and knowledge base (Liebowitz, 1995). The dialog structure is the user interface of the expert system that allows the user to interact with the expert systems components. The inference engine is the control structure of the expert system that allows the expert to use search strategies to test different hypotheses. The knowledge base is a set of facts, rules and heuristics about the expert system domain. The knowledge base is the most important component of the expert system as the power of the expert system lies in its knowledge. Therefore, the performance of a system depends on how good the knowledge is. Excel VBA expert systems can be integrated with other systems, like databases, simulators, existing information systems and other sub-systems.

In rule based expert systems, the knowledge base is composed of two structures, facts and rules. Facts define a piece of information that is known to be true, whereas rules are (if/then) statements that define the set of facts that must be true before a set of actions can be executed. In other words, the if/then statement is used in VBA to execute a block of code if a specified logical condition is true. Moreover, it can execute another block only if the condition is false.

Multiple conditions can be checked using the “ElseIf” keyword. According to Aitken (2003), when the multiple conditions are encountered during execution, each condition is tested starting from the top and when the block code associated with the first true condition is executed, then execution passes to the code after the “End If” statement. In case no condition is true, the block of code associated with the Else keyword is executed. Figure 3.5, illustrates VBA syntax for multiple conditions rules.

```
Sub Rule-Name()

 '
 '      Optional Documentation String
 '
     If condition-1 Then
          block-1
     ElseIf condition-2 Then
          block-2
     …
     …
     …
     ElseIf condition-n Then
          block-n
     Else
          block-else
     End If
End Sub
```

Figure 3.5: General form of a VBA decision function with multiple conditions.

The two main inference methods used in expert system problem solving strategies are forward and backward chaining. A chain is a group of multiple inferences that connect a problem with a solution. The chain is called a forward chain when it is searched from problem to solution, or it can be described as reasoning from facts to the conclusions. Backward chaining is reasoning from conclusions to facts. For more specific needs other inference methods can be used, such as backtracking, hierarchical planning, means-ends, constraint handling, plan-generate-test, least commitment principal and problem reduction. The forward chaining is suitable for solving design problem in the proposed IKBS. The user provides information on the process (facts) and then the IKBS do the reasoning and suggest a set of suitable reactors and separators (conclusion).

Raman and Grossmann (1991) demonstrated that expert systems using either forward or backward chaining search techniques can miss solutions if heuristics conflict. This is because expert systems search for a single path to a goal (Flowers et al., 1994). The first such path identified by the expert system represents the solution.

VBA code has been written to link Excel to Aspen HYSYS process simulator as illustrated in Appendix A. Using the developed VBA programming code, users can for example change the makeup feed temperature, pressure and flowrate in the Excel worksheet. Furthermore, users can also change and explore the effect of reactor feed temperature. These variables are exported to Aspen HYSYS and subsequently run the simulation case. Then, the new results from Aspen HYSYS are imported to Excel worksheet.

The decision to use the Microsoft Excel and Excel VBA expert system to implement the knowledge based portion of the project was based on the following advantages:

1. the nature of process flowsheet development suggests a forward chaining inference engine which can be established using VBA
2. the availability of the decision functions in VBA, which are the backbone of chemical processes synthesis decision making approach
3. the databases can easily be constructed using MS Excel spreadsheets
4. the possibility to perform calculations easily using MS Excel spreadsheets
5. VBA has the capability to develop simple and user-friendly interfaces which provides an effective way of communication between the program and the user
6. Microsoft VBA is widely available as it is built into all MS Office applications
7. debugging in VBA is much easer than many other programming languages/expert system tools such as CLIPS
8. the possibility to integrate other software such as Aspen HYSYS which even can be customised using VBA (Aspen Technology, 2006a).

Table 3.1, illustrates the computer specification required by Excel 2003.

Table 3.1: Excel 2003 system requirements. (Adapted from Microsoft, 2008)

Component	Requirement
Computer and processor	Personal computer with an Intel Pentium 233 MHz or faster processor (Pentium III recommended)
Memory	128 MB of RAM or greater
Hard disk	150 MB of available hard disk space; optional installation files cache (recommended) requires an additional 200 MB of available hard disk space
Drive	CD-ROM or DVD drive
Display	Super VGA (800 × 600) or higher-resolution monitor
Operating system	Microsoft® Windows® 2000 with Service Pack 3 (SP3), Windows XP or later

3.4 Databases

Process synthesis, design and optimisation depend on availability and reliability of property data for the mixtures involved. The selection of an appropriate unit operation is determined by there being specific differences in the components which are quantified in term of physical property data. Sizing calculations of the selected equipment involves physical property data of the components. To carry out an efficient process synthesis, it is important to avoid duplication activity by considering the use of existing knowledge and exploiting it. Therefore, it is important to make use of both internal and external databases.

Excel VBA has the capability to import data from other applications inside Excel and from external databases into the spreadsheet. There are four fundamental data manipulation operations that can be performed on the data in a data source. These are: retrieving existing data, adding new data, modifying data and deleting data. Data manipulation operations are performed on the data source by passing plain text SQL (Structured Query Language) statements directly to the data source using ADO (ActiveX Data Objects) (Bullen et al., 2005).

The integrated knowledge based system, makes use of available databases such as the Knovel® Library database which has been used as an internal database within Excel. The internal databases incorporated in the integrated knowledge based system include a list of possible azeotropes, mass separating agents, chemical prices, safety and environmental impacts, and general physical properties.

An initial chemical prices database has been created in Excel using the Chemical Marketing Reporter prices. These prices may not reflect the market situation at a particular location. However, it can be used for the primary economic evaluation. Price forecast can be used to predict the future prices based on the market history. This technique may not be always reliable in the present volatile oil market.

Toxicity data for raw materials, products, by-products, mass separating agents and any other intermediates incorporated in the process design can be obtained using environmental and safety databases. A number of common chemicals have severe toxic effect to humans and the environment and need to be avoided in the process. One source of data on chemical toxicity is the Toxic Chemical Release Inventory (TRI) which is maintained by the US Environmental Protection Agency (EPA) (Seider et al., 1999). The database contains information on over 600 chemicals.

Another source is provided by the National Fire Protection Association (NFPA). These chemicals are tabulated by Wood (1995b). Chemicals are rated based on three categories, “Hazard to Health”, “Flammability Hazard”, and “Reactivity and Stability Hazard”. The rating system is from 0 to 4, where “0” minimal hazard, “1” slight hazard, “2” moderate hazard, “3” serious hazard, “4” severe hazard. The health and flammability hazard category helps in choosing from a list of possible competing agents in the process. The Reactivity and Stability Hazard rating is the most useful information as it may effect the overall design decision The NFPA ratings provide less quantitative source of information under chemical flammability hazard compared with the Knovel® Library database, which lists the flash point, lower and upper flammability limits, and autoignition temperature.

The accuracy of a process simulation depends strongly on the thermodynamic models used to describe the physical behaviour of the process chemical species. To achieve this model needs both reliable property data as well as a full featured data regression package. Extensive database for over 1,000 components are provided by many process simulators such as Aspen HYSYS which is used in this proposed integrated knowledge based system. Database in Aspen HYSYS can be accessed by the IKBS using VBA programming code or using Aspen Simulation Workbook (ASW). Imported data can be saved in Excel in the form of tables in the worksheet.

Examples of the type of data which are important for process synthesis activities include: material properties, physicochemical data, and cost of chemicals. Basic properties such as molecular weight, liquid/gas density and viscosity, heat capacity, vapour pressure, enthalpy, entropy normal boiling point, melting point, etc. which are often available at 20 ^{o}C. Furthermore, as phase equilibria is one of the most important data in chemical process design, the DECHEMA data bank is an example of a database that can be used to provide vapour-liquid and liquid-liquid equilibrium data. In the DECHEMA data bank each set of data has been regressed to determine interaction coefficients for the binary pairs to be used to estimate liquid phase activity coefficients (Seider et al., 2003). Yet when developing a chemical process, phase equilibrium data needs to be calculated at temperature and pressure ranges anticipated in order to obtain reasonable predictions of the phase conditions and separations of a specific mixture. Therefore, physical property data must be presented in the form of parameters.

One of the world largest databases collections is the DETHERM®. The DETHERM® database consists of several packages as illustrated in Table 3.2.

Table 3.2: Packages of the DETHERM database. (adapted from Westhaus et al., 1999)

Package name	No. of data tables	Contents
DDB, The Dortmund Database	245,000	Vapour–liquid equilibria of normal and low substances and electrolytes, liquid–liquid equilibria, activity coefficients at infinite dilution, gas solubilities, solid–liquid equilibria, azeotropic data, excess properties, pure component data
ELDAR, Electrolyte data collection	50,622	Densities, heats of solution, heat capacities, molar volumes, osmotic coefficients, solubilities, vapour pressures, electric conductivities, viscosities, dielectric properties, etc.
INFOTHERM, Thermophysical database	71,272	PVT-data, transport and surface properties, caloric properties, phase equilibria VLE, GLE, LLE, SLE , basic data.
COMDOR, Thermophysical parameters	20,131	Phase equilibria VLE , excess enthalpies, transport and surface properties, caloric and acoustic data
C-DATA, Data collection Prague	7,043	20 physico-chemical properties for 593 components
BDBB, Base database Bohlen	18,041	Propertyrconstant matrix with 24 fields for 1126 components
OTHERS, Several smaller packages	208,671	Chebyshev-and Antoine-constants, transport properties, caloric data, PVT-data, critical data

The packages are property-oriented, and produced and maintained by external experts. DETHERM® is an acronym for DECHEMA thermophysical property database. Example of the data available in DETHERM® include: phase equilibria (vapour–liquid, liquid–liquid, gas–liquid, solid–liquid), azeotropic data, vapour pressures, critical data, heat capacities, enthalpies, entropies, densities, activity coefficients, compressibility, viscosity, thermal conductivities, diffusion coefficients, surface tensions etc. (Westhaus et al., 1999).

There are three possibilities to access the DETHERM® database: online via the STN International database hosts, in-house with a locally installed system, or with the DETHERM® Internet client via internet connections. Parts of the data from the DETHERM® database are also published in printed form as the ‘DECHEMA Chemistry

Data Series'. In the online access, users can either initiate a terminal session or use a graphical interface under Windows. Users can also export the retried data to excel. The in-house version can also export and import files to various data format. The database is updated yearly and grows with around 8% yearly. DETHERM® contains 5.88 million data sets for around 26,500 pure components and 101,300 mixtures are stored (Westhaus and Sass, 2004).

The data may be downloaded in a variety of different formats optimized for either direct viewing (HTML) or for direct usage in process simulation packages such as ASPEN HYSYS, or data regression tools such as the DECHEMA Data Preparation Package. The DECHEMA Data Preparation Package inks the raw thermophysical data such as in the DETHERM® database and model based process simulation such as Aspen Plus® and Aspen HYSYS®. Figure 3.6, illustrates the five main components of DECHEMA Data Preparation Package. The GUI links the end user and the system. The Data Preparation Package CORE manages the transfer of information between the different components.

The Graphics Subsystem allows graphical representation of measured raw data and model derived data in different plots. The Neutral File Interface is able to read and write raw thermophysical data and model parameters in the neutral IK-CAPE PPDX format. Regressed model parameters can be exported to a file and loaded from the targeted process simulation package. Any thermodynamics module having an open interface can be used with Data Preparation Package utilizing the THERMO interface. The optimizer is the backbone of the Data Preparation Package system. During optimization the property calculation is performed with help of the external thermodynamics package, using the thermo interface (Westhaus and Sass, 2004).

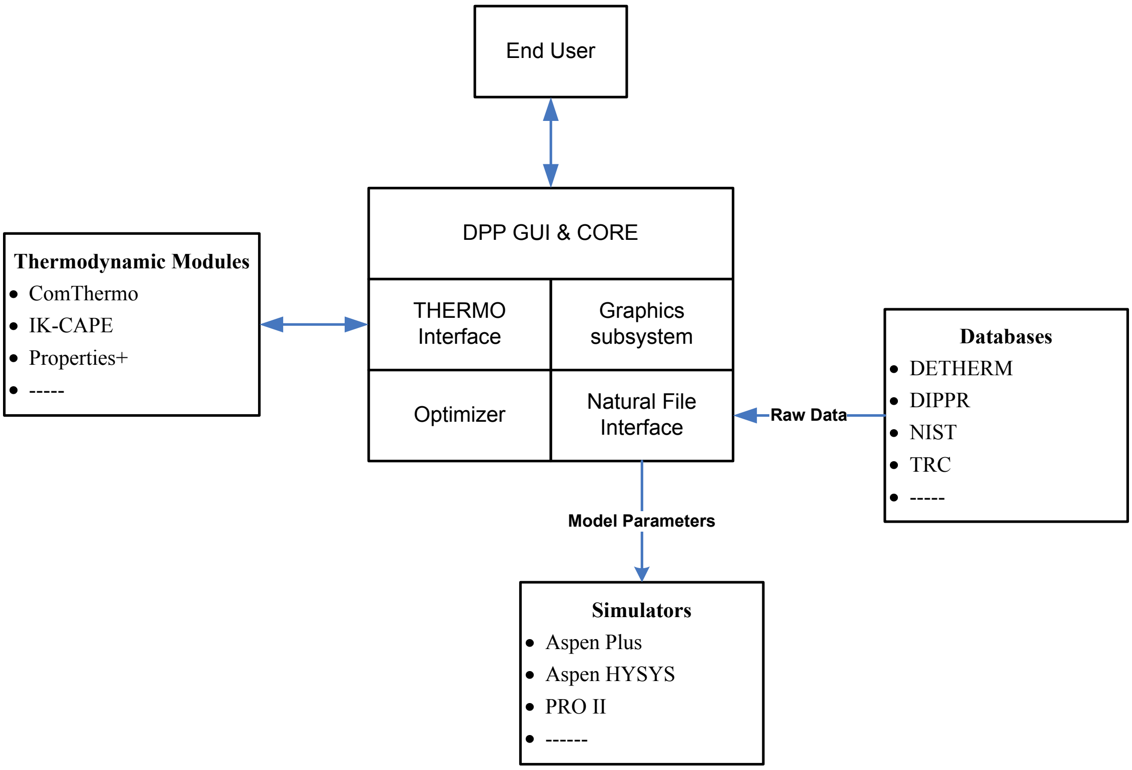


Figure 3.6: General Architecture of DECHEMA Data Preparation Package. (modified from Westhaus and Sass, 2004)

A large number of organisations have developed computer based data banks. Some of the data banks which are commercially available are tabulated in Table 3.3. Among the data banks in Table 3.2, DECHEMA retrieval bank and Dortmund data bank (DDB) contain stored measurements with source reference, whereas most of the other data banks consist of collections of parameters limits without measured data or source references (Wells and Rose, 1986).

Table 3.3: Thermophysical properties databanks. (adapted from Resnick, 1981; Wells and Rose, 1986)

Data bank	Organisations
ASPEN-PLUS, HYSYS	AspenTech, Boston, USA
APPES	AIChE, New York, USA
CHEMCO	EURECHA, E.E.H., Zurich, Switzerland
CHESS	Washington University, Washington, USA
DATABANK	Imperial Chemical Industries, London, UK
DDB	Dortmund University, Dortmund, Germany
DSD, SDC, SDR	DECHEMA, Frankfurt, Germany
EPIC	University of Liege, Liege Belgim
FLOWTRAN	Monsanto Company, St. Louis, USA
NEL-APPES	National Engineering laboratory, Glasgow, UK
PHYSCO	Milan Polytechnic, Milan, Italy
PPDS	Institution of Chemical Engineers, Rugby, UK
PROPDAD	University of Connecticut, Storrs, Connecticut
TISDATA	Dutch State Mines, Mausstricht, Nederlands
TRC/API	Texas AandM University, College Station, Texas, USA
TRL	Washington University, St Louis, Missouri, USA
UHDE SDC	Uhde, Frankfurt, Germany

3.5 Aspen HYSYS Process Simulator

Process simulation is the representation of a chemical process by mathematical models as a computer program. By solving the model, information about the process performance can be obtained. Since the first process simulator was published in 1958 (Resnick, 1981), process simulators have been widely used as useful tools in process design and synthesis. Process simulators can create a rigorous steady state and dynamic model for plant design and troubleshooting. In process design, computer-aided process design programs often are referred to as process simulators, flowsheet simulators, or flowsheet packages (Seider et al., 2003).

Process simulation software structure consists of four essential parts (Bumble, 2000):

1. user interfaces
2. execution program
3. thermodynamic unit operations
4. constants, databases , and equations

Figure 3.7, illustrates the structure of a typical process simulator. Users input the data, using the software interface, such as stream temperature, pressure and composition, and design parameters such as distillation column number of stages, volume of reactor, and pressure drop in process units. The execution program takes the user input information and follows the instruction to control the calculation sequence and convergence routines to find a solution in which all recycle loops and process unit have converged and all user specifications have been met. The thermodynamic unit operations, the chemical, physical and thermodynamic properties are calculated.

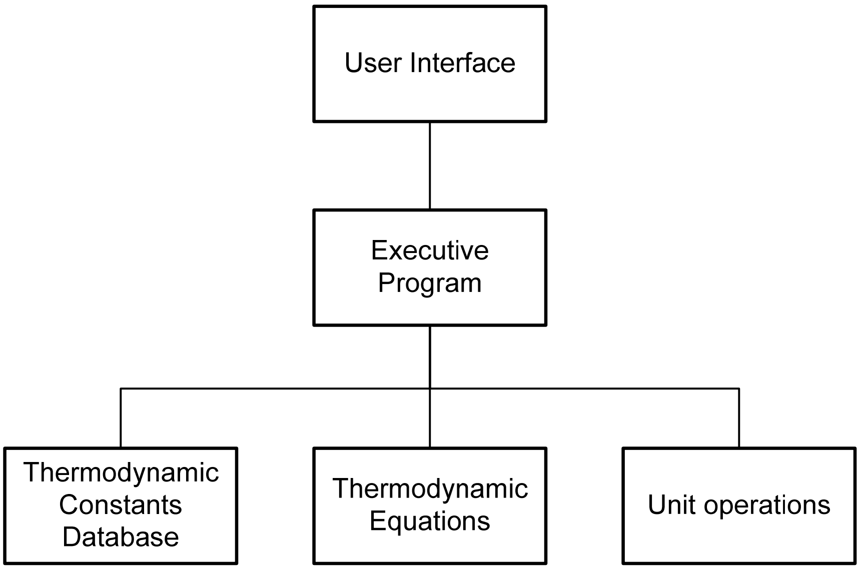


Figure 3.7: Structure of process simulators. (adapted from Bumble, 2000)

There are two types of simulation, the sequential modular and simultaneous equation. The sequential modular simulators are more commonly used simulators. The sequential modular approach sequentially calculates modules. It performs the unit operation calculations based on the process feed input information. The output is the conditions of the calculated outlet streams and the unit operation information such as size and duty etc. The input to the subsequent unit is the outlet from the previous unit operation. Thus the calculations process sequentially. If recycle streams are present, the user is required to provide an initial estimation of the stream specifications. The simulator calculates around the loops and revises the input streams value until the input and output streams match. This means the sequential simulators first converge individual unit operations and then seek to converge recycle loops. The main disadvantages of sequential modular approach are (Vogel, 2005):

- Convergence problems in flowsheet with many recycle streams,
- Incomprehensible convergence behaviour in large flowsheets
- Slow convergence of large flowsheets with many recycle streams and complex design specifications. However, recycle sequence can be selected.

Simultaneous equation simulators, combine the equations for the linking of flowsheet and units model in a matrix which are then simultaneously solved. As in the sequential modular approach, substance properties and phase equlibria are solved by subprograms. The main advantage of the simultaneous equation approach is that it gives optimum and fast convergence behaviour in flowsheet with many recycle streams. The disadvantages of simultaneous equation approach are (Vogel, 2005):

- Requires large storage space
- Difficult to find errors
- No insight into the process units
- The necessity to specify initial values

The major simulation packages used in the chemical industry includes: Aspen PLUS, SPEEDUP, DYNAPLUS, SPLIT, ADVENT, ADSIM, HYSIM, HYSYS, HYCON by Aspen Technology Inc., PRO/II, PROVISION, PROTISS, HEXTRAN by Simulation Sciences Inc., ProMax by Bryan Research and Engineering Inc., and CHEMCAD by Chemstations Inc.

Despite the significant progress that has been made in process simulations since the 1960s, there are some limitations that still require remedies. Examples include membrane separation, adsorption, ion-exchange, crystallization, reactive separation, and non-ideal reactors models need to be added to the unit operation library. Equilibrium calculations need to be extended to handle solid phases.

gPROMS is a hybrid modelling and simulation software for process flowsheet simulation and optimization. Tanvir and Mujtaba (2008) indicated that gPROMS provides an easy and flexible platform to build a process flowsheet graphically and during simulation and optimization the corresponding master model automatically connects individual unit model equations. Most commercial process simulators can only simulate conventional reactors and separators, gPROMS can be used to simulate and optimize advanced reactors and separators.

Aspen HYSYS process simulator is a comprehensive flowsheeting tool that is used to screen alternative designs and to examine the effect of parametric changes on the entire process. It is also used to model existing plants to ensure equipment is performing to specification and to perform mass and energy balances. It can be used to provide depth of knowledge about complete system behaviour and facilitate cost calculations (Aspen Technology, 2006a). Rigorous material and energy balance calculations using detailed equipment models will be carried out to determine flow rates, composition, and energy flow for all streams in the process.

Aspen HYSYS which is being used in the integrated knowledge based system is an interactive, object oriented program and event-driven graphical environment. Aspen HYSYS uses subroutines, or procedures, to model the conventional process units operations. It differs from the other simulators in two respects (Seider et al., 2003): the first, Aspen HYSYS has the facility for interactively interpreting commands once they are entered; whereas the other simulators require the user to run the simulation each time when the new entries are completed. The second aspect is that Aspen HYSYS has a unique feature that information propagates in both forward and reverse directions. These two features make Aspen HYSYS process simulator very fast responding and relatively easy to use.

There are four interfaces in Aspen HYSYS:

1. process flow diagram for construction of the simulation process flowsheet
2. workbook, which is a collection of pages to display information in tabular form similar to a spreadsheet
3. property view, which is collection of pages that contain information about the flowsheet objects such as stream or process units
4. summary view, which displays a list of all currently installed streams and process units

As Aspen HYSYS is an integrated simulation environment and fully object-oriented software design, it is fully Object Linking and Embedding (OLE) compliant which allows for complete user customization. Through a completely transparent interface, the OLE extensibility lets the design engineer perform the following (Babu, 2004):

- Develop customized steady state and dynamic unit operations
- Specify proprietary reaction kinetic expressions
- Create specialised property packages using HYSYS customization extensibility method

The automation features within Aspen HYSYS expose many of the internal objects to other OLE compliant software such as Excel, Visual Basic and Visio. By using industrial OLE automation and extension, the user can customize the simulation. This open architecture allows the user to extend the simulation functionality in response to the changing needs of the design.

Table 3.4, illustrates the hardware requirement for Aspen HYSYS and Icarus. It is recommended to select the fastest CPU and to use at lease 1 GB or higher physical memory for the proposed generic flowsheet. According Aspen Ltd, Aspen HYSYS 2006 and Icarus have been tested on Windows 2000 and Windows XP. There is no significant speed difference with different operating systems.

Table 3.4: Aspen HYSYS and Icarus hardware requirements. (adapted from Aspen, 2006a)

Resource	Recommended Requirements
CPU	Intel Pentium III 866 MHz (or faster) processor.
Monitor	A colour monitor with 1024 x 768 resolution.
Physical Memory	256-512 MB; 1 GB or higher for large plant models.
Hard Disk Space	Up to 2.0 GB of free disk space, depending on which Aspen products are installed; 200 MB for system components on the Windows drive.
Virtual memory	1 GB consisting of physical memory and swap file.
	Large plant models or multiple open applications may require additional virtual memory.
Pointing device	A mouse or other pointing device.
DVD drive	Available on the local PC or through the network during the installation.
Licensing	Software License Manager (SLM) requires a network adapter to connect to a license manager server. A parallel port or USB port is required if the software is to be run in a standalone configuration.

3.6 Aspen Simulation Workbook (ASW)

Aspen Simulation Workbook (ASW) is a tool for interfacing Aspen HYSYS process simulation models directly to MS Excel worksheets. This allows modelling experts to develop simple and user-friendly interfaces to process models. The model end user can run models and view key model predictions in Excel. ASW also allows model variables to be linked to tables in an Excel worksheet through the ASW organizer. The resulting Excel worksheets can be used to run “what-if scenario” (Aspen Technology, 2006d).

Due to licensing difficulties, the ASW was not implemented. However a VBA program was written to link Aspen HYSYS flowsheet to Excel as illustrated in Appendix A. Appendix A, is only a short form of the more complicated developed VBA code which covers currently 43 streams of the more that 300 streams in the generic flowsheet. The written VBA program can be further developed to provide similar capability to ASW.

3.7 Flowsheet Optimization

Once the flowsheet is developed, it can be optimized to meet the objective function and take in consideration of the constraints. Linear and nonlinear programming optimization problems, and mixed integer nonlinear programming (Seider et al., 2003; Aspen Technology, 2006e) can be solved using HYSYS Optimizer. In the current phase of the software development, HYSYS optimizer was not implemented. There are five modes of optimizer in HYSYS, Original, Hyprotech Sequential Quadratic Programming (SQP), MDC Optim, DataRecon and Selection Optimization (Aspen Technology, 2006e). The Original mode is the most common optimization on HYSYS.

The optimization schemes for the Original Optimizer includes five types of built-in algorithm, BOX, Mixed, SQP, Fletcher-Reeves, and Quasi-Newton methods. The Box, Mixed and SQP methods are available for constrained minimization or maximization with inequality constraints. Equality constraints can only be handled by the Original and Hyprotech SQP methods. The Fletcher-Reeves and Quasi-Newton methods are available for unconstrained optimization problems. The capabilities of the five optimization schemes are summarized in Table 3.5.

Table 3.5: Summary of the optimization schemes for the Original Optimizer. (adapted from Aspen Technology, 2006e)

Method	Unconstrained Problems	Constrained Problems: Inequality	Constrained Problems: Equality	Calculates Derivatives
BOX	X	X		
Mixed	X	X		X
SQP	X	X	X	X
Fletcher-Reeves	X			X
Quasi-Newton	X			X

3.8 Aspen Icarus Process Evaluator (IPE)

Cost estimation can have a significant impact on project profitability and process synthesis alternatives evaluation. Aspen Icarus Process Evaluator (IPE) is a software system provided by Aspen Technology Inc. for economic evaluation of process designs. Aspen IPE extends the results of process simulation, generates rigorous size and cost estimates for processing equipment, performs preliminary mechanical designs and estimates purchase and installation costs, indirect costs, the total capital investment, the engineering, procurement, construction and profitability analyses (Seider et al., 2003). In the current phase of the IKBS development Aspen IPE was not implemented.

3.9 Conclusion

The proposed structure of the integrated knowledge based system (IKBS) uses Excel and Visual Basic for Application (VBA) as a backbone to the expert system. Excel and Excel VBA are integrated with third party software such as Aspen HYSYS and Aspen Icarus Process Evaluator (IPE) to obtain a rigorous design and sizing of flowsheet units, and to estimate the cost of alternative flowsheets. Internal databases were successfully incorporated to provide key information on the process chemical species such as physical properties, prices, safety and environmental impacts, azeotropes etc. The flowsheet optimization, sizing and detailed economic evaluation were not implemented in the prototype integrated knowledge based system, but are suggested as a future development. A VBA programming code was developed to link Aspen HYSYS process simulator with Excel. This integration between Excel and Aspen HYSYS provides the user with an easy way to explore the effect of changing design parameters on the process performance.

Chapter 4

Framework for Total Chemical Process Flowsheet Synthesis

4.1 Introduction

The process design activity must start with a goal, constraints within which the goal must be achieved and a criterion by which the solution might be recognized. Process design establishes the sequence of chemical and physical operations, operating conditions, duties, and specifications and arrangement of all process equipment. The goal of conceptual design is to find the best process flowsheet by selecting the process units and interactions among these units, and to estimate the optimum or near optimum design conditions. These design decisions come from establishing efficient procedures for the synthesis of process flowsheets and from acquiring valuable decision making knowledge which can be used throughout the process synthesis. The required knowledge for process synthesis may be structured or unstructured, numerical or symbolic, precise or imprecise, and certain or uncertain.

Linnhoff et al. (1994) and Smith (2005) have used the “onion” diagram to emphasize the sequential or hierarchical nature of process design as illustrated in Figure 4.1. The onion model starts with the reactor and following with subsequent layers of separation/recycle systems, heat exchanger networks and utility systems. Unlike the “onion” model, in the proposed integrated systematic procedure, the process synthesis starts with collecting information on the process followed by a preliminary chemistry and economic analyses. Furthermore, safety and environmental impact evaluation takes place before studying the reactor system synthesis. This proposed approach can reduce the number of reactors and separators evaluated in the reaction-separation-recycle systems synthesis.

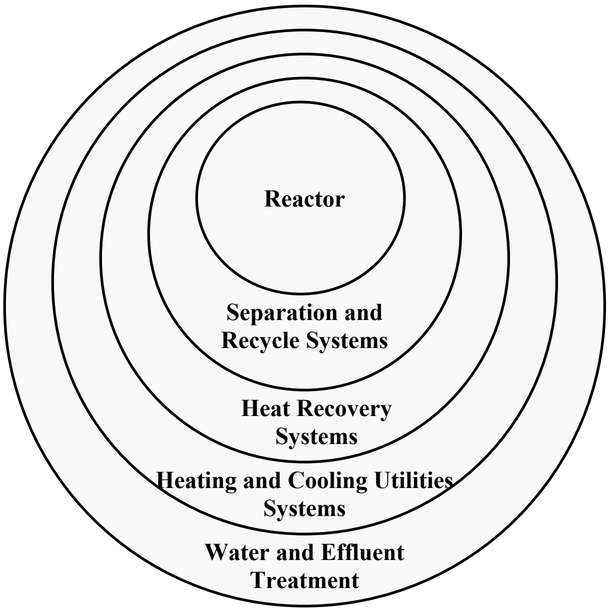


Figure 4.1: The onion model of process design. (Adapted from Smith, 2005)

In the early stages of process design, it is necessary to reduces alternative options in order to come up with reasonable decisions. This can be achieved by using chemical engineering experience in the form of rules of thumb or heuristics. Despite the fact that some heuristics may contradict other heuristics, it may lead to a near optimum design and remove optimal solutions which are non-sensible. Furthermore, the use of heuristics can save a significant amount of time and money during the preparation of the preliminary process design.

A list of design rules or heuristics for process equipment selection and design was produced by Jordan (1968). This list was further extended by Happel and Jordan (1975). This was followed by different set of heuristics by Ulrich (1984). A longer list of rules of thumb was developed by Walas (1988). Seider et al (2003) have reproduced the Walas list in their process design principles textbook. The list of process equipment design heuristics include important units such as compressors, cooling towers, crystallisers, distillation columns, absorbers, dryers, evaporators, extractors, filters, reactors and refrigerators. Recently, Wood (2007) produced a wide range of design rules for the selection of process unit operations. The design rules illustrated in his book are related to: transportation, energy exchange, homogeneous separations, heterogeneous separations, reactors, mixing, size reduction, size enlargement, and process vessels.

4.2 Systematic Procedure for Process Flowsheet Synthesis

The development of process flowsheet following a hierarchical approach is essentially a top-down analysis organized as a sequence of synthesis levels. Each level contains a decision making mechanism based on identification of dominant design decisions to generate flowsheet alternatives. An evaluation procedure eliminates unfeasible alternatives. Finally, the procedure leads to a base case flowsheet which can be used for detailed analysis and refinement.

In the proposed integrated systematic approach, analyses of the possible ways of processing a set of basic physical-chemical operations can be achieved by using basic and detailed information. The general synthesis problem statement for this type of system is:

Given a set of raw materials, the reaction path and kinetics, the desired product specification, with the aid of input information on the process species from the database and third party software, synthesis of alternative process flowsheets with a set of design options that can be considered further for optimal process design.

In this research, the proposed systematic procedure integrates heuristics with process simulation, flowsheet optimization and economic evaluation in a set of synthesis levels as illustrated in Figure 4.2. This work addresses the synthesis of process configurations that exploit interactions between reaction and separation processes.

The user starts by specifying some process relevant data required by IKBS to build a knowledge base for the process in a form of input/output information. There are often a number of alternative reaction paths to manufacture a certain product. Economic potential is used to perform a preliminary elimination as some of the alternative reaction paths are not economically viable. Chemical prices can be obtained from the database or predicted based on price forecasting. A preliminary safety and environmental evaluation step uses the available databases to identify potential safety and environmental impacts from the process. The main task of the reactor system synthesis consists of selecting the reaction paths, and reactor types, configurations and operating conditions. Up to three reaction systems can be synthesised by the IKBS.

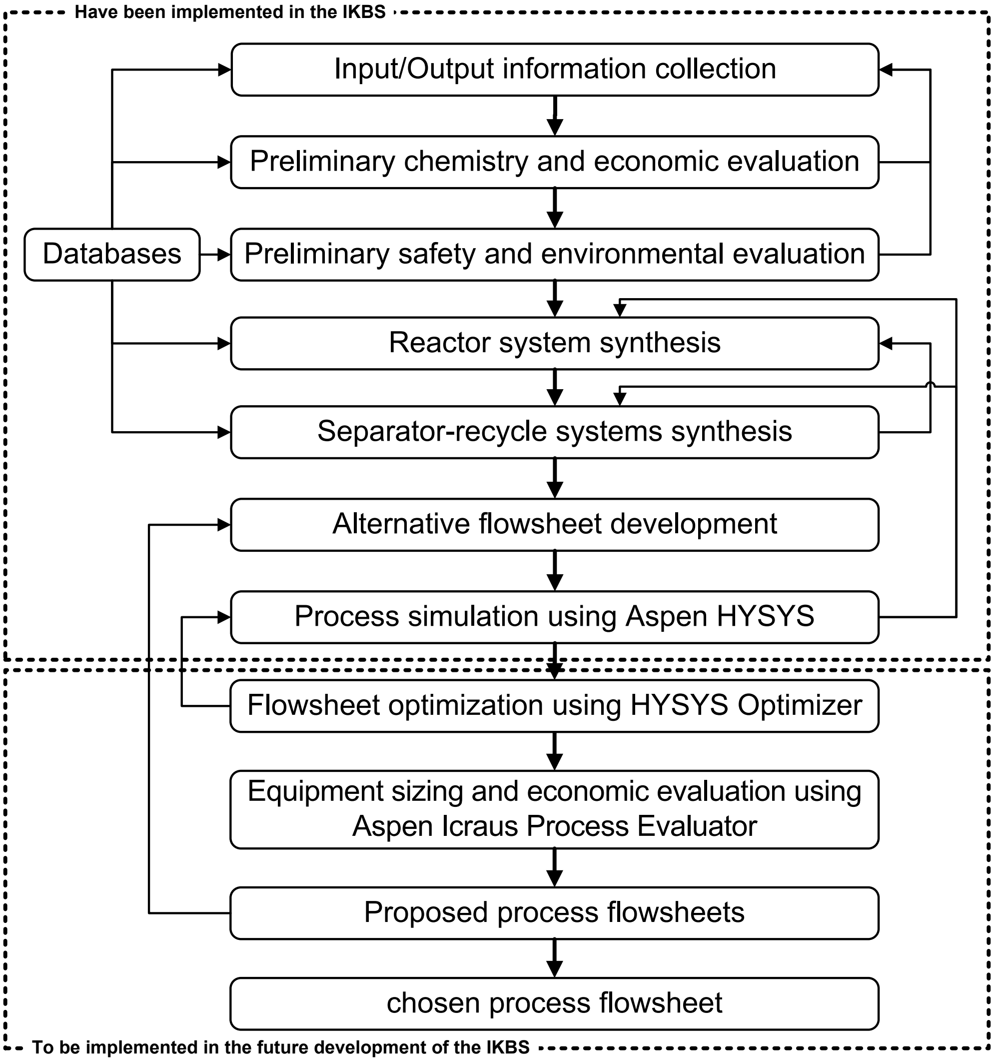


Figure 4.2: Flowchart of the proposed systematic procedure.

For the separation-recycle systems synthesis step, the main task consists of selecting the type, location, sequences and operating conditions of the separation system. The design of recycle from separators to reactor involves recycle component classifications, number of recycle streams determination, and the specifications and locations of liquid/vapour recycles and purges.

These alternative flowsheets can be simulated using Aspen HYSYS to solve the mass and energy balances given by the user, calculate the thermodynamic properties of process streams, and determine operating conditions. HYSYS can be customized to develop steady state unit operation. In HYSYS, a generic flowsheet is used to simulate the different alternative reactor-separator-recycle systems. A matrix of splitter ratios is used in Excel to specify the direction and magnitude of streams between the reactors.

HYSYS Optimizer provides a tool for chemical process flowsheet optimization. It uses an advanced algorithm for optimization based on sequential quadratic program (SQP) technology. Optimized flowsheets are subsequently loaded into Aspen IPE for sizing and economic evaluation. A limited number of process flowsheets are proposed based on meeting the design requirements of low investment cost and high profit. The flowsheet optimization, sizing and economic evaluation are part of the second phase of the future software development.

The closed loop from the preliminary chemistry and economic evaluation, and the safety and environmental evaluation has been implemented to adjust the input/output information collection. The closed loop between the reactor system and separator-recycle systems synthesis steps can be used for example in case of reactive separation processes. The closed loop from Aspen HYSYS to the reactor-separator-recycles system can be used after the flowsheet optimization. This is due to the fact that the simulation results may change after the optimization step. The last loop between proposed flowsheets and the alternative flowsheet development can be used to change the flowsheet alternatives in the IKBS superstructure.

The final decision criteria to select a specific process alternative, relies mainly on the economic evaluation of this alternative. The economic model used to evaluate each alternative takes into account the capital and operating costs associated with the process. It also takes into consideration the fact that the most environmentally friendly process might not be the most economical. At each level of the synthesis, the user is guided in a step by step manner to generate process alternatives.

Once the process is synthesised, the user can give feedback on the suggested flowsheet. The feedback can be used for future synthesis problems. This structured method allows systematic identification of the most economical process flowsheet. The step of the integrated systematic procedure is discussed below. Detailed discussion of the systematic procedure for the synthesis of reactor systems and separator recycle systems synthesis are presented in Chapters 5 and 6 respectively.

4.3 Input Information

The user starts the IKBS by selecting the start button in the initial screen illustrated in Figure 4.3. The user is guided in a step by step manner to provide the required information and view the synthesis results. At this early level of the process synthesis, the user must specify some process input/output information which is required by the software. Examples of the required information include, feed stream specifications (temperature, pressure, phase, composition) and costs, product specifications and value, plant throughput, reaction kinetics information, and key separation information. The user may not be required to provide all physical properties and chemical prices as it might be available in the databases. A short questionnaire (see Appendix B) was completed by 12 Process Engineers at the Saudi Basic Industries Corporation Industrial Complex for Research and Technology. The result shows that there is diversity in the availability of the process input/Output information. The limitations on the user's input/output information requirements were considered during the development of the software.

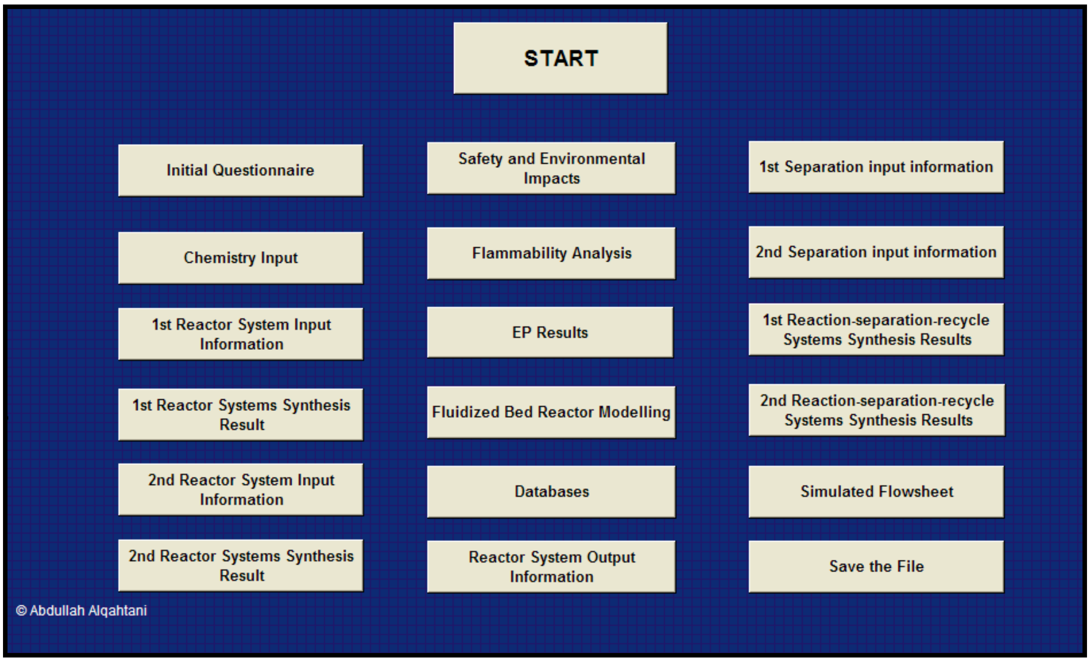
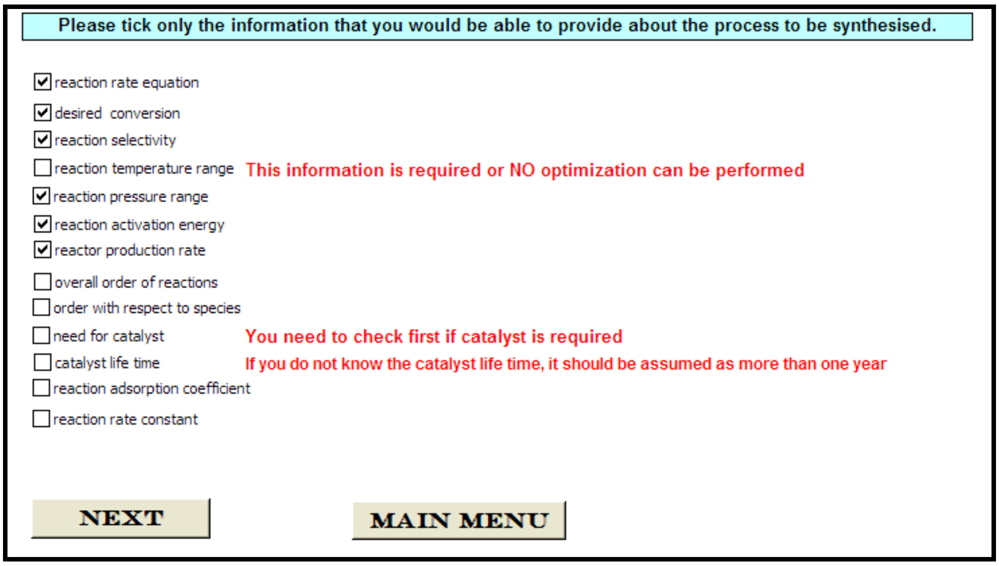


Figure 4.3: Initial screen of the IKBS.

The user is required to fill in a similar electronic questionnaire as an initial step of the process synthesis before they start using the software. Figure 4.4, illustrates the questioner on reaction system synthesis information.



Please tick only the information that you would be able to provide about the process to be synthesised.

☑ reaction rate equation
☑ desired conversion
☑ reaction selectivity
☐ reaction temperature range This information is required or NO optimization can be performed
☑ reaction pressure range
☑ reaction activation energy
☑ reactor production rate
☐ overall order of reactions
☐ order with respect to species
☐ need for catalyst You need to check first if catalyst is required
☐ catalyst life time If you do not know the catalyst life time, it should be assumed as more than one year
☐ reaction adsorption coefficient
☐ reaction rate constant

Figure 4.4: Input information questionnaire

The initial questionnaire verifies the availability of some key information on the process such as: reaction rate equation, conversion, selectivity, temperature and pressure range, activation energy, overall order of reaction, order with respect to reaction species, need for catalyst and catalyst life time, reaction adsorption coefficients, and reaction rate constant. It is not necessary to provide all of this information. The IKBS will inform the user about the consequences of not providing particular information. For example if the range of temperature, pressure, or concentration that the kinetic equation is valid for is not provided, no optimization can be performed. To quote another example, if catalyst life time is not provided, a one year life time is assumed.

This is required to ensure that users have the minimum required knowledge about the process to make full use of the software. If the users are not able to provide that basic information, they will be asked to look for it before they start providing the process chemistry information. Depending on the answers, users are going to provide the information related to the available information. This can improve the efficiency of the software as it will only ask for information, during the synthesis process, which the user knows based on the questionnaire results. If all minimum required information is provided, other not supplied information can be imported from a database or determined by the software.

4.4 Preliminary Economic Evaluation

There are often a number of alternative reaction paths to manufacture a certain product. Economic potential can be used to eliminate some of the alternatives that are not economically viable based on the cost of the raw materials and the value of the product. Douglas (1988) and Kirkwood (1987), suggest the calculation of economic potential at level 2, 3 and 4 of his hierarchical procedure discussed in Chapter 2.

Level 2 (Input Output Structure) economic potential is given by:

$$PE_2 = \text{(Primary product value)} + \text{(By-product values)} - \text{(Raw material cost)} - \text{(Feed compressor cost [if applicable])} \qquad (4.1)$$

Level 3 (Recycle Structure) economic potential is given by:

$$PE_3 = (PE_2) - (\text{Recycle compressor cost [if applicable]}) - (\text{reactor system cost}) - (\text{pre-heating/cooling system cost}) \quad (4.2)$$

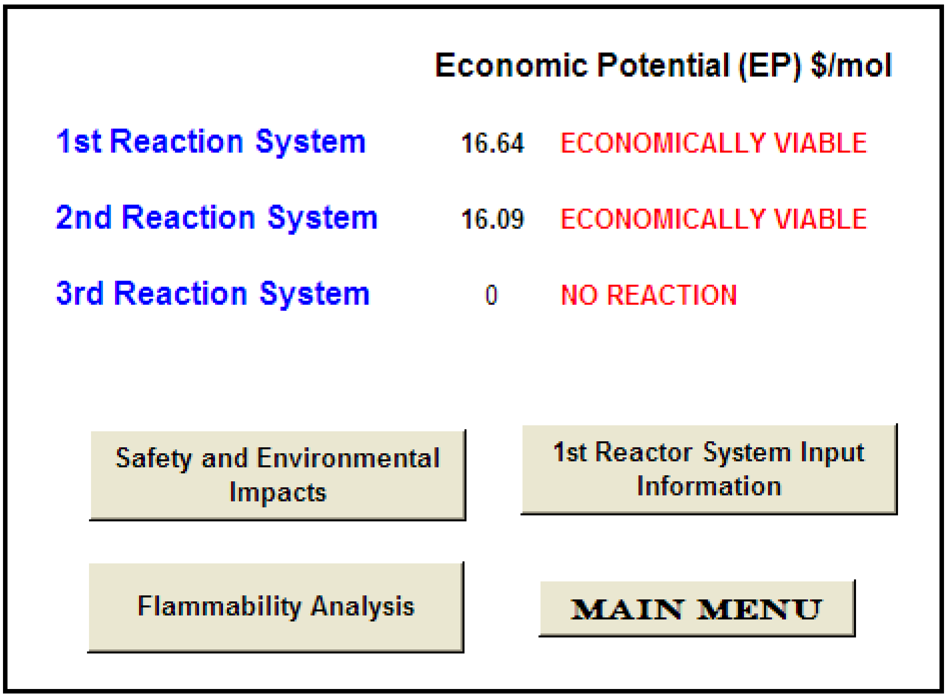
Level 4 (Separation System Structure) economic potential is given by:

$$PE_4 = (PE_3) - (\text{Absorber cost [if applicable]}) - (\text{total analysed cost of distillation sequence}) \quad (4.3)$$

If the economic potential at any level becomes negative, Douglas suggests three decision options:

1. Terminating the design study,
2. searching for a better process alternative,
3. Increasing the product price so that the economic potential is zero, and continue with the design.

The IKBS follows a different strategy to that of Douglas. In the IKBS preliminary economic evaluation at this early stage of process synthesis, only accounts for the reaction conversion and selectivity as well as the separation of reactor effluent and recycle of unreacted materials based on a heuristic design rule suggested by Douglas (1988). Douglas (1988) suggests the recovery of more than 99% of all valuable materials. Therefore, the IKBS preliminary economic evaluation does not consider the capital and operating costs. Considering the capital and operating costs of the process flowsheet is part of sizing and economic evaluation step by Aspen IPE in the future development of the software. By following this strategy, good potential design will not be eliminated before the detailed calculation of the flowsheet operating and capital cost using Aspen IPE is accomplished. Furthermore, optimization may make certain combination of process units not attractive based on the optimal process unit sizing and operating conditions. Figure 4.5, illustrate the preliminary economic potential to select the reaction path.



	Economic Potential (EP) $/mol	
1st Reaction System	16.64	ECONOMICALLY VIABLE
2nd Reaction System	16.09	ECONOMICALLY VIABLE
3rd Reaction System	0	NO REACTION

Figure 4.5: Economic potential calculation results.

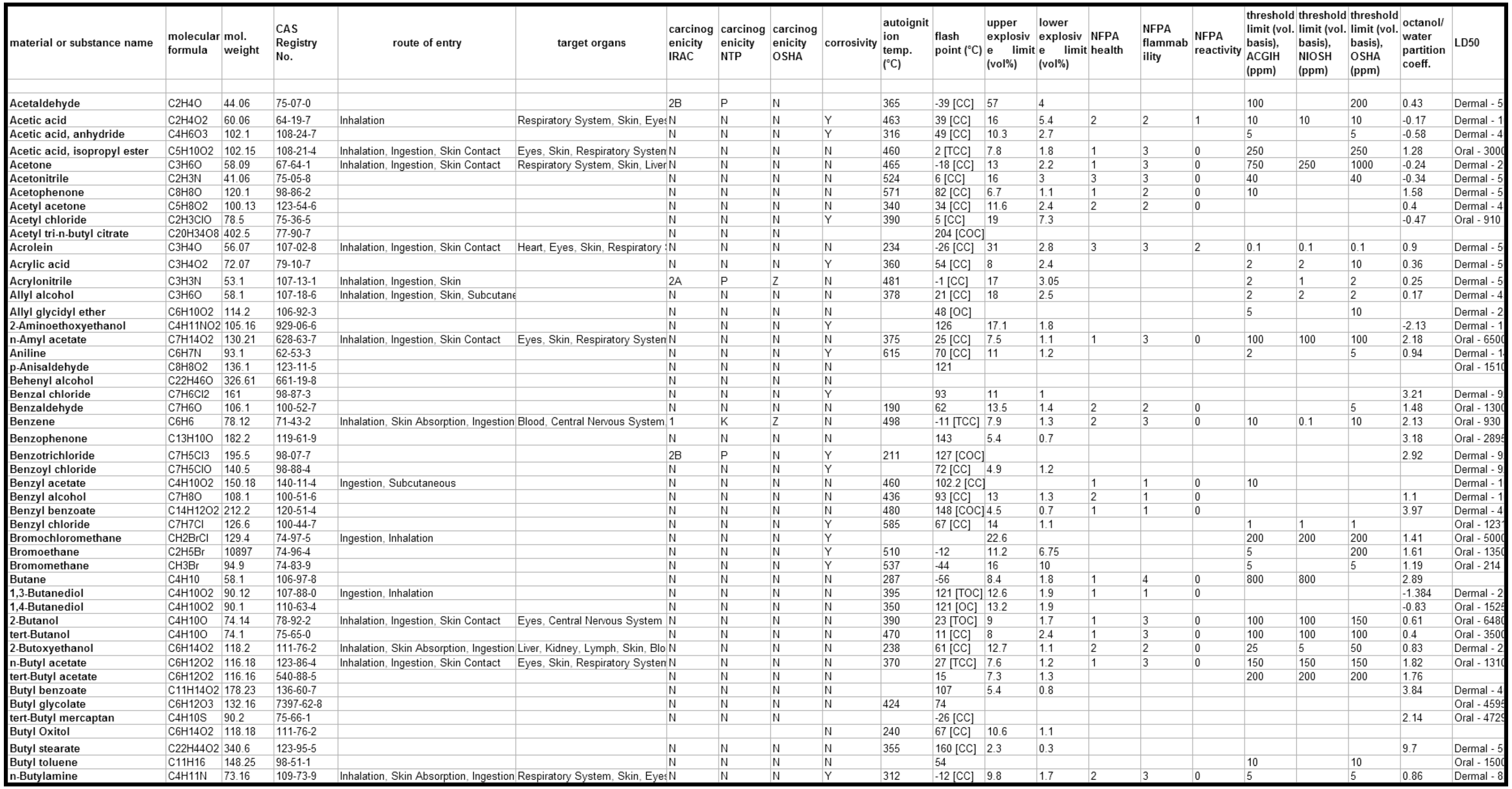
Chemical prices can be obtained from the Chemical Market Reporter, or from the IKBS internal database. It also can be predicted based on price forecasting. Forecasting the future prices of petrochemicals can be achieved by using qualitative or quantitative techniques. The qualitative forecasting techniques are based on individual estimation based on personal experience. Qualitative forecasting can be obtained from considering the estimates of sales personnel. The two basic models used in the quantitative techniques are the time-series models and causal models. The time-series models use past time ordered sequences of observations of forecasted variables. This time-series history variable is used to develop a model for predicting future value, and then forecasts are made by extrapolating the fitted model. The causal models, relate statistically time-series of interest (dependent variable) to one or more other time-series (independent variables) over the same time period (Al-Sharrah, 2007). Uncertainties in cost can have a major impact in evaluating the feasibility of a process. The price of the raw materials is more uncertain than the price of the product which is regulated by the market.

4.5 Preliminary Safety and Environmental Evaluation

The chemical process industry is faced with the need to manufacture products at the required quality while minimizing production costs and complying with a variety of safety and environmental regulations. To achieve these, the process design must simultaneously satisfy economic, safety, environment, and social objectives. In the preliminary safety and environmental evaluation step of the integrated systematic procedure, potential hazardous materials are identified based on available information in the database. Explosion and fire risks as well as toxicity are the main safety and environmental elements and deserve attention. The IKBS database provides the key information on these elements as illustrated in Figure 4.6 and give a warning to the user if any chemical species is potentially dangerous. Examples of safety and environmental information in the database include:

- route of entry
- target organs
- carcinogenicity, IRAC, NTP, OSHA
- corrosivity
- autoignition temperature
- flash point
- upper and lower explosive limits
- the NFPA health, flammability, and reactivity codes
- threshold limit**,** ACGIH, , NIOSH , OSHA
- octanol/water partition coefficient
- LD50
- Montreal protocol

Once the reaction equations are identified, all related safety and environmental information to the species are imported from the database. Therefore, the user can indentify any potential safety and environmental impacts of the process species such as reactants, products, by-products, mass separation agents, solvents, diluents etc. This can assist design engineers in the development of inherently safer and environmentally friendlier chemical processes.

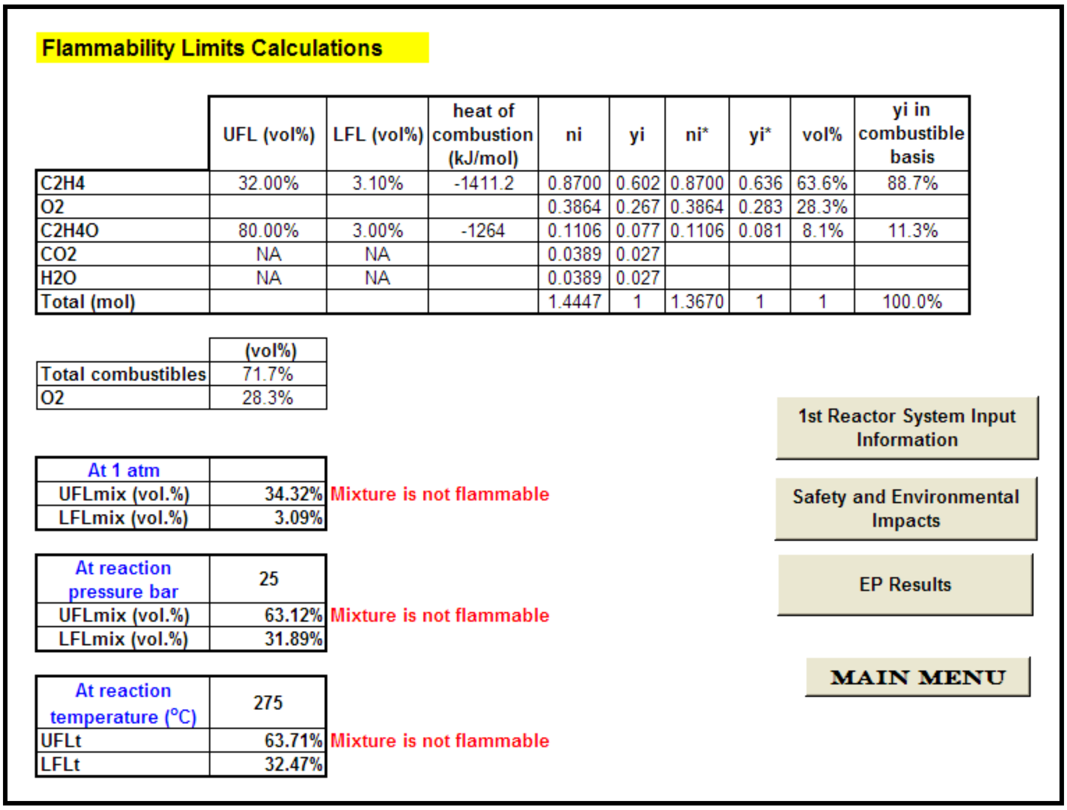


material or substance name	molecular formula	mol. weight	CAS Registry No.	route of entry	target organs	carcinogenicity IRAC	carcinogenicity NTP	carcinogenicity OSHA	corrosivity	autoignition temp. (°C)	flash point (°C)	upper explosive limit (vol%)	lower explosive limit (vol%)	NFPA health	NFPA flammability	NFPA reactivity	threshold limit (vol. basis), ACGIH (ppm)	threshold limit (vol. basis), NIOSH (ppm)	threshold limit (vol. basis), OSHA (ppm)	octanol/ water partition coeff.	LD50
Acetaldehyde	C2H4O	44.06	75-07-0			2B	P	N		365	-39 [CC]	57	4				100		200	0.43	Dermal - 5
Acetic acid	C2H4O2	60.06	64-19-7	Inhalation	Respiratory System, Skin, Eyes	N	N	N	Y	463	39 [CC]	16	5.4	2	2	1	10	10	10	-0.17	Dermal - 1
Acetic acid, anhydride	C4H6O3	102.1	108-24-7			N	N	N	Y	316	49 [CC]	10.3	2.7				5		5	-0.58	Dermal - 4
Acetic acid, isopropyl ester	C5H10O2	102.15	108-21-4	Inhalation, Ingestion, Skin Contact	Eyes, Skin, Respiratory Systen	N	N	N	N	460	2 [TCC]	7.8	1.8	1	3	0	250		250	1.28	Oral - 3000
Acetone	C3H6O	58.09	67-64-1	Inhalation, Ingestion, Skin Contact	Respiratory System, Skin, Liver	N	N	N	N	465	-18 [CC]	13	2.2	1	3	0	750	250	1000	-0.24	Dermal - 2
Acetonitrile	C2H3N	41.06	75-05-8			N	N	N	N	524	6 [CC]	16	3	3	3	0	40		40	-0.34	Dermal - 5
Acetophenone	C8H8O	120.1	98-86-2			N	N	N	N	571	82 [CC]	6.7	1.1	1	2	0	10			1.58	Dermal - 5
Acetyl acetone	C5H8O2	100.13	123-54-6			N	N	N	N	340	34 [CC]	11.6	2.4	2	2	0				0.4	Dermal - 4
Acetyl chloride	C2H3ClO	78.5	75-36-5			N	N	N	Y	390	5 [CC]	19	7.3							-0.47	Oral - 910
Acetyl tri-n-butyl citrate	C20H34O8	402.5	77-90-7			N	N	N			204 [COC]										
Acrolein	C3H4O	56.07	107-02-8	Inhalation, Ingestion, Skin Contact	Heart, Eyes, Skin, Respiratory	N	N	N	N	234	-26 [CC]	31	2.8	3	3	2	0.1	0.1	0.1	0.9	Dermal - 5
Acrylic acid	C3H4O2	72.07	79-10-7			N	N	N	Y	360	54 [CC]	8	2.4				2	2	10	0.36	Dermal - 5
Acrylonitrile	C3H3N	53.1	107-13-1	Inhalation, Ingestion, Skin		2A	P	Z	N	481	-1 [CC]	17	3.05				2	1	2	0.25	Dermal - 5
Allyl alcohol	C3H6O	58.1	107-18-6	Inhalation, Ingestion, Skin, Subcutane		N	N	N	N	378	21 [CC]	18	2.5				2	2	2	0.17	Dermal - 4
Allyl glycidyl ether	C6H10O2	114.2	106-92-3			N	N	N	N		48 [OC]						5		10		Dermal - 2
2-Aminoethoxyethanol	C4H11NO2	105.16	929-06-6			N	N	N	Y		126	17.1	1.8							-2.13	Dermal - 1
n-Amyl acetate	C7H14O2	130.21	628-63-7	Inhalation, Ingestion, Skin Contact	Eyes, Skin, Respiratory Systen	N	N	N	N	375	25 [CC]	7.5	1.1	1	3	0	100	100	100	2.18	Oral - 6500
Aniline	C6H7N	93.1	62-53-3			N	N	N	Y	615	70 [CC]	11	1.2				2		5	0.94	Dermal - 1
p-Anisaldehyde	C8H8O2	136.1	123-11-5			N	N	N	N		121										Oral - 1510
Behenyl alcohol	C22H46O	326.61	661-19-8			N	N	N	N												
Benzal chloride	C7H6Cl2	161	98-87-3			N	N	N	Y		93	11	1							3.21	Dermal - 9
Benzaldehyde	C7H6O	106.1	100-52-7			N	N	N	N	190	62	13.5	1.4	2	2	0			5	1.48	Oral - 1300
Benzene	C6H6	78.12	71-43-2	Inhalation, Skin Absorption, Ingestion	Blood, Central Nervous System,	1	K	Z	N	498	-11 [TCC]	7.9	1.3	2	3	0	10	0.1	10	2.13	Oral - 930
Benzophenone	C13H10O	182.2	119-61-9			N	N	N	N		143	5.4	0.7							3.18	Oral - 2895
Benzotrichloride	C7H5Cl3	195.5	98-07-7			2B	P	N	Y	211	127 [COC]									2.92	Dermal - 9
Benzoyl chloride	C7H5ClO	140.5	98-88-4			N	N	N	Y		72 [CC]	4.9	1.2								Dermal - 9
Benzyl acetate	C4H10O2	150.18	140-11-4	Ingestion, Subcutaneous		N	N	N	N	460	102.2 [CC]			1	1	0	10				Dermal - 1
Benzyl alcohol	C7H8O	108.1	100-51-6			N	N	N	N	436	93 [CC]	13	1.3	2	1	0				1.1	Dermal - 1
Benzyl benzoate	C14H12O2	212.2	120-51-4			N	N	N	N	480	148 [COC]	4.5	0.7	1	1	0				3.97	Dermal - 4
Benzyl chloride	C7H7Cl	126.6	100-44-7			N	N	N	Y	585	67 [CC]	14	1.1				1	1	1		Oral - 123
Bromochloromethane	CH2BrCl	129.4	74-97-5	Ingestion, Inhalation		N	N	N	Y			22.6					200	200	200	1.41	Oral - 5000
Bromoethane	C2H5Br	10897	74-96-4			N	N	N	Y	510	-12	11.2	6.75				5		200	1.61	Oral - 1350
Bromomethane	CH3Br	94.9	74-83-9			N	N	N	Y	537	-44	16	10				5		5	1.19	Oral - 214
Butane	C4H10	58.1	106-97-8			N	N	N	N	287	-56	8.4	1.8	1	4	0	800	800		2.89	
1,3-Butanediol	C4H10O2	90.12	107-88-0	Ingestion, Inhalation		N	N	N	N	395	121 [TOC]	12.6	1.9	1	1	0				-1.384	Dermal - 2
1,4-Butanediol	C4H10O2	90.1	110-63-4			N	N	N	N	350	121 [OC]	13.2	1.9							-0.83	Oral - 1525
2-Butanol	C4H10O	74.14	78-92-2	Inhalation, Ingestion, Skin Contact	Eyes, Central Nervous System	N	N	N	N	390	23 [TOC]	9	1.7	1	3	0	100	100	150	0.61	Oral - 6480
tert-Butanol	C4H10O	74.1	75-65-0			N	N	N	N	470	11 [CC]	8	2.4	1	3	0	100	100	100	0.4	Oral - 3500
2-Butoxyethanol	C6H14O2	118.2	111-76-2	Inhalation, Skin Absorption, Ingestion	Liver, Kidney, Lymph, Skin, Blo	N	N	N	N	238	61 [CC]	12.7	1.1	2	2	0	25	5	50	0.83	Dermal - 2
n-Butyl acetate	C6H12O2	116.18	123-86-4	Inhalation, Ingestion, Skin Contact	Eyes, Skin, Respiratory Systen	N	N	N	N	370	27 [TCC]	7.6	1.2	1	3	0	150	150	150	1.82	Oral - 1310
tert-Butyl acetate	C6H12O2	116.16	540-88-5			N	N	N	N		15	7.3	1.3				200	200	200	1.76	
Butyl benzoate	C11H14O2	178.23	136-60-7			N	N	N	N		107	5.4	0.8							3.84	Dermal - 4
Butyl glycolate	C6H12O3	132.16	7397-62-8			N	N	N	N	424	74										Oral - 4595
tert-Butyl mercaptan	C4H10S	90.2	75-66-1			N	N	N			-26 [CC]									2.14	Oral - 4729
Butyl Oxitol	C6H14O2	118.18	111-76-2						N	240	67 [CC]	10.6	1.1								
Butyl stearate	C22H44O2	340.6	123-95-5			N	N	N	N	355	160 [CC]	2.3	0.3							9.7	Dermal - 5
Butyl toluene	C11H16	148.25	98-51-1			N	N	N	N		54						10		10		Oral - 1500
n-Butylamine	C4H11N	73.16	109-73-9	Inhalation, Skin Absorption, Ingestion	Respiratory System, Skin, Eyes	N	N	N	Y	312	-12 [CC]	9.8	1.7	2	3	0	5		5	0.86	Dermal - 8

Figure 4.6: Safety and environmental impact database.

It also can assist in evaluating and considering alternative reaction paths, separating agents, or techniques that are acceptable from safety and environmental points view. This should also satisfy the other constrains such as the process economic and reaction/separation feasibility.

Figure 4.7, illustrates one of the uses of safety and environmental databases in assisting the elimination of gas mixture flammability in the ethylene oxide reactor. Within the upper and lower flammability limits, flames and explosions might occur. Therefore, it is necessary to keep the concentration outside the flammability range. The IKBS determines if the current mixture is flammable at the reaction conditions and gives a warning to the user accordingly.



Flammability Limits Calculations

	UFL (vol%)	LFL (vol%)	heat of combustion (kJ/mol)	ni	yi	ni*	yi*	vol%	yi in combustible basis
C2H4	32.00%	3.10%	-1411.2	0.8700	0.602	0.8700	0.636	63.6%	88.7%
O2				0.3864	0.267	0.3864	0.283	28.3%	
C2H4O	80.00%	3.00%	-1264	0.1106	0.077	0.1106	0.081	8.1%	11.3%
CO2	NA	NA		0.0389	0.027				
H2O	NA	NA		0.0389	0.027				
Total (mol)				1.4447	1	1.3670	1	1	100.0%

	(vol%)
Total combustibles	71.7%
O2	28.3%

At 1 atm		
UFLmix (vol.%)	34.32%	Mixture is not flammable
LFLmix (vol.%)	3.09%	

At reaction pressure bar	25	
UFLmix (vol.%)	63.12%	Mixture is not flammable
LFLmix (vol.%)	31.89%	

At reaction temperature (°C)	275	
UFLt	63.71%	Mixture is not flammable
LFLt	32.47%	

Figure 4.7: Flammability limits analysis.

Reactor gas mixture flammability limits are calculated using information from the database on the upper and lower flammability of each species. Information is imported from the database to the flammability limits calculation worksheet. The molar fraction of each species in the mixture is calculated based on the mass balance. Another calculation of the molar fraction accounts only for the combustion gases and oxygen concentration. Thus volume % of the total combustibles is calculated. The flammability limits can be calculated at different pressure and temperatures depending on the reactor conditions.

For mixtures, the flammability limits are estimated using the Le Chatelier equation as illustrated below (Seider et al., 2003).

Flammability limits of the mixture at ambient condition:

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}} \tag{4.4}$$

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \tag{4.5}$$

Where:

LFL_i and UFL_i: flammability limits of species i

y_i : mole fraction of species i in the vapour

Flammability limits at reaction pressure:

$$UFL_p = UFL_{mix} + 20.6(\log P + 1) \tag{4.6}$$

$$LFL_p = LFL_{mix} + 20.6(\log P + 1) \tag{4.7}$$

Flammability limits at reaction temperature:

$$UFL_T = UFL_{25}\left[1 - \frac{0.75(T-25}{\Delta Hc})\right] \tag{4.8}$$

$$LFL_T = LFL_{25}\left[1 - \frac{0.75(T - 25)}{\Delta Hc}\right] \qquad (4.9)$$

Where:
P : reaction pressure in k Pa
ΔHc: net heat of combustion from the IKBS database
T : reaction temperature in ^{o}C
UFL_{25} and $LFL_{25:}$ flammability limits at 25101.3 k Pa

As the flammability limits are affected by the temperature and pressure, IKBS calculates the upper and lower flammability limits at the desired range of reaction pressure and temperature. Results from safety and environmental impact analysis should be considered throughout the process development. For example, the optimization results should not contradict with the safety and environmental restrictions. In process synthesis, safety and hazard problems can justify important design decisions.

4.6 Reaction-Separation-Recycle Systems Synthesis

After collecting process input and output information, chemistry and preliminary economic evaluation, and safety and environmental impact analysis, the synthesis of reactor-separator-recycle systems takes place. The main tasks to be considered during reactor system synthesis include: selecting reactor types and number, and operating conditions. The main phases of general separation-recycle systems synthesis consist of the selection of the type, location and operating conditions of the separation systems, and separation sequencing. The user provides input information to the reactor-separator-recycle systems synthesis at multi levels of increasing complexity. Other information can be imported from the internal databases and from Aspen HYSYS simulated generic flowsheet using the developed VBA programming code.

The detailed discussion of the systematic procedure for reaction-separation-recycle systems synthesis is in Chapter 5 and 6.

4.7 Generic Superstructure

Chemical process flowsheet can be constructed in a reduced structure known as a superstructure that has embedded within it all feasible process options and feasible interconnections which can be alternative options for optimal design configurations. Douglas (1988) developed a generic superstructure for conceptual design of chemical processes as illustrated in Figure 4.8.

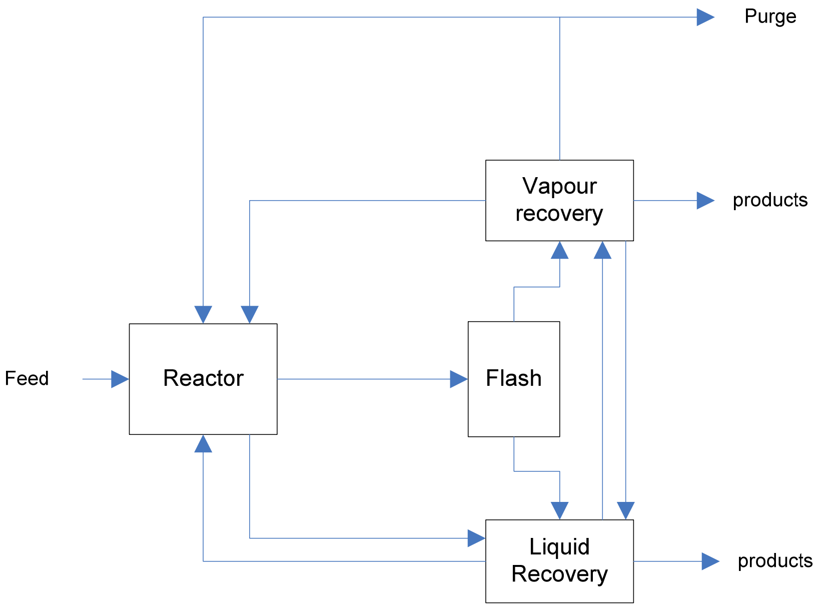


Figure 4.8: Douglas' general superstructure for reactor-separator-recycle.

The superstructure contains a reactor system and a flash separator, liquid recovery and vapour recovery. The vapour recovery can be after the phase separation, in the purge stream, or in the recycle stream. The selection of the location of the vapour recovery system is based on four possibilities. If the flash vapour stream contains a significant amount of a valuable component that would be lost in the purge stream, the vapour recovery system can be located on the purge stream as it normally has the smallest flowrate.

If it is important to prevent the recycle of certain components that are deleterious to the reactor operation or degrade the product distribution, the vapour recovery should be placed in the gas recycle stream which normally has the second smallest flowrate as some of the main recovery stream is sent to purge. To prevent the loss of valuable reactants, the recycle of the undesirable material, the vapour recovery system can be located on the flash vapour stream. Vapour recovery system may not be required if the loss of valuable reactants or the recycle of the undesirable material is not significant.

Among the suggested separation units in Douglas' generic superstructure for the vapour recovery are: partial condensers, cryogenic distillation, absorption, adsorbers and membrane separation process. For liquid mixture separation the following separation units are considered: distillation, stripping towers, extractive distillation, azeotropic distillation, reactive distillation, liquid-liquid extraction and adsorbers. These alternatives show that all evaluated separation processes are conventional and no reactive, or hybrid separation system is considered. The superstructure does not account for multiple reactor or separation systems in a complex flowsheet.

A generic superstructure of reactor-separator-recycle systems is proposed for total process flowsheet optimization. The proposed generic superstructure illustrated in Figure 4.9, consists of reactor system (RS), phase separation system (PSS), vapour and liquid recovery system (LSS and VSS), recycle separation system (RSS), and liquid recycle to the reactor system. The direction of the flow is controlled by the IKBS. For example, if the decision is to use a reactor system followed by a liquid recovery system, the splitter after the reactor will only direct the flow to the liquid recovery system.

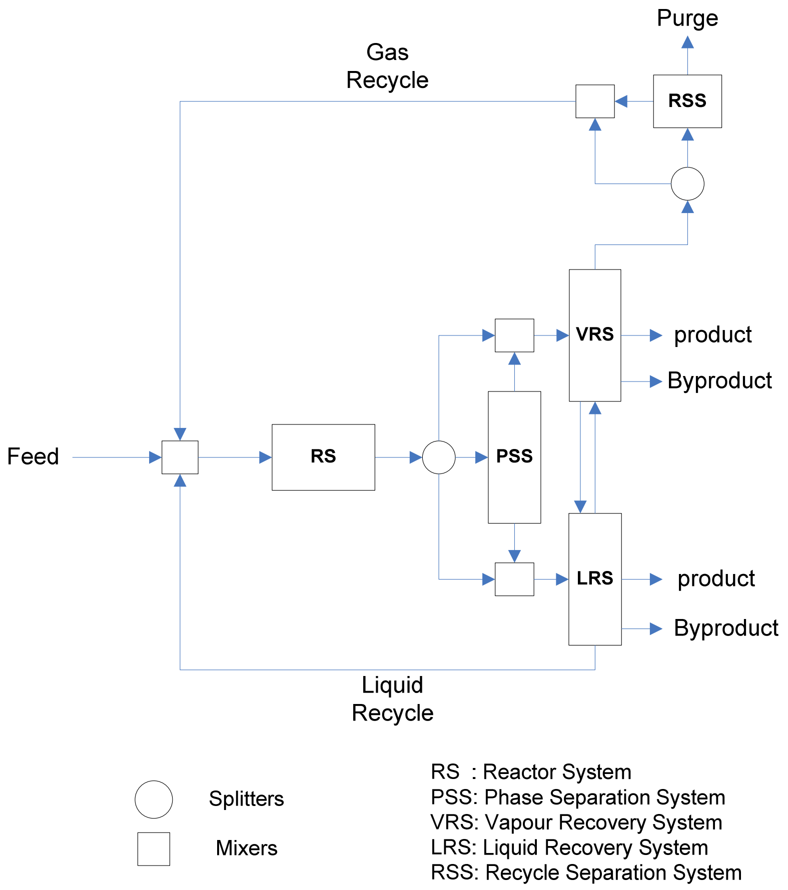


Figure 4.9: Proposed general superstructure for reactor-separator-recycle.

In the detailed reactor system (RS) superstructure, illustrated in Figure 4.10, the reactor system contains a series of multiple reaction zones. A series of four non-ideal CSTRs are in parallel with another series of four non-ideal fixed bed/plug flow reactors. The decision to use four reactors/reaction zones is based on the maximum for very slow reaction. The use of four reactors/reaction zones when studying reactor systems is discussed in Chapter 5 based on the work in modular simulation of fluidized bed reactor by Jafari et al. (2004) and reactor selection guide by Wood (2007). There is interchange between each reactor to examine different configurations of multiple reactors.

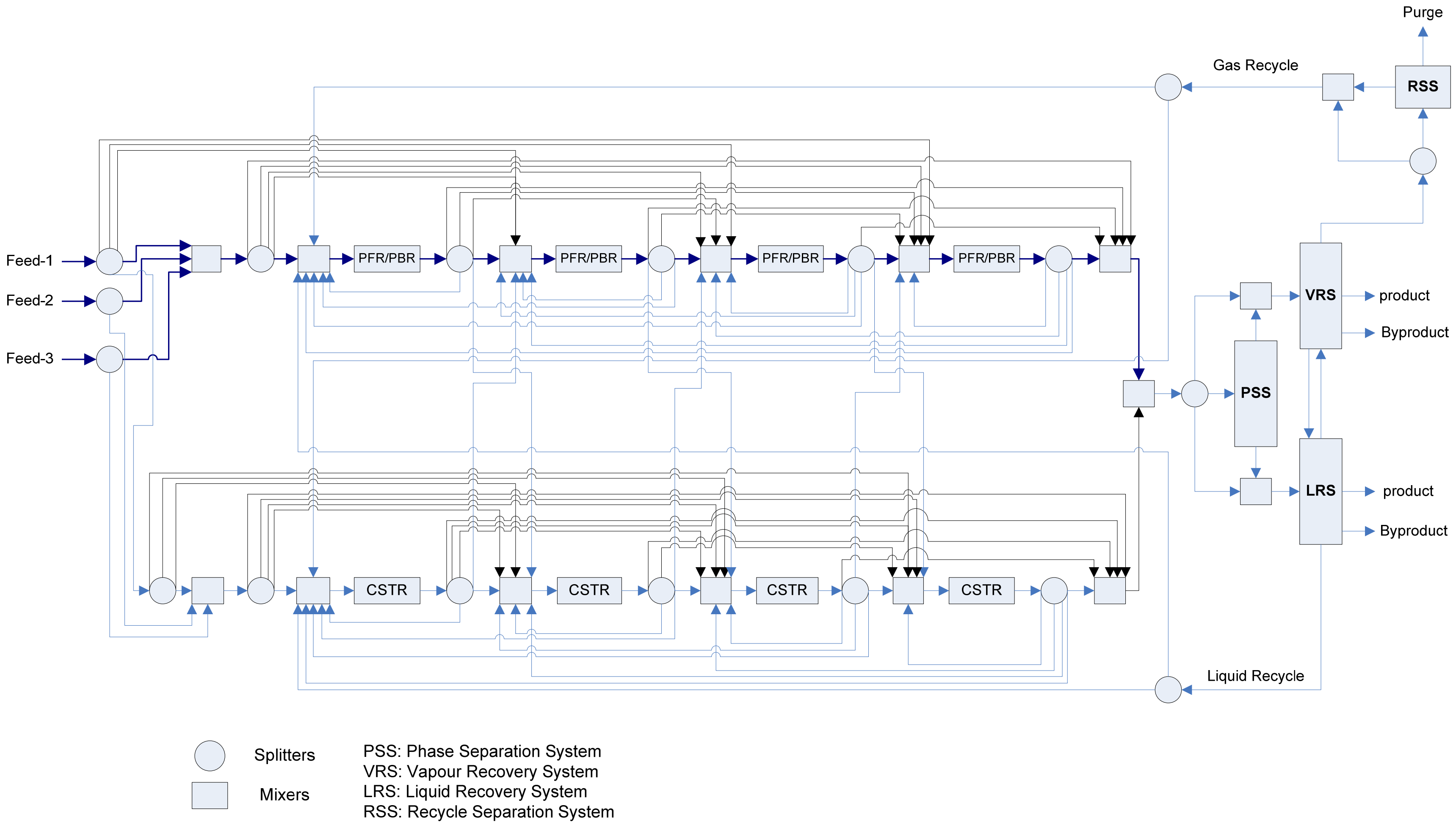


Figure 4.10: Detailed reactor system as a part of the generic superstructure for reactor-separation-recycle systems synthesis and optimization.

The interchange between reactors is used in the modular simulation of a fluidized bed reactor to account for the interchange between the bubble and emulsion phases. The superstructure also includes an internal recycle, a distribution of reactants to each reactor and a bypass. The internal recycle around the reactors and the distribution of reactants between reactors are also used to examine different configurations. For example, introducing one of the reactants to different reaction zones to study the over all performance of the reactor systems. It also can be used in a very exothermic reaction to control the heat transfer. The internal recycle can also be used to study the effect of recycling reactor influent to different position in the reactor system such as improving the reaction conversion. Streams are connected by mixing and splitting units to direct the flow based on the IKBS decisions. The control of the direction of the streams is governed by an Excel expert system matrix. The matrix contains the ratio of each splitter output streams.

The detailed generic separation superstructure is illustrated in Figure 4.11. It contains a reactor (RS) system, two phase separation systems (PSS-1 and PSS-2), vapour separation systems (VSS-1 and VSS-2) and liquid separation systems (LSS-1 and LSS-2). Recycle gas can be separated in two recycle separation systems (RSS-1 and RSS-2). Each separation system in the generic superstructure can have a combination of several units, such as a train of vacuum distillation columns or hybrid separation systems.

If the reactor effluent is in the liquid phase, it is sent directly to liquid separation systems. If the reactor effluent is vapour phase, it can be separated into liquid and vapour phase using the phase separation or sent directly to vapour recovery systems based on the design heuristic rules discussed in Chapter 6. If the reactor effluent contains immiscible liquids it is sent directly to the phase separation system. In the generic superstructure, all separation systems are connected to each other in many possible design options. Options can be for example, interchange between vapour and liquid recovery systems, and connectivity within each separation system.

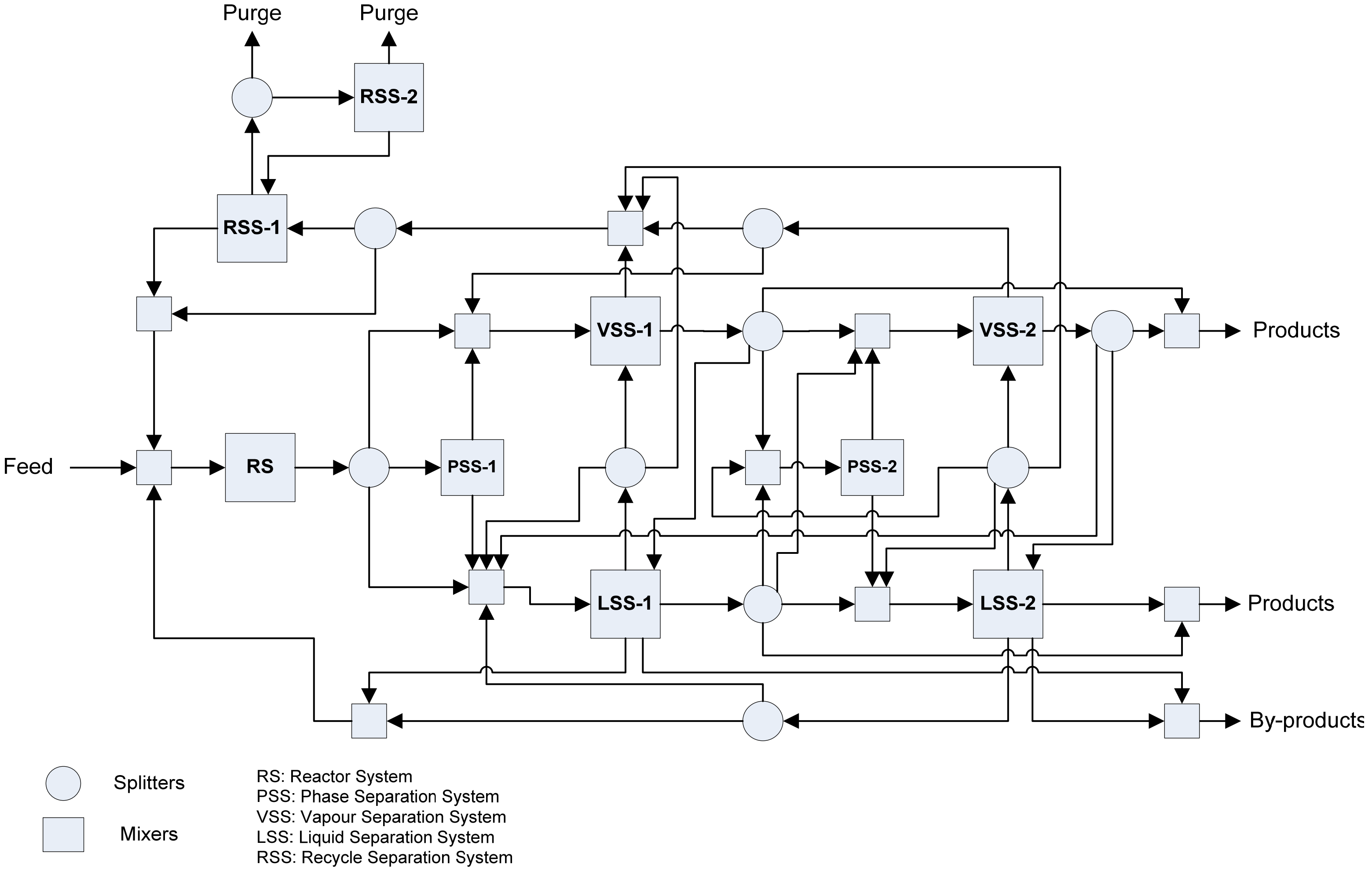


Figure 4.11: Detailed separator system in the generic superstructure for reactor-separation-recycle systems synthesis and optimization.

Unlike the Douglas' superstructure, the proposed generic superstructure contains two recycled gas separation systems in addition to the vapour recovery systems. This can account for all possible arrangements for gas recycle separation and recovery. As in the reactor systems superstructure, streams in the separation systems superstructure are connected by mixing and splitting units to direct the flow based on the IKBS decisions, and the control of the direction of the streams is governed by an Excel expert system matrix.

The generic superstructure has been constructed and tested against several existing commercial petrochemical process flowsheets such as methanol, formaldehyde, ammonia, acetic acid, maleic anhydride, isopropanol, ethylbenzene, styrene and aniline using published data from Chauvel and Lefebvre, (1989); Matar and Hatch (2001); Moulijn, et al. (2001); Meyers (2005).

4.8 Flowsheet Simulation

The role of process simulation is to improve the understanding of the process so that design engineers can make the best process decisions. The developed alternative flowsheet is simulated using Aspen HYSYS to solve the mass and energy balances, calculate the thermodynamic properties of process streams, and to provide the proper physical data for the components involved in the process.

The output from Excel VBA expert system can be used to prepare an input file to obtain a rigorous design using the HYSYS process simulator. The input data to Aspen HYSYS contains the process structure, the unit design and operation parameters, the composition and state of the process feed streams, and any recycle streams estimate. Aspen HYSYS unit subroutines include mixers, tees, components separators, splitters, flash drums, 3-phase separator, shortcut columns, distillation columns, absorbers, strippers, rectifiers, liquid-liquid extractions, heat exchangers, pumps, compressors, turbines, expander, valves, and reactors such as conversion, equilibrium, Gibbs, CSTR and PFR. This rigorous simulation is being used to validate the screening procedure and to assess and compare different design options in reactor-separator systems.

A generic process flowsheet was developed based on the proposed generic superstructure. Figure 4.12, illustrates the proposed generic process flowsheet, which is used to simulate different alternative reactor-separator-recycle systems configurations. Bigger scale figures of the reaction and separation recycle systems are illustrated in Chapters 5 and 6. The generic process flowsheet contains a series of four CSTRs which are parallel with another series of four fixed bed/plug flow reactors with interchange between each reactor to examine different configurations of multiple reactors. The separation systems contain two phase separators, two absorbers, one stripper, five distillation columns and an extraction column. The generic process flowsheet also contains gas and liquid recycle to account for many possible design configurations. Recycled gas is simulated using components splitter. Streams are connected using mixing and splitting units to direct the flow based on the IKBS decisions. Detailed description of the generic flowsheet construction and applications are discussed in the subsequent chapters.

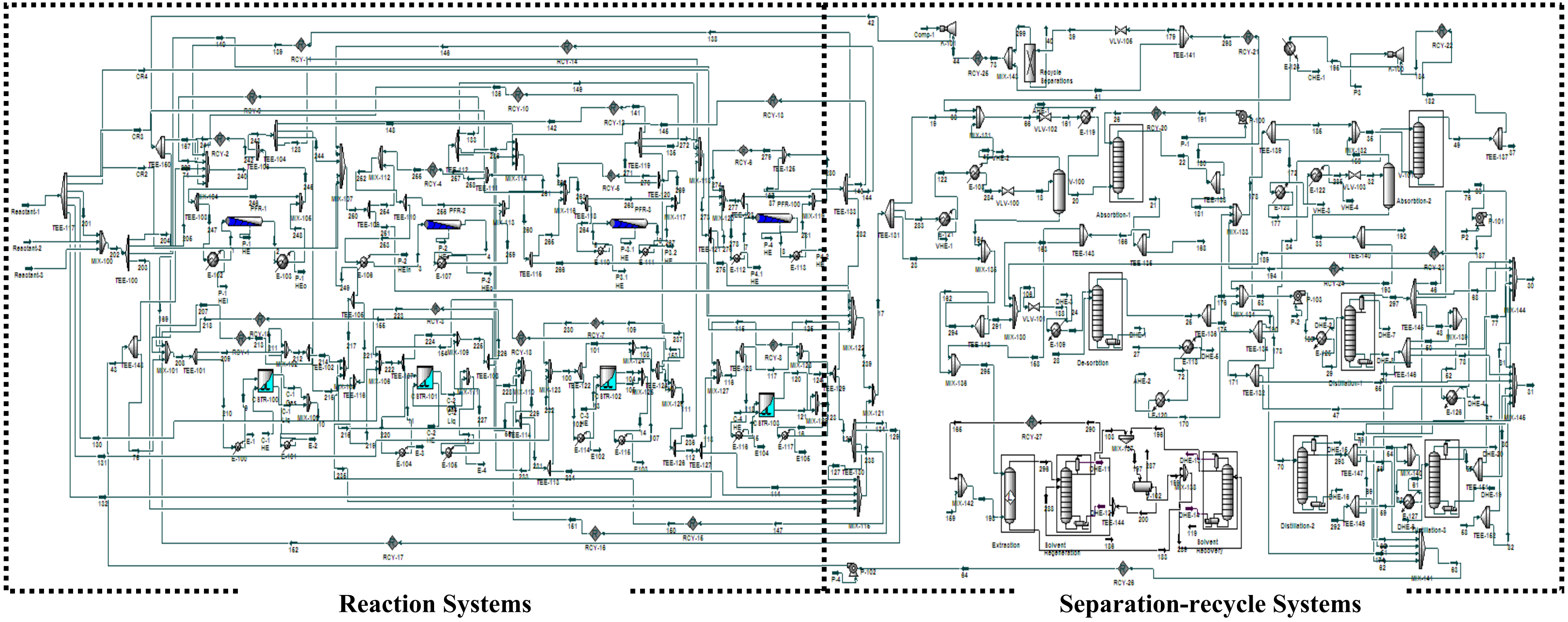


Figure 4.12: Generic flowsheet for reaction-separation-recycle systems simulation.

A key step in solving a simulation problem is to select the appropriate thermodynamic model and to supply the correct parameters. Modern thermodynamic methods make the treatment of complex mixtures possible. This includes hydrocarbons, polar species, supercritical, water, etc. Table 4.1, lists some models used in the industrial process simulation. In Aspen HYSYS, the UNIQUAC (UNIversal QUAsi-Chemical model) property package is being used in this project as it is appropriate to the synthesis of petrochemical processes. Other property packages can also be used, such as Peng-Robinson, UNIFAC, Soave-Redlich-Kwong, PSRK (predictive Soave-Redlich-Kwong) and NRTL (non-random two-liquids).

Table 4.1: Simulation thermodynamic models. (adapted from Chen and Mathias, 2002)

Chemical Systems	Primary Choice Models	Secondary Choice Models	Problem Areas
Air Separation	Peng-Robinson, Soave-Redlich-Kwong	Corresponding States	
Gas Processing	Peng-Robinson, Soave-Redlich-Kwong	BWRS	
Gas Treating	Kent-Eisenberg, Electrolyte NRTL		Data, Parameters, Models for mixed amines
Petroleum Refining	BK10, Chao-Seader, Grayson-Streed, Peng-Robinson, Soave-Redlich-Kwong, Lee-Kessler-Plöcker		Heavy crude characterization
Petrochemicals— VLE	Peng-Robinson, Soave-Redlich-Kwong, PSRK	NRTL, UNIQUAC, UNIFAC	Data, Parameters
Petrochemicals— LLE	NRTL, UNIQUAC		Data, Parameters, Models for VLLE systems
Chemicals	NRTL, UNIQUAC, PSRK	UNIFAC	Data, Parameters
Electrolytes	Electrolyte NRTL, Zemaitis	Pitzer	Data, Parameters, Databanks, Models for polyelectrolytes
Oligomers	Polymer NRTL	UNIQUAC, UNIFAC	Pure component fugacity, Databanks
Polymers	Polymer NRTL, PC-SAFT	Sanchez-Lacombe, SAFT, UNIFAC-FV	Data, Parameters, Databanks, Flash algorithms, Models for polar polymers, block copolymers
Steam	NBS/NRC		
Environmental	UNIFAC+Henry's Law		Data
Pharma/Biological	None		Data, Databanks, Models

4.9 Flowsheet Optimization

Aspen HYSYS contains a multi-variable steady state flowsheet optimizer. Once the flowsheet has been developed and a converged solution has been obtained, the optimizer can be used to find the optimum operating condition which minimizes or maximizes the objective function. HYSYS Optimizer uses its spreadsheet for defining the objective function and constraint expressions. The proposed generic superstructure can be optimized using HYSYS Optimizer in the second phase of the IKBS future development to suggest optimal design conditions and configurations.

4.10 Process Equipment Sizing and Economic Evaluation

At the beginning of the systematic procedure, the preliminary economic evaluation did not consider the capital and operating costs. To generate rigorous size and cost estimates of process flowsheet equipment, Aspen Icarus Process Evaluator (IPE) can be used. IPE has an expert system which links it to HYSYS simulator. Once the flowsheet is simulated, the user can export the results to IPE using the Aspen HYSYS Tools bar. This task can be considered in the second phase of the IKBS future development.

4.11 Proposed Process Flowsheet

In the final stage of the software development, the IKBS proposes a limited number of process flowsheets based on meeting the design requirements at low investment cost and high profit. Eventually the chosen flowsheet is illustrated along with decision justifications, optimum operating conditions, detailed economic evaluation and summary report on the process.

4.12 Conclusion

A new proposed framework for chemical process synthesis starts with collecting process information from the user at multi levels of complexity. Other information is imported from the IKBS internal database. Early stages of the systematic procedure account for preliminary economic evaluation to identify all economically viable reaction paths. Safety and environmental impacts are identified, based on the database information. This can improve the users understanding of the process safety and environmental impacts, and can also be used in the future development of the software to suggest different alternative solvents, or reaction routes. The reactor-separator-recycle systems synthesis step analyses the process and uses industrial experience to select alternative process units and configurations. Developed flowsheets are simulated using a proposed generic superstructure and flowsheet in Aspen HYSYS. The generic flowsheet is being used to simulate the alternative flowsheet configurations. The generic superstructure can also be used to optimize the process flowsheet in the future. The proposed combination of qualitative and quantitative approach to the synthesis of the total process flowsheet was not yet fully investigated in the previous work.

Chapter 5

Chemical Reactor Systems Synthesis

5.1 Introduction

Chemical reactor system synthesis is the task of identifying the network of reactors which transform raw materials to products at optimum cost whilst meeting design constraints. Synthesis of reactor systems is an important part of the overall chemical process flowsheet development. In a chemical process, feed preparation, product recovery and recycle steps are directly influenced by the reactor system. Reactor systems should not be designed in isolation such as the work by Schembecker et al (1995a,b) and Jacobs et al. (2000a,b), but rather as an important part of an overall chemical process flowsheet. For example, if the design decisions suggest the use of a diluent or heat carrier, then the overall material balances will have to be changed. Moreover, the design and specification for the separation systems will change due to the addition of an extraneous component. These previous works also do not use third-party software and databases to support the design decisions. The types of reactors widely used in most of reactor system synthesis are the ideal CSTR and PFR. However, industrial reactors are non-ideal.

Information on reactor design and heuristic rules for reactor system synthesis can be obtained from different textbooks such as Walas (1989); Froment and Bischoff (1990); Ullmann's Encyclopaedia of Industrial Chemistry by Elvers et al. (1996); Schmidt (1998); Levenspiel (1999); Missen (1999); Silla (2003); Trambouze and Euzen (2004); Fogler (2005), Wood (2007).

5.2 Reactor Systems Synthesis Procedure

The design strategy used by the IKBS can be described as a logical sequence of analysis and synthesis steps grouped in levels of development based on design decisions. There are some important factors that need to be weighed for the synthesis of reaction schemes, reactor selection and configuration. Factors that need to be considered include equilibrium conversion, kinetics, downstream separations, process economic, safety, and environmental issues.

In the present work, the proposed strategy for reactor system synthesis as a part of the total chemical flowsheet development is illustrated in Figure 5.1. As explained in the previous chapter, the integrated knowledge based system starts by collecting process chemistry information from the user. This early level of process synthesis, considers the number of raw material and product streams. It also considers the presence of by-products and inert components and how they participate in the process chemistry. The feed to the reactor system is always a combined feed consisting of a fresh feed mixed with one or more recycle streams. The fresh feeds may contain inert chemicals, potential reactants for side reactions and catalyst poisons.

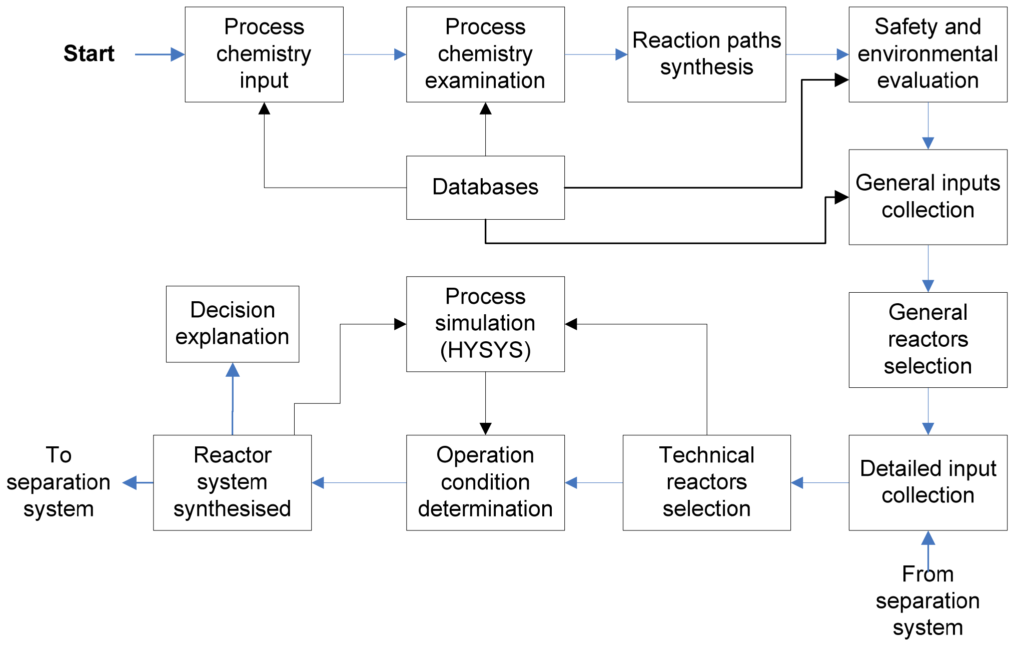
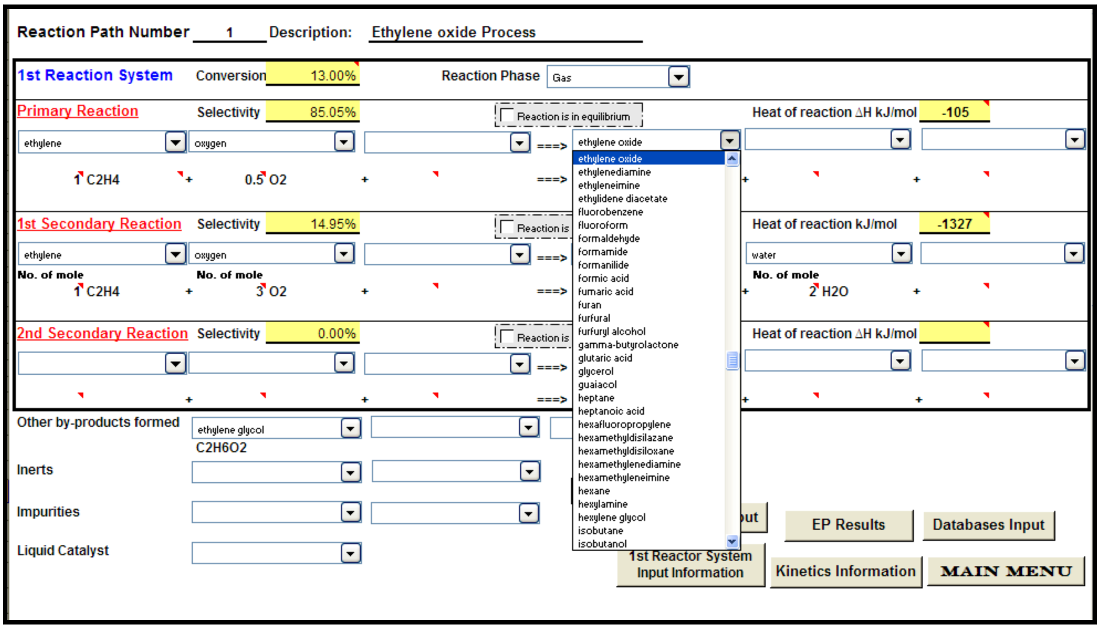


Figure 5.1: Reactor system synthesis strategy.

Currently, the IKBS assumes that the fresh feed contains only reactants for desired reactions. Recycle streams are intended to contain only unconverted reactants and product of desired reactions in addition to by-products and inert chemicals.

In the IKBS, by using the chemistry input interface (see Figure 5.2), chemical equations are provided by selecting reactant and product chemical names from a database from which chemical information and physical properties are imported automatically as illustrated in Figure 5.3. Users can also specify the reaction conversion and selectivity. Heats of reaction can also be provided by the user, or calculated using the heat of formation from the database. If the reaction is in equilibrium, users can indicate the fact and further kinetic information will be required in kinetic input information steps. For reverse reactions, the rate equations will include information on the reverse reaction concentrations and adsorption coefficients in addition to the equilibrium constants.



Reaction Path Number 1 Description: Ethylene oxide Process

1st Reaction System Conversion 13.00% Reaction Phase Gas

Primary Reaction Selectivity 85.05% ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol -105

ethylene + oxygen ===> ethylene oxide

1 C_2H_4 + 0.5 O_2 + ===> + +

1st Secondary Reaction Selectivity 14.95% ☐ Reaction is Heat of reaction kJ/mol -1327

ethylene + oxygen ===> water

No. of mole 1 C_2H_4 + No. of mole 3 O_2 + ===> + No. of mole 2 H_2O +

2nd Secondary Reaction Selectivity 0.00% ☐ Reaction is Heat of reaction ΔH kJ/mol

Other by-products formed: ethylene glycol $C_2H_6O_2$

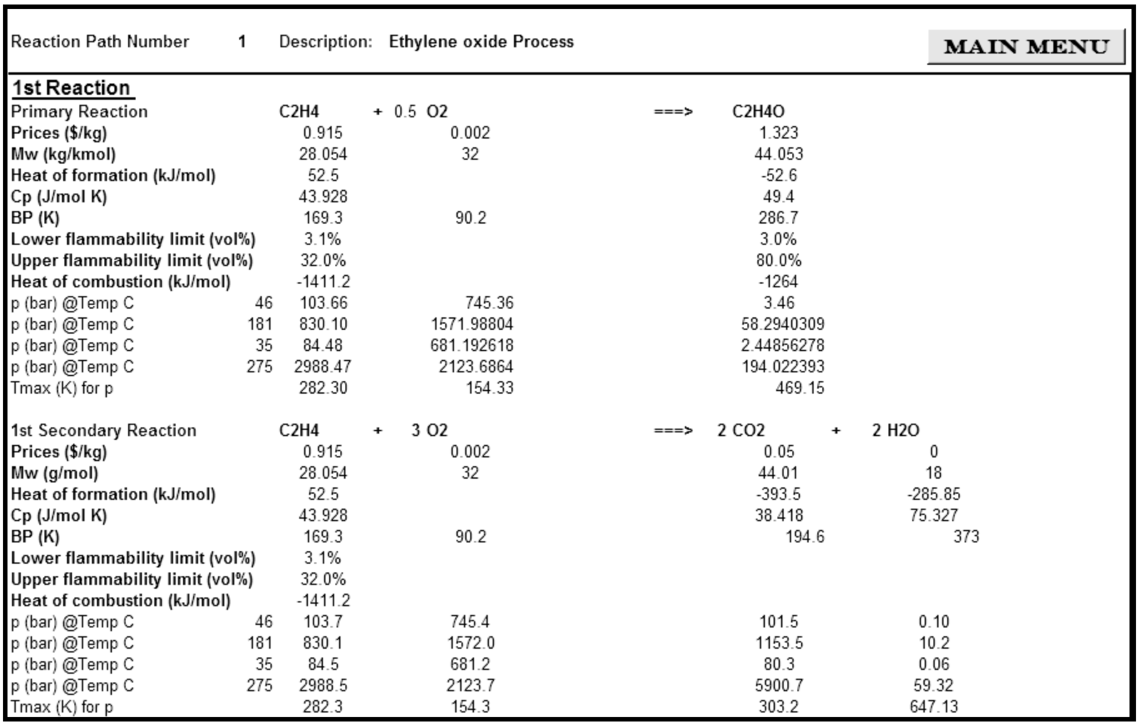
Inerts

Impurities

Liquid Catalyst

Figure 5.2: Chemistry input information interface in the IKBS.

Users can also specify any inert, or impurities and liquid catalyst involved in the process. Also any by-products without available chemical equations can be specified. Related information to these chemical species is also imported automatically from the database accordingly as illustrated in Figure 5.4.



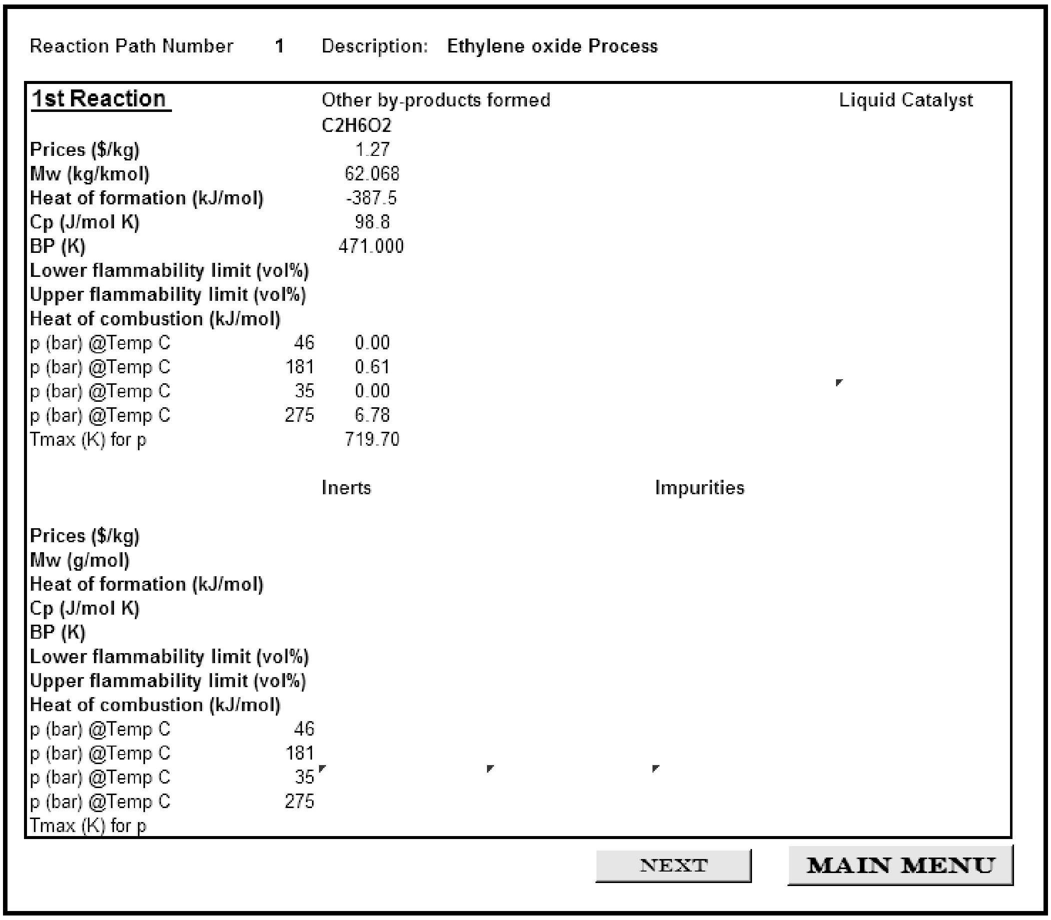
Reaction Path Number 1 Description: Ethylene oxide Process

1st Reaction

Primary Reaction		C2H4	+	0.5 O2	===>	C2H4O		
Prices ($/kg)		0.915		0.002		1.323		
Mw (kg/kmol)		28.054		32		44.053		
Heat of formation (kJ/mol)		52.5				-52.6		
Cp (J/mol K)		43.928				49.4		
BP (K)		169.3		90.2		286.7		
Lower flammability limit (vol%)		3.1%				3.0%		
Upper flammability limit (vol%)		32.0%				80.0%		
Heat of combustion (kJ/mol)		-1411.2				-1264		
p (bar) @Temp C	46	103.66		745.36		3.46		
p (bar) @Temp C	181	830.10		1571.98804		58.2940309		
p (bar) @Temp C	35	84.48		681.192618		2.44856278		
p (bar) @Temp C	275	2988.47		2123.6864		194.022393		
Tmax (K) for p		282.30		154.33		469.15		
1st Secondary Reaction		C2H4	+	3 O2	===>	2 CO2	+	2 H2O
Prices ($/kg)		0.915		0.002		0.05		0
Mw (g/mol)		28.054		32		44.01		18
Heat of formation (kJ/mol)		52.5				-393.5		-285.85
Cp (J/mol K)		43.928				38.418		75.327
BP (K)		169.3		90.2		194.6		373
Lower flammability limit (vol%)		3.1%						
Upper flammability limit (vol%)		32.0%						
Heat of combustion (kJ/mol)		-1411.2						
p (bar) @Temp C	46	103.7		745.4		101.5		0.10
p (bar) @Temp C	181	830.1		1572.0		1153.5		10.2
p (bar) @Temp C	35	84.5		681.2		80.3		0.06
p (bar) @Temp C	275	2988.5		2123.7		5900.7		59.32
Tmax (K) for p		282.3		154.3		303.2		647.13

Figure 5.3: Example of reactor system synthesis input information from the databases.

As illustrated in Figure 5.3 and Figure 5.4, Input information from the database at this early level of synthesis includes chemical prices, molecular weight, heat of formation, heat capacities, boiling points, lower and upper flammability limits, heat of combustion and partial pressure at different temperatures. This information is used for the process chemistry analysis and reactor selection in addition to the safety and environmental evaluation as explained in Chapter 4. If there is any safety and environmental concern about the economically viable paths, warnings will be issued to the user based on the available information from safety and environmental database illustrated in Figure 5.5. Reaction conversion and selectivity and the recycle of unreacted material are considered in the economic evaluation step.



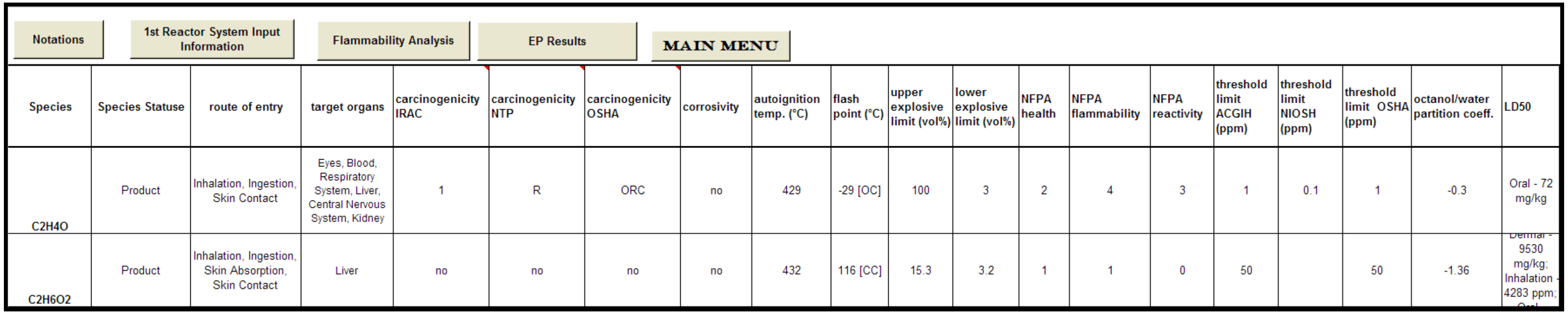
Reaction Path Number **1** Description: **Ethylene oxide Process**

1st Reaction		Other by-products formed	Liquid Catalyst
		C2H6O2	
Prices ($/kg)		1.27	
Mw (kg/kmol)		62.068	
Heat of formation (kJ/mol)		-387.5	
Cp (J/mol K)		98.8	
BP (K)		471.000	
Lower flammability limit (vol%)			
Upper flammability limit (vol%)			
Heat of combustion (kJ/mol)			
p (bar) @Temp C	46	0.00	
p (bar) @Temp C	181	0.61	
p (bar) @Temp C	35	0.00	
p (bar) @Temp C	275	6.78	
Tmax (K) for p		719.70	

		Inerts	Impurities
Prices ($/kg)			
Mw (g/mol)			
Heat of formation (kJ/mol)			
Cp (J/mol K)			
BP (K)			
Lower flammability limit (vol%)			
Upper flammability limit (vol%)			
Heat of combustion (kJ/mol)			
p (bar) @Temp C	46		
p (bar) @Temp C	181		
p (bar) @Temp C	35		
p (bar) @Temp C	275		
Tmax (K) for p			

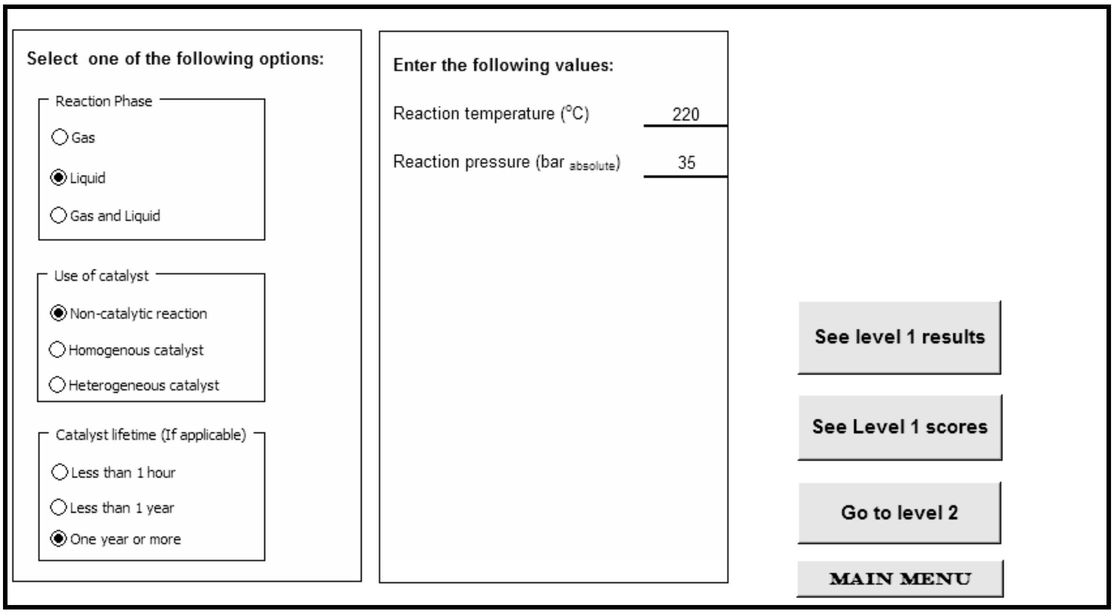
Figure 5.4: Further input information from the database on the process chemistry.

General input information about the process such as reaction phase, temperature and pressure, the use of catalyst and its lifetime are provided by the user to start the general reactor selection process as illustrated in Figure 5.6. This key information is used to select the main types of reactor. This early level of reactor system synthesis demonstrates the possibility to select suitable reactors by providing minimum information as illustrated in Figure 5.7. In the next level of reactor selection, more reactors and reactor configurations are evaluated based on additional input information.



Species	Species Statuse	route of entry	target organs	carcinogenicity IRAC	carcinogenicity NTP	carcinogenicity OSHA	corrosivity	autoignition temp. (°C)	flash point (°C)	upper explosive limit (vol%)	lower explosive limit (vol%)	NFPA health	NFPA flammability	NFPA reactivity	threshold limit ACGIH (ppm)	threshold limit NIOSH (ppm)	threshold limit OSHA (ppm)	octanol/water partition coeff.	LD50
C2H4O	Product	Inhalation, Ingestion, Skin Contact	Eyes, Blood, Respiratory System, Liver, Central Nervous System, Kidney	1	R	ORC	no	429	-29 [OC]	100	3	2	4	3	1	0.1	1	-0.3	Oral - 72 mg/kg
C2H6O2	Product	Inhalation, Ingestion, Skin Absorption, Skin Contact	Liver	no	no	no	no	432	116 [CC]	15.3	3.2	1	1	0	50		50	-1.36	Dermal - 9530 mg/kg; Inhalation - 4283 ppm;

Figure 5.5: Safety and environmental impacts from the IKBS database.



Select one of the following options:

Reaction Phase
- ○ Gas
- ● Liquid
- ○ Gas and Liquid

Use of catalyst
- ● Non-catalytic reaction
- ○ Homogenous catalyst
- ○ Heterogeneous catalyst

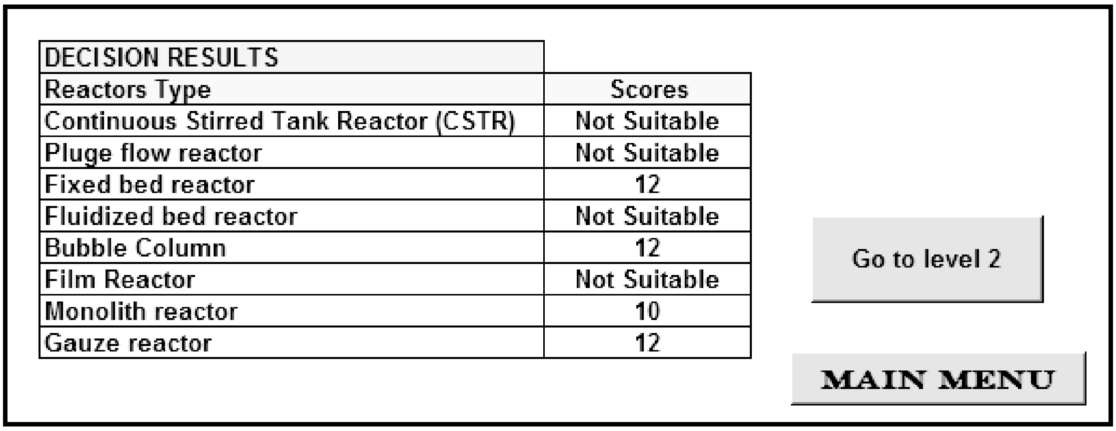
Catalyst lifetime (If applicable)
- ○ Less than 1 hour
- ○ Less than 1 year
- ● One year or more

Enter the following values:

Reaction temperature (^{o}C) 220

Reaction pressure (bar $_{absolute}$) 35

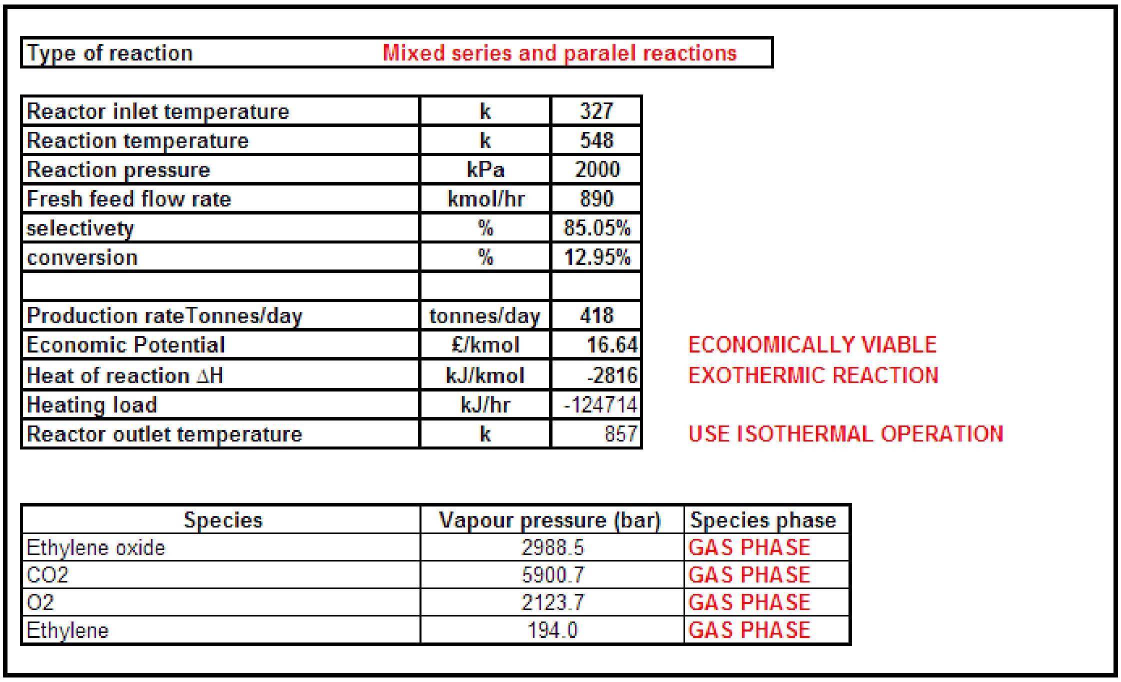
Figure 5.6: Reactor system synthesis level-1 input information.



DECISION RESULTS	
Reactors Type	Scores
Continuous Stirred Tank Reactor (CSTR)	Not Suitable
Pluge flow reactor	Not Suitable
Fixed bed reactor	12
Fluidized bed reactor	Not Suitable
Bubble Column	12
Film Reactor	Not Suitable
Monolith reactor	10
Gauze reactor	12

Figure 5.7: Reactor system synthesis level-1 results.

One of the key pieces of information in reactor selection is the phase of reaction. The phase of reaction can be given by the user or predicted. The reaction phase can be determined by the IKBS at reaction operating conditions based on Antoine equation vapour pressure calculations. Antoine equation constants are imported from the database. Figure 5.8, illustrates an example of the process analysis step. The IKBS analysis can indicate the type of reaction such single, series, parallel, and mixed series and parallel.



Type of reaction	Mixed series and paralel reactions

Reactor inlet temperature	k	327
Reaction temperature	k	548
Reaction pressure	kPa	2000
Fresh feed flow rate	kmol/hr	890
selectivety	%	85.05%
conversion	%	12.95%
Production rateTonnes/day	tonnes/day	418
Economic Potential	£/kmol	16.64
Heat of reaction ∆H	kJ/kmol	-2816
Heating load	kJ/hr	-124714
Reactor outlet temperature	k	857

ECONOMICALLY VIABLE

EXOTHERMIC REACTION

USE ISOTHERMAL OPERATION

Species	Vapour pressure (bar)	Species phase
Ethylene oxide	2988.5	GAS PHASE
CO2	5900.7	GAS PHASE
O2	2123.7	GAS PHASE
Ethylene	194.0	GAS PHASE

Figure 5.8: Reactor system analysis step.

The IKBS can also predict if the reaction is exothermic or endothermic based on the heat of formation calculations. Other calculation suggests the mode of reactor operation as an isothermal or adiabatic based on the calculation of the adiabatic temperature change. To make decisions on the reactor heat effects, the reactor heat load is estimated to calculate the adiabatic temperature change. Assuming steady state and no heat lost, the reactor heat load calculated as:

$$Q_R = \Delta H_R F_{FT} \tag{5.1}$$

Where:

Q_R: Reactor heat load (kJ/hr)

ΔH_R : Heat of reaction (kJ/kmol)

F_{FT}: Fresh feed rate (kmol/hr)

Once the reactor heat load is determined, the adiabatic temperature change is calculated from:

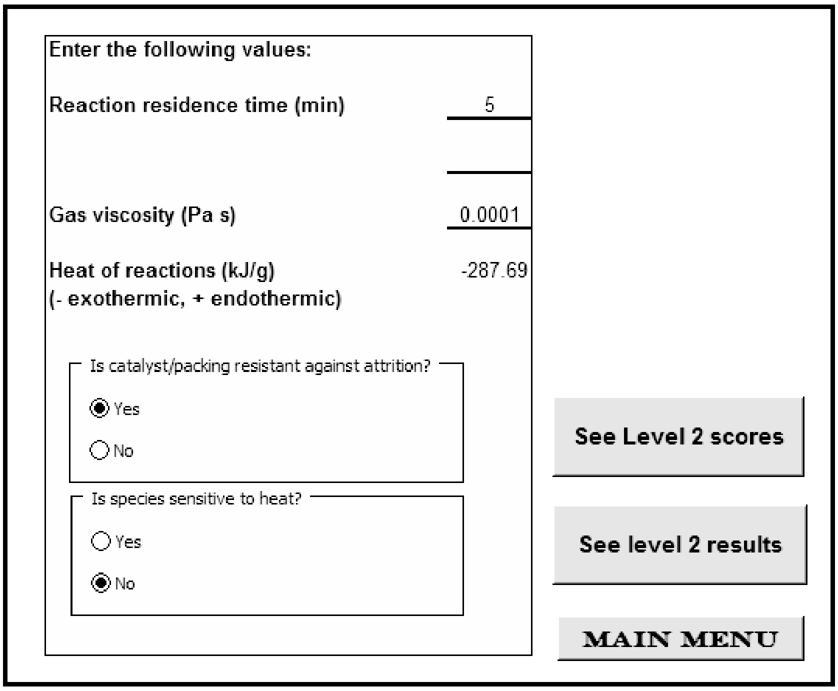
$$Q_R = FC_p(T_{R,in} - T_{R,out}) \tag{5.1}$$

Where:
Cp: heat capacity of the reactor feed stream (kJ/kmol K)
F : reactor feed stream flowrate (kmol/hr)
$T_{R,in}$: reactor inlet temperature (K)
$T_{R,out}$: reactor outlet temperature (K)

According to Douglas (1988), if the reaction is exothermic and the calculated reactor output temperature is more than the desired reaction temperature, isothermal operation is required to control the temperature. Smith (2005) suggests that if the adiabatic temperature change is less than 10 ^{o}C the reactor can be operated adiabatically. These calculations can be used to make a design decision on whether the reactor can be operated adiabatically, with direct heating or cooling, or whether a diluent or heat carrier is needed to control the reaction temperature with the allowable limits.

Highly exothermic reactions require safe control of the released heat, for example by using a multitubular reactor which is designed like a heat exchanger with a large number of tubes. Other methods involve external heat exchangers with circulation or heat exchangers between multiple reaction segments.

Further details such as the reaction exotherm, residence time, species viscosities and sensitivity to heat, potential catalyst attrition are given in the second level of input information (see Figure 5.9). This is followed by detailed kinetics information which can lead to a suggested list of single and multiple technical reactors. The required kinetics information is discussed in the subsequent sections. Other input information can be imported from the separation system once it is synthesised as a part of the reactor-separator-recycle system. Multiple reactor systems can be synthesised and decisions can be explained to the user.



Enter the following values:

Reaction residence time (min) 5

Gas viscosity (Pa s) 0.0001

Heat of reactions (kJ/g) -287.69
(- exothermic, + endothermic)

Is catalyst/packing resistant against attrition?
● Yes
○ No

Is species sensitive to heat?
○ Yes
● No

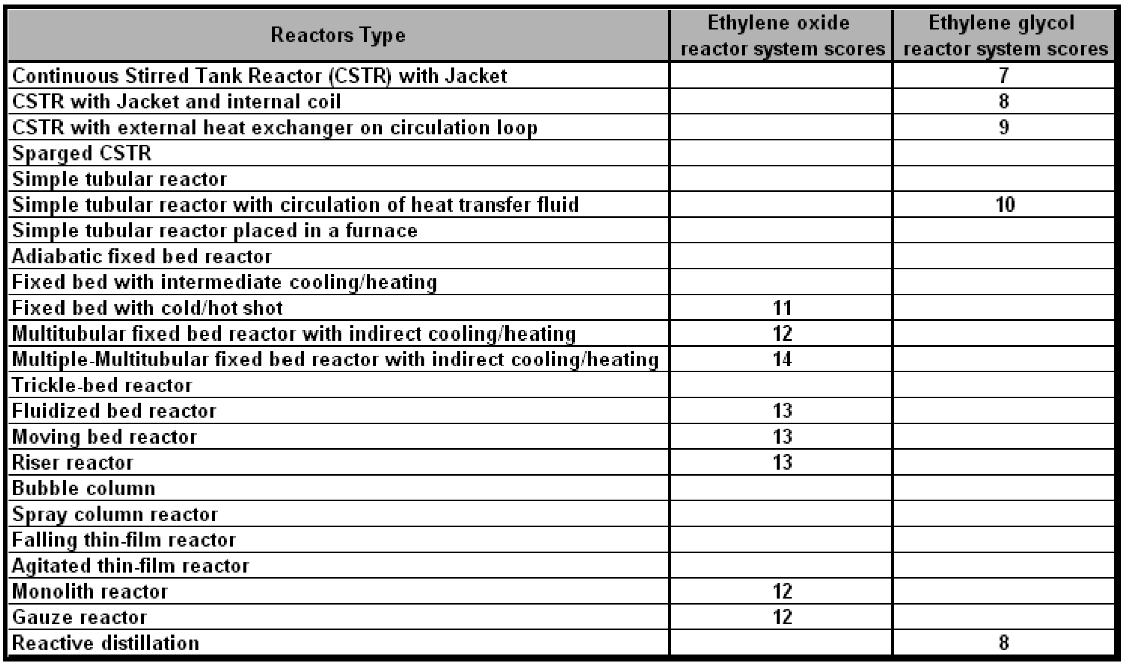
Figure 5.9: Reactor system synthesis level-2 input information.

The IKBS, lists suitable reactors in a table with the total scores given to each reactor as illustrated in Table 5.1. The allocated scores to each reactor is the sum of all relevant decision criteria scores. Reactors without scores are not suitable because one relevant criterion, or more, indicates that the reactor is not suitable for the process requirements. The scoring system implemented in the IKBS is described in the subsequent sections.

The proposed reactor systems are then simulated using a generic flowsheet in Aspen HYSYS process simulator. Figure 5.10, illustrates the reactor systems of proposed generic flowsheet. The reactor system contains a series of four CSTRs which are parallel with another series of four fixed bed/plug flow reactors with interchange between each reactor to examine different configurations of multiple reactors. Reactor systems can comprise a single reactor, or a combination of reactors of the same type such as fixed bed reactors in parallel. It also can be a combination of different type of reactors such as CSTR followed by PFR. Each reactor input and output streams include a heat exchanger to adjust the stream temperature based on the design requirements.

There is also a bypass around each reactor and internal recycle between reactors. Reactor systems output streams are connected to the separation systems.

Table 5.1: List of suggested reactors by the IKBS for two reaction stages system.



Reactors Type	Ethylene oxide reactor system scores	Ethylene glycol reactor system scores
Continuous Stirred Tank Reactor (CSTR) with Jacket		7
CSTR with Jacket and internal coil		8
CSTR with external heat exchanger on circulation loop		9
Sparged CSTR		
Simple tubular reactor		
Simple tubular reactor with circulation of heat transfer fluid		10
Simple tubular reactor placed in a furnace		
Adiabatic fixed bed reactor		
Fixed bed with intermediate cooling/heating		
Fixed bed with cold/hot shot	11	
Multitubular fixed bed reactor with indirect cooling/heating	12	
Multiple-Multitubular fixed bed reactor with indirect cooling/heating	14	
Trickle-bed reactor		
Fluidized bed reactor	13	
Moving bed reactor	13	
Riser reactor	13	
Bubble column		
Spray column reactor		
Falling thin-film reactor		
Agitated thin-film reactor		
Monolith reactor	12	
Gauze reactor	12	
Reactive distillation		8

Results from reactor and separator systems are linked for total flowsheet synthesis. The connectivity of reactor and separator systems are also achieved by gas and liquid recycle from the separation systems. The reactor streams are connected with a set of mixing and splitting units. A matrix of splitters ratio is used in Excel to specify the direction and magnitude of streams between the reactors as illustrated in Figure 5.11. These design flexibilities can be used to assess the process performance at different configurations.

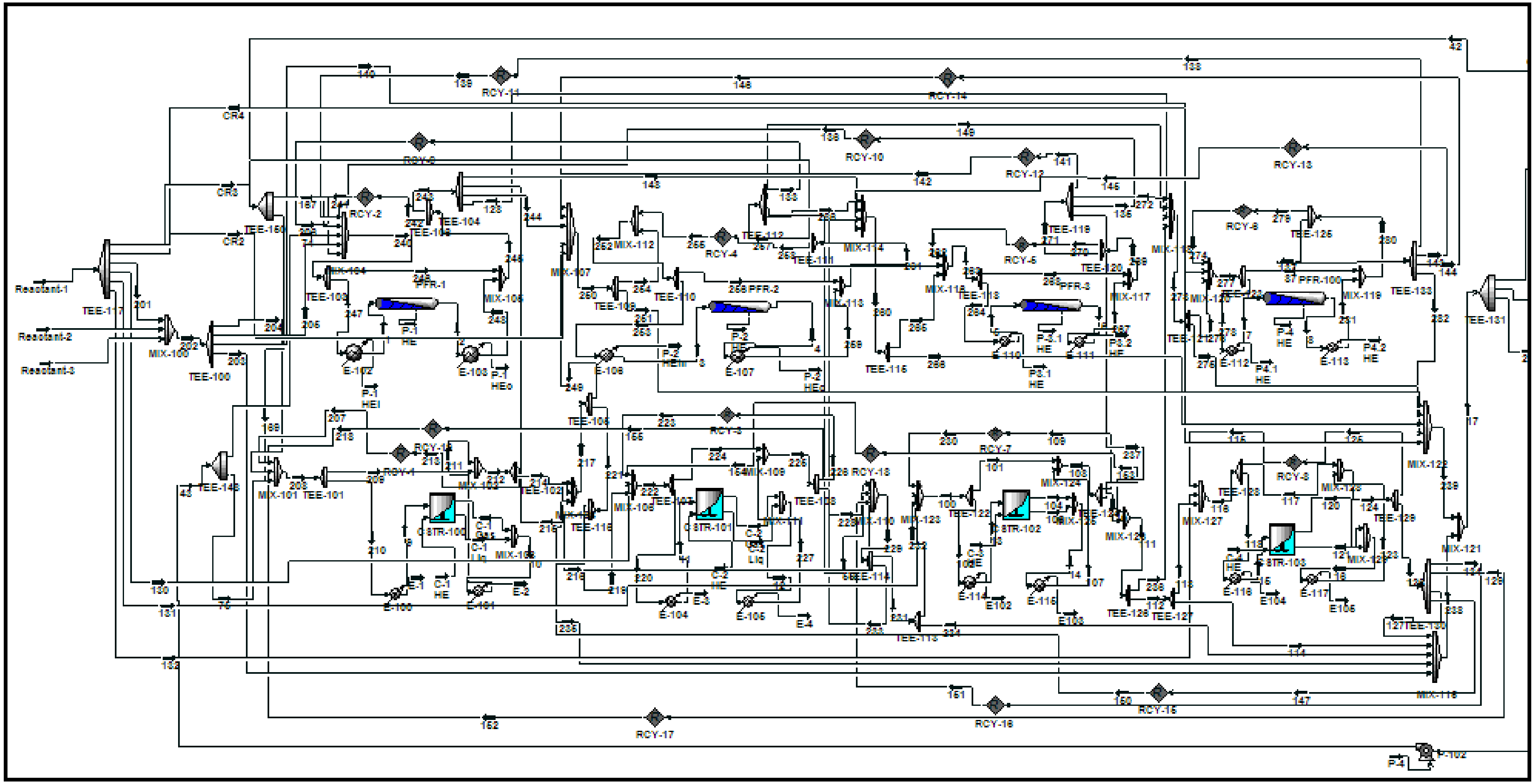
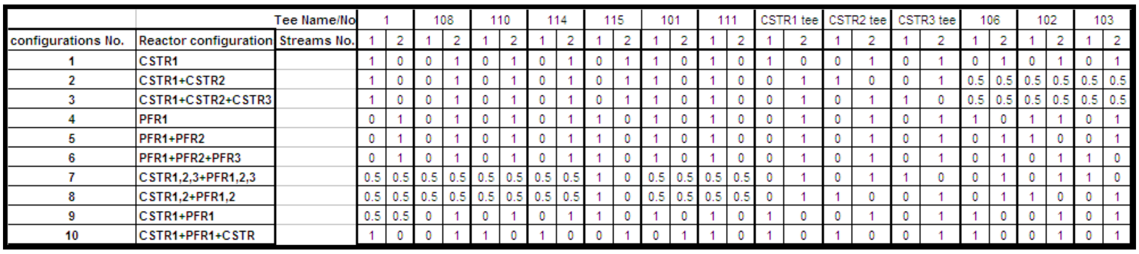


Figure 5.10: Reactor systems in HYSYS generic process flowsheet



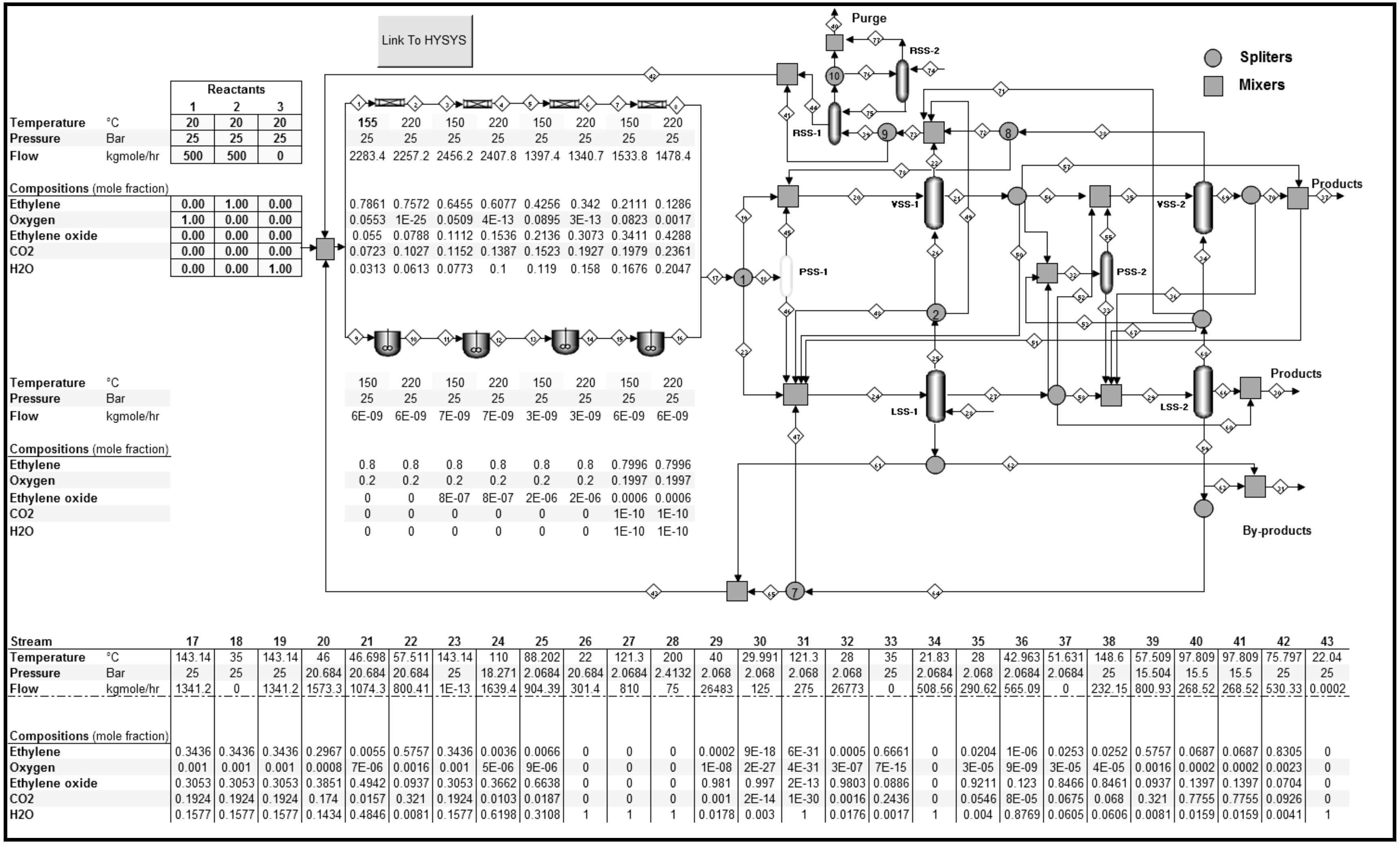
		Tee Name/No	1		108		110		114		115		101		111		CSTR1 tee		CSTR2 tee		CSTR3 tee		106		102		103	
configurations No.	Reactor configuration	Streams No.	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1	CSTR1		1	0	0	1	0	1	0	1	0	1	1	0	1	0	1	0	0	1	0	1	0	1	0	1	0	1
2	CSTR1+CSTR2		1	0	0	1	0	1	0	1	0	1	1	0	1	0	0	1	1	0	0	1	0.5	0.5	0.5	0.5	0.5	0.5
3	CSTR1+CSTR2+CSTR3		1	0	0	1	0	1	0	1	0	1	1	0	1	0	0	1	0	1	1	0	0.5	0.5	0.5	0.5	0.5	0.5
4	PFR1		0	1	0	1	0	1	0	1	1	0	1	0	1	0	0	1	0	1	0	1	1	0	1	1	0	1
5	PFR1+PFR2		0	1	0	1	0	1	0	1	1	0	1	0	1	0	0	1	0	1	0	1	0	1	1	0	0	1
6	PFR1+PFR2+PFR3		0	1	0	1	0	1	0	1	1	0	1	0	1	0	0	1	0	1	0	1	0	1	0	1	1	0
7	CSTR1,2,3+PFR1,2,3		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	0	0.5	0.5	0.5	0.5	0	1	0	1	1	0	0	1	0	1	1	0
8	CSTR1,2+PFR1,2		0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	1	0	0.5	0.5	0.5	0.5	0	1	1	0	0	1	0	1	1	0	0	1
9	CSTR1+PFR1		0.5	0.5	0	1	0	1	0	1	1	0	1	0	1	0	1	0	0	1	0	1	1	0	0	1	0	1
10	CSTR1+PFR1+CSTR		1	0	0	1	1	0	1	0	0	1	0	1	1	0	1	0	1	0	0	1	1	0	0	1	0	1

Figure 5.11: The IKBS matrix of splitters ratio to specify the direction and magnitude of streams between the generic flowsheet reactors.

In the reactor system synthesis, non-ideal behaviour of reactors can be considered, such as the modular simulation of fluidized bed reactors based on the use of a series of four CSTRs and PFRs in parallel with interchange between the different reactor types. Application of this approach is presented in the ethylene oxide case study in Chapter 7. It is also possible to customize Aspen HYSYS by creating custom unit operations.

The generic process flowsheet gives the capabilities of exploring and optimizing different reactor configurations. This includes studying the effect of feed distribution, the recycle of products between reactions zones and the use of a combination of different reactors. In the IKBS, users can adjust the make-up feed temperature, pressure and reactants ratio, and each reaction zone feed temperature, to examine the effect on reactor system performance. Once these variables have changed, it will be exported to Aspen HYSYS for simulation, and then the results are imported to the IKBS as illustrated in Figure 5.12.

Current imported results from Aspen HYSYS simulated generic flowsheet include the main 43 streams flowrate, temperature, pressure and composition. This link between the IKBS and Aspen HYSYS was performed by VBA program as illustrated in Appendix B. The “what-if” scenario can enable the users to explore the effect of the design variables and visualize the optimization results in the IKBS.



		Reactants		
		1	2	3
Temperature	°C	20	20	20
Pressure	Bar	25	25	25
Flow	kgmole/hr	500	500	0
Compositions (mole fraction)				
Ethylene		0.00	1.00	0.00
Oxygen		1.00	0.00	0.00
Ethylene oxide		0.00	0.00	0.00
CO2		0.00	0.00	0.00
H2O		0.00	0.00	1.00

155	220	150	220	150	220	150	220
25	25	25	25	25	25	25	25
2283.4	2257.2	2456.2	2407.8	1397.4	1340.7	1533.8	1478.4
0.7861	0.7572	0.6455	0.6077	0.4256	0.342	0.2111	0.1286
0.0553	1E-25	0.0509	4E-13	0.0895	3E-13	0.0823	0.0017
0.055	0.0788	0.1112	0.1536	0.2136	0.3073	0.3411	0.4288
0.0723	0.1027	0.1152	0.1387	0.1523	0.1927	0.1979	0.2361
0.0313	0.0613	0.0773	0.1	0.119	0.158	0.1676	0.2047

Temperature	°C	150	220	150	220	150	220	150	220
Pressure	Bar	25	25	25	25	25	25	25	25
Flow	kgmole/hr	6E-09	6E-09	7E-09	7E-09	3E-09	3E-09	6E-09	6E-09
Compositions (mole fraction)									
Ethylene		0.8	0.8	0.8	0.8	0.8	0.8	0.7996	0.7996
Oxygen		0.2	0.2	0.2	0.2	0.2	0.2	0.1997	0.1997
Ethylene oxide		0	0	8E-07	8E-07	2E-06	2E-06	0.0006	0.0006
CO2		0	0	0	0	0	0	1E-10	1E-10
H2O		0	0	0	0	0	0	1E-10	1E-10

Stream		17	18	19	20	21	22	23	24	25	26	27	28	29	30
Temperature	°C	143.14	35	143.14	46	46.698	57.511	143.14	110	88.202	22	121.3	200	40	29.991
Pressure	Bar	25	25	25	20.684	20.684	20.684	25	18.271	2.0684	20.684	2.0684	2.4132	2.068	2.068
Flow	kgmole/hr	1341.2	0	1341.2	1573.3	1074.3	800.41	1E-13	1639.4	904.39	301.4	810	75	26483	125
Compositions (mole fraction)															
Ethylene		0.3436	0.3436	0.3436	0.2967	0.0055	0.5757	0.3436	0.0036	0.0066	0	0	0	0.0002	9E-18
Oxygen		0.001	0.001	0.001	0.0008	7E-06	0.0016	0.001	5E-06	9E-06	0	0	0	1E-08	2E-27
Ethylene oxide		0.3053	0.3053	0.3053	0.3851	0.4942	0.0937	0.3053	0.3662	0.6638	0	0	0	0.981	0.997
CO2		0.1924	0.1924	0.1924	0.174	0.0157	0.321	0.1924	0.0103	0.0187	0	0	0	0.001	2E-14
H2O		0.1577	0.1577	0.1577	0.1434	0.4846	0.0081	0.1577	0.6198	0.3108	1	1	1	0.0178	0.003

Stream		31	32	33	34	35	36	37	38	39	40	41	42	43
Temperature	°C	121.3	28	35	21.83	28	42.963	51.631	148.6	57.509	97.809	97.809	75.797	22.04
Pressure	Bar	2.068	2.068	25	2.0684	2.068	2.0684	2.0684	25	15.504	15.5	15.5	25	25
Flow	kgmole/hr	275	26773	0	508.56	290.62	565.09	0	232.15	800.93	268.52	268.52	530.33	0.0002
Compositions (mole fraction)														
Ethylene		6E-31	0.0005	0.6661	0	0.0204	1E-06	0.0253	0.0252	0.5757	0.0687	0.0687	0.8305	0
Oxygen		4E-31	3E-07	7E-15	0	3E-05	9E-09	3E-05	4E-05	0.0016	0.0002	0.0002	0.0023	0
Ethylene oxide		2E-13	0.9803	0.0886	0	0.9211	0.123	0.8466	0.8461	0.0937	0.1397	0.1397	0.0704	0
CO2		1E-30	0.0016	0.2436	0	0.0546	8E-05	0.0675	0.068	0.321	0.7755	0.7755	0.0926	0
H2O		1	0.0176	0.0017	1	0.004	0.8769	0.0605	0.0606	0.0081	0.0159	0.0159	0.0041	1

Figure 5.12: Generic flowsheet results from linking the IKBS with Aspen HYSYS simulation.

5.3 Reactor Selection Decision Criteria

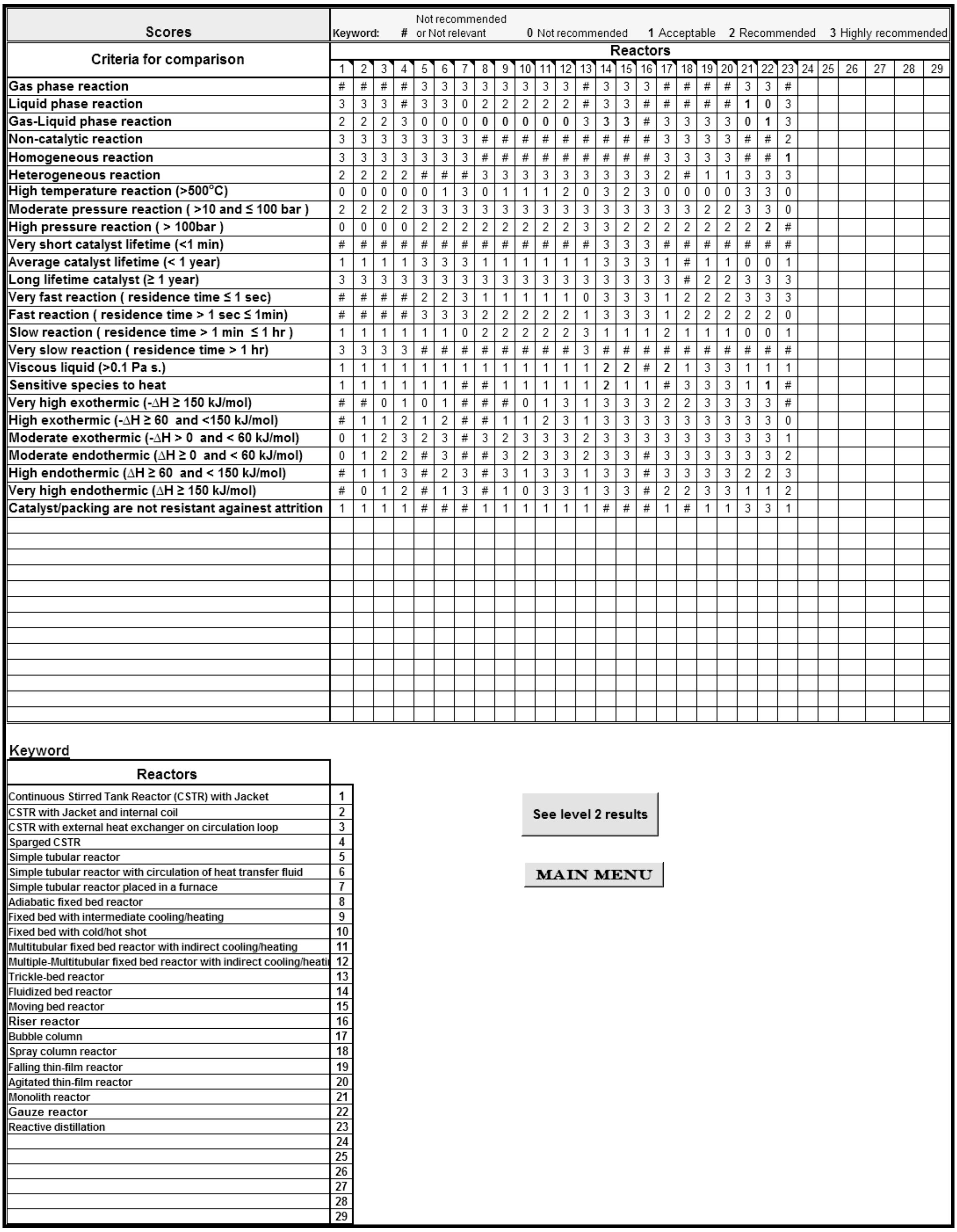
The goal of chemical reactor systems synthesis is to find the type, arrangements and operating conditions of reactors which meet design constraints based on reaction kinetics and other key properties of reaction species. The general factors that affect the selection of a chemical reactor are discussed here.

Initial reactor system selection criteria in the IKBS start with positive economic potential and acceptable safety and environmental impacts as discussed in Chapter 4. Subsequent analyses are based on a set of criteria. Figure 5.13, illustrates, the IKBS criteria for reactor selection and associated scores. The main criteria are the following:

- phase of reaction
- reaction pressure and temperature
- speed of reaction
- use of catalyst, catalyst lifetime and potential attrition
- reaction exotherm
- viscosity
- heat transfer requirements

The reactor selection scoring worksheet contains 25 selection criteria and 23 reactors and reactor configurations. Figure 5.13, illustrates that the IKBS has the flexibility to add more criteria, reactors, and scores. There can be 6 more reactors and 13 criteria added to the reactor evaluation and selection, without significant modification of the program.

As illustrated in Figure 5.13, the scoring system used in the selection process ranges from "not suitable" (given the sign #), which immediately eliminates the choice. For example, a typical CSTR is not suitable for gas phase reaction. Therefore, it is given the score "#" which eliminates it. For suitable reactors, the selection scores range from 0 to 3 where 0 can be given to "not recommended", or "not relevant", 1 "acceptable", 2 "recommended" and 3 "highly recommended". The highly recommended score is given to selection criteria, which have been implemented in many existing commercial processes using the same reactor type.



Scores

Keyword: # Not recommended or Not relevant 0 Not recommended 1 Acceptable 2 Recommended 3 Highly recommended

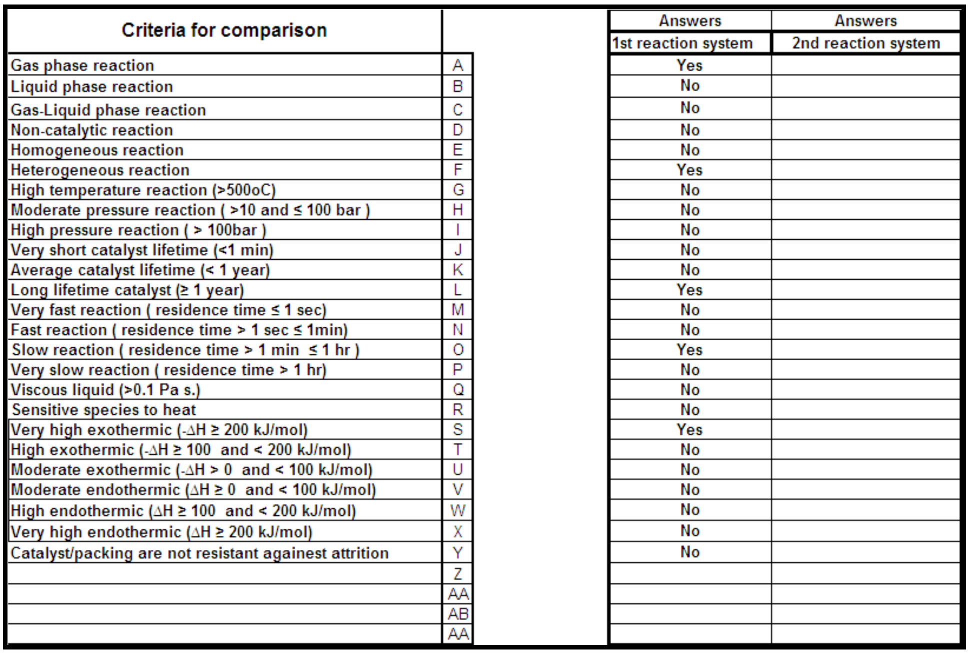
Criteria for comparison	Reactors																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Gas phase reaction	#	#	#	#	3	3	3	3	3	3	3	3	#	3	3	3	#	#	#	#	3	3	#						
Liquid phase reaction	3	3	3	#	3	3	0	2	2	2	2	2	#	3	3	#	#	#	#	#	1	0	3						
Gas-Liquid phase reaction	2	2	2	3	0	0	0	0	0	0	0	0	3	3	3	#	3	3	3	3	0	1	3						
Non-catalytic reaction	3	3	3	3	3	3	3	#	#	#	#	#	#	#	#	#	3	3	3	3	#	#	2						
Homogeneous reaction	3	3	3	3	3	3	3	#	#	#	#	#	#	#	#	#	3	3	3	3	#	#	1						
Heterogeneous reaction	2	2	2	2	#	#	#	3	3	3	3	3	3	3	3	3	2	#	1	1	3	3	3						
High temperature reaction (>500°C)	0	0	0	0	0	1	3	0	1	1	1	2	0	3	2	3	0	0	0	0	3	3	0						
Moderate pressure reaction (>10 and ≤ 100 bar)	2	2	2	2	3	3	3	3	3	3	3	3	3	3	3	3	3	3	2	2	3	3	0						
High pressure reaction (> 100bar)	0	0	0	0	2	2	2	2	2	2	2	2	3	3	2	2	2	2	2	2	2	2	#						
Very short catalyst lifetime (<1 min)	#	#	#	#	#	#	#	#	#	#	#	#	#	3	3	3	#	#	#	#	#	#	#						
Average catalyst lifetime (< 1 year)	1	1	1	1	3	3	3	1	1	1	1	1	1	3	3	3	1	#	1	1	0	0	1						
Long lifetime catalyst (≥ 1 year)	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	#	2	2	3	3	3						
Very fast reaction (residence time ≤ 1 sec)	#	#	#	#	2	2	3	1	1	1	1	1	0	3	3	3	1	2	2	2	3	3	3						
Fast reaction (residence time > 1 sec ≤ 1min)	#	#	#	#	3	3	3	2	2	2	2	2	1	3	3	3	1	2	2	2	2	2	0						
Slow reaction (residence time > 1 min ≤ 1 hr)	1	1	1	1	1	1	0	2	2	2	2	2	3	1	1	1	2	1	1	1	0	0	1						
Very slow reaction (residence time > 1 hr)	3	3	3	3	#	#	#	#	#	#	#	#	3	#	#	#	#	#	#	#	#	#	#						
Viscous liquid (>0.1 Pa s.)	1	1	1	1	1	1	1	1	1	1	1	1	1	2	2	#	2	1	3	3	1	1	1						
Sensitive species to heat	1	1	1	1	1	1	#	#	1	1	1	1	1	2	1	1	#	3	3	3	1	1	#						
Very high exothermic (-ΔH ≥ 150 kJ/mol)	#	#	0	1	0	1	#	#	#	0	1	3	1	3	3	3	2	2	3	3	3	3	#						
High exothermic (-ΔH ≥ 60 and <150 kJ/mol)	#	1	1	2	1	2	#	#	1	1	2	3	1	3	3	3	3	3	3	3	3	3	0						
Moderate exothermic (-ΔH > 0 and < 60 kJ/mol)	0	1	2	3	2	3	#	3	2	3	3	3	2	3	3	3	3	3	3	3	3	3	1						
Moderate endothermic (ΔH ≥ 0 and < 60 kJ/mol)	0	1	2	2	#	3	#	#	3	2	3	3	2	3	3	#	3	3	3	3	3	3	2						
High endothermic (ΔH ≥ 60 and < 150 kJ/mol)	#	1	1	3	#	2	3	#	3	1	3	3	1	3	3	#	3	3	3	3	2	2	3						
Very high endothermic (ΔH ≥ 150 kJ/mol)	#	0	1	2	#	1	3	#	1	0	3	3	1	3	3	#	2	2	3	3	1	1	2						
Catalyst/packing are not resistant againest attrition	1	1	1	1	#	#	#	1	1	1	1	1	1	#	#	#	1	#	1	1	3	3	1						

Keyword

Reactors	
Continuous Stirred Tank Reactor (CSTR) with Jacket	1
CSTR with Jacket and internal coil	2
CSTR with external heat exchanger on circulation loop	3
Sparged CSTR	4
Simple tubular reactor	5
Simple tubular reactor with circulation of heat transfer fluid	6
Simple tubular reactor placed in a furnace	7
Adiabatic fixed bed reactor	8
Fixed bed with intermediate cooling/heating	9
Fixed bed with cold/hot shot	10
Multitubular fixed bed reactor with indirect cooling/heating	11
Multiple-Multitubular fixed bed reactor with indirect cooling/heati	12
Trickle-bed reactor	13
Fluidized bed reactor	14
Moving bed reactor	15
Riser reactor	16
Bubble column	17
Spray column reactor	18
Falling thin-film reactor	19
Agitated thin-film reactor	20
Monolith reactor	21
Gauze reactor	22
Reactive distillation	23
	24
	25
	26
	27
	28
	29

Figure 5.13: Example of reactors selection criteria

Once the required information for the synthesis of the chemical reactor systems is provided by the user, imported from the databases, or calculated by the IKBS, the answers to each criterion is tabulated in the reactor selection scoring worksheet as illustrated in Figure 5.14. If the answer is “YES” then the score in Figure 5.13 is considered and the criterion is accounted for in the selection of the reactor. If the answer is “NO”, the score in Figure 5.13 is ignored.

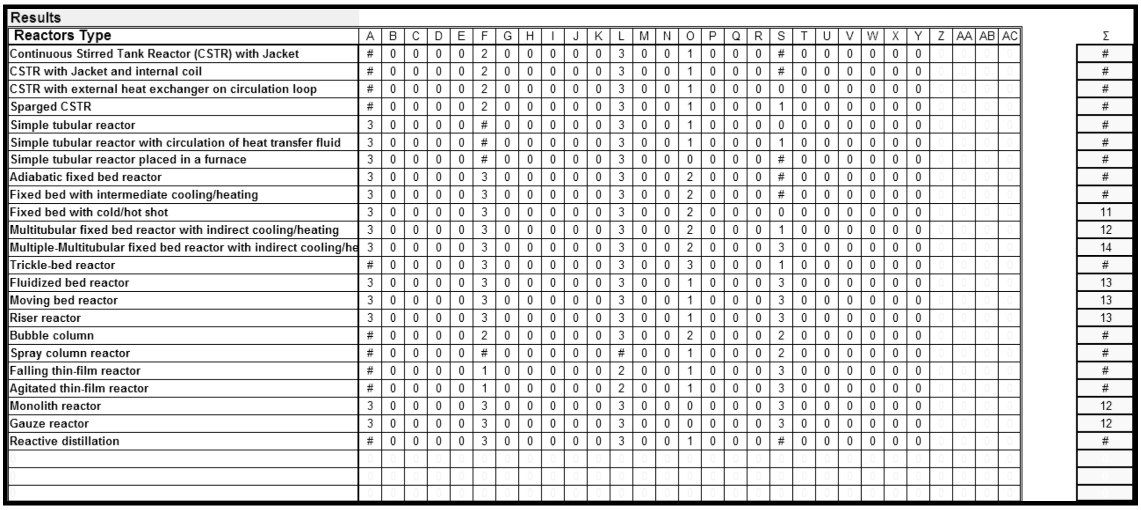


Criteria for comparison		Answers	Answers
		1st reaction system	2nd reaction system
Gas phase reaction	A	Yes	
Liquid phase reaction	B	No	
Gas-Liquid phase reaction	C	No	
Non-catalytic reaction	D	No	
Homogeneous reaction	E	No	
Heterogeneous reaction	F	Yes	
High temperature reaction (>500oC)	G	No	
Moderate pressure reaction (>10 and ≤ 100 bar)	H	No	
High pressure reaction (> 100bar)	I	No	
Very short catalyst lifetime (<1 min)	J	No	
Average catalyst lifetime (< 1 year)	K	No	
Long lifetime catalyst (≥ 1 year)	L	Yes	
Very fast reaction (residence time ≤ 1 sec)	M	No	
Fast reaction (residence time > 1 sec ≤ 1min)	N	No	
Slow reaction (residence time > 1 min ≤ 1 hr)	O	Yes	
Very slow reaction (residence time > 1 hr)	P	No	
Viscous liquid (>0.1 Pa s.)	Q	No	
Sensitive species to heat	R	No	
Very high exothermic (-ΔH ≥ 200 kJ/mol)	S	Yes	
High exothermic (-ΔH ≥ 100 and < 200 kJ/mol)	T	No	
Moderate exothermic (-ΔH > 0 and < 100 kJ/mol)	U	No	
Moderate endothermic (ΔH ≥ 0 and < 100 kJ/mol)	V	No	
High endothermic (ΔH ≥ 100 and < 200 kJ/mol)	W	No	
Very high endothermic (ΔH ≥ 200 kJ/mol)	X	No	
Catalyst/packing are not resistant againest attrition	Y	No	
	Z		
	AA		
	AB		
	AA		

Figure 5.14: Input information answers in the IKBS for reactor selection

The sum of all criteria scores is given to each suitable reactor as illustrated in Figure 5.15. For example, when a multi-tubular reactor is examined for a highly exothermic gas phase catalytic reaction, IKBS gives the score “3” for each of the three criteria (phase of reaction, reaction exotherm and use of heterogeneous catalyst) with the total score of “9”. Weighting the selection criteria of process units by allocating different values to each criterion can improve the design decision. This can be an important future task to account for the fact that some criteria may have a bigger effect on the selection of the reactor-separator-recycle system than others.

In the IKBS, scores can be changed based on further assessments and experience. For example, the design engineer will be given the chance to evaluate the proposed flowsheet and give feedback which may yield a change of the scores. If any of the scores for the examined reactor is “#” i.e. not suitable, the sum of the sores in Figure 5.15, is given the sign “#” regardless the other suitable criteria scores values.

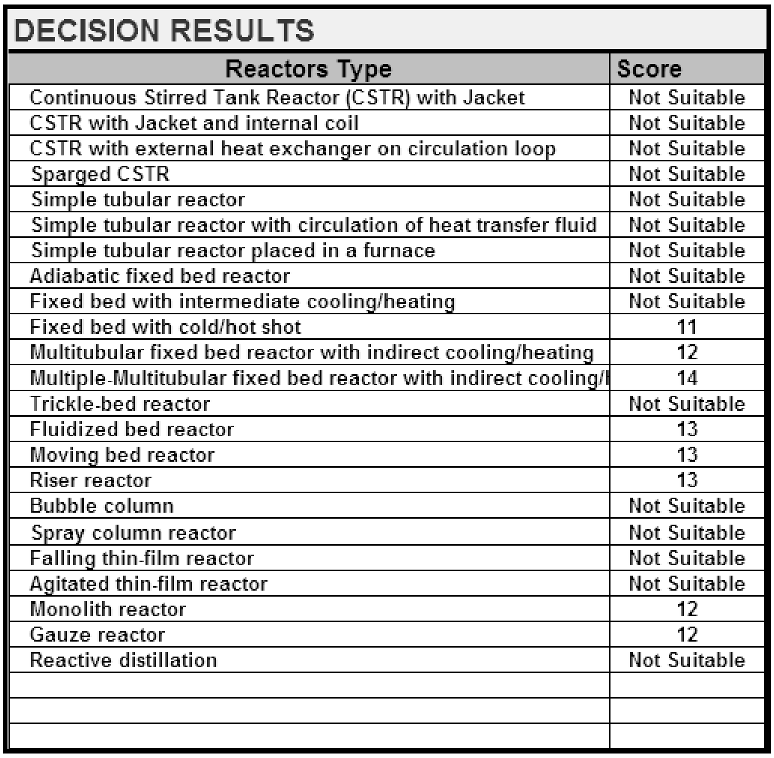


Results

Reactors Type	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	Σ
Continuous Stirred Tank Reactor (CSTR) with Jacket	#	0	0	0	0	2	0	0	0	0	0	3	0	0	1	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
CSTR with Jacket and internal coil	#	0	0	0	0	2	0	0	0	0	0	3	0	0	1	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
CSTR with external heat exchanger on circulation loop	#	0	0	0	0	2	0	0	0	0	0	3	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#
Sparged CSTR	#	0	0	0	0	2	0	0	0	0	0	3	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	#
Simple tubular reactor	3	0	0	0	0	#	0	0	0	0	0	3	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#
Simple tubular reactor with circulation of heat transfer fluid	3	0	0	0	0	#	0	0	0	0	0	3	0	0	1	0	0	0	1	0	0	0	0	0	0	0	0	0	0	#
Simple tubular reactor placed in a furnace	3	0	0	0	0	#	0	0	0	0	0	3	0	0	0	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
Adiabatic fixed bed reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	2	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
Fixed bed with intermediate cooling/heating	3	0	0	0	0	3	0	0	0	0	0	3	0	0	2	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
Fixed bed with cold/hot shot	3	0	0	0	0	3	0	0	0	0	0	3	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	11
Multitubular fixed bed reactor with indirect cooling/heating	3	0	0	0	0	3	0	0	0	0	0	3	0	0	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	12
Multiple-Multitubular fixed bed reactor with indirect cooling/he	3	0	0	0	0	3	0	0	0	0	0	3	0	0	2	0	0	0	3	0	0	0	0	0	0	0	0	0	0	14
Trickle-bed reactor	#	0	0	0	0	3	0	0	0	0	0	3	0	0	3	0	0	0	1	0	0	0	0	0	0	0	0	0	0	#
Fluidized bed reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	13
Moving bed reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	13
Riser reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	13
Bubble column	#	0	0	0	0	2	0	0	0	0	0	3	0	0	2	0	0	0	2	0	0	0	0	0	0	0	0	0	0	#
Spray column reactor	#	0	0	0	0	#	0	0	0	0	0	#	0	0	1	0	0	0	2	0	0	0	0	0	0	0	0	0	0	#
Falling thin-film reactor	#	0	0	0	0	1	0	0	0	0	0	2	0	0	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	#
Agitated thin-film reactor	#	0	0	0	0	1	0	0	0	0	0	2	0	0	1	0	0	0	3	0	0	0	0	0	0	0	0	0	0	#
Monolith reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	12
Gauze reactor	3	0	0	0	0	3	0	0	0	0	0	3	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	12
Reactive distillation	#	0	0	0	0	3	0	0	0	0	0	3	0	0	1	0	0	0	#	0	0	0	0	0	0	0	0	0	0	#
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Figure 5.15: The IKBS reactor scores calculation

If any of the scores in Figure 5.15 for the examined reactor is "#", the reactor decision results show "not suitable" as illustrated in Figure 5.16. The suitable reactors are given the sum of the criteria scores.



DECISION RESULTS

Reactors Type	Score
Continuous Stirred Tank Reactor (CSTR) with Jacket	Not Suitable
CSTR with Jacket and internal coil	Not Suitable
CSTR with external heat exchanger on circulation loop	Not Suitable
Sparged CSTR	Not Suitable
Simple tubular reactor	Not Suitable
Simple tubular reactor with circulation of heat transfer fluid	Not Suitable
Simple tubular reactor placed in a furnace	Not Suitable
Adiabatic fixed bed reactor	Not Suitable
Fixed bed with intermediate cooling/heating	Not Suitable
Fixed bed with cold/hot shot	11
Multitubular fixed bed reactor with indirect cooling/heating	12
Multiple-Multitubular fixed bed reactor with indirect cooling/	14
Trickle-bed reactor	Not Suitable
Fluidized bed reactor	13
Moving bed reactor	13
Riser reactor	13
Bubble column	Not Suitable
Spray column reactor	Not Suitable
Falling thin-film reactor	Not Suitable
Agitated thin-film reactor	Not Suitable
Monolith reactor	12
Gauze reactor	12
Reactive distillation	Not Suitable

Figure 5.16: The IKBS reactor selection decision results

Perry and Green, (1997) tabulated about 120 industrial chemical reactions with the associated types of reactors, reactor phase, catalyst, temperature, pressure, and residence time. The information from this list is summarized in Table 5.2 and used by the IKBS to construct the decision making criteria for selecting reactors with similar conditions.

Table 5.2: Examples of industrial chemical reactor applications. (modified and summarized from Perry and Green, 1997)

Reactor	Phase	Temperature range ^{o}C	Pressure range (atm)	Residence time
CSTR	L	5 - 165	1-100	0.5 min- 140 hr
PFR	G,L,G+L	70- 860	1-200	0.015 s – 7.5 s
Fixed bed	G,L,G+L	40-600	1-1000	0.5 s -1 hr
Fluidized bed	G	270-550	1-10	0.1-5 s
Multitubular fixed bed	G,L,G+L	50-790	1-13	0.2 s – 2.5 hr
Tower	G,L,G+L	15-800	1-500	0.07 s – 10 hr
Gauze	G	450-1150	1-8	0.0026-0.01 s
Furnace	G	500-700	1	1 s
Riser	G	530-540	2-3	2-4 s

5.3.1 Reaction Phase

The phase of reaction is one of the basic criteria which eliminates a range of reactor types. The phases that can be involved in chemical reactions are: gas (G), liquid (L), liquid/solid (L/S), gas/solid (G/S), gas/liquid (G/L), gas/liquid/solid (G/L/S) and liquid/liquid/solid (L/L/S).

An example for the elimination of a reactor based on reaction phase is the CSTR which is not suitable for a gas phase reaction due to the mixing characteristics of CSTRs.

However, a lab scale CSTR with rotating catalyst basket can be used for catalytic gas phase reaction, such as Carberry and Berty reactors by Autoclaves Ltd. Wood (2007) summarised a list of reactors with suitable reaction phases in the range starting from "1" for suitable to "3" for widely used. Wood also highlighted the key advantages and applications of each reactor as illustrated in Table 5.3.

A comparison of the suggested scores in Table 5.3 with the proposed scores in the IKBS shows that the IKBS cover a wider range of application and scores are more applicable to engineering practice. For example, the IKBS suggests the use of multi bed reactor with quench or heat transfer for gas or liquid catalytic reaction, whereas Table 5.3 suggests the same reactor for only gas catalytic reaction. Furthermore, moving bed reactors can be used for catalytic and non catalytic reactions as suggested by the IKBS, whereas Table 5.3 only suggests it for catalytic reaction.

Reactive distillation in Table 5.3 is only recommended for liquid phase homogeneous reactions, where it can also be used for catalytic heterogeneous reactions as suggested by the IKBS. The monolith reactor is given the same score (2) for liquid and gas reaction in Table 5.3, the IKBS give higher score for gas phase (3) than the liquid phase (1) due to the difference in pressure drop and mixing characteristics.

In the IKBS, the list of reactors considered is wider than in most pervious work such as Kirkwood et al. (1988) and Han et al. (1996a,b), which restricts reactor choices to CSTR for liquid, or mixed phase, and PFR for liquid or gas phase reactions.

Table 5.3: Effect of reaction phase on the choice of reactor (modified from Wood, 2007).

Type of reactor	Homo-geneous			Heterogeneous							Comments
						non-catalytic		Catalytic			
	G	L	S	GL	LL	GS	LS	GS	LS	GLS	
Simple Plug Flow Reactor (PFR)	3	2									Used for fast and High temperature reactions. Good for consecutive reactions. High heat transfer area.
Moving bed reactor								2	2	2	Used for very fast reactions. Good for consecutive reactions. Large transfer area, temperature can be controlled by injection.
Fixed bed catalyst								3	1	3	Used for fast reactions. Good for consecutive reactions. Not suitable for high exothermic and endothermic reactions.
Multi-bed reactor, adiabatic with quench or heat exchange								2			Used for primarily for equilibrium reactions that are temperature sensitive. Large transfer area.
Multi-tube fixed bed catalyst non adiabatic							1	3	2		Used for fast, reactions. Good for consecutive reactions. Large transfer area. Handle exothermic reactions.
Bubble reactor				2	2					2	Used for slow reactions, consecutive reactions, irreversible and reversible with high equilibrium constant. Relatively isothermal. Limited I range of temperature and pressures.
Spray reactor				2	1					2	Used for fast reactions. Low pressure drop
Trickle bed reactor									1	3	Used for very fast reactions. All reaction is in the liquid film and is mass transfer controlled.
Monolithic reactor								2	2	1	Used when mass transfer affects selectivity or reactivity, not for highly exothermic reaction because limited in radial heat transfer unless cross flow is used.
Thin film		1		1	1					1	Mass transfer controlled, fast absorption and highly exothermic or endothermic reaction. Good for viscous liquids.
Shaft furnace			1			1					Highly endothermic reaction.
Series of CSTR		1		1					1	2	Used for slow reaction.
Fluidized bed						1	1	2	1	3	Used for very fast reaction.
Reactive distillation		1									Reaction equilibrium can be shifted by removing one or more of the species from the reaction space.

5.3.2 Reaction Temperature and Pressure

Reaction temperature and pressure have an important effect on reaction kinetics and reactor selection. For rate or kinetically controlled reactions, at low temperature and for moderate activation energy, the rate of reaction doubles for a temperature increase of 10 ^{o}C (Smith, 2005; Wood, 2007). According to Smith (2005), if the logarithm of the reaction rate constant is plotted against the inverse of the absolute temperature, tends to follow straight line. The reaction rate constant is given by Arrhenius equation:

$$\ln k = \ln A_o - \frac{E}{RT} \tag{5.3}$$

Or

$$k = \ln A_o \exp - \frac{E}{RT} \tag{5.4}$$

Where:

A_o : pre-exponential factor or frequency factor, (same dimensions as k)

E : activation energy (J/mol)

R : gas constant = 8.314 (J/mol K)

T : absolute temperature (K)

At the same concentration and two different temperatures T1 and T2:

$$\ln \frac{r_2}{r_1} = \ln \frac{k_2}{k_1} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{5.5}$$

In Equation 5.5, the activation energy is assumed to be constant and increasing the temperature by 10 ^{o}C would double the rate of the reaction.

There can be three possible extreme cases when studying the effect of temperature on heterogeneous catalytic reaction rate as illustrated in Figure 5.17 (Trambouze and Euzen, 2004). The first case is at slow reaction with low temperature and there is no limitation due to the mass transfer. The second case is when the reaction is fast but not limited by external diffusion. The temperature can be considered uniform in both the fluid and particles. The third case is when the reaction is very fast and entirely controlled by external diffusion. In this case the activation energy is insensitive to temperature.

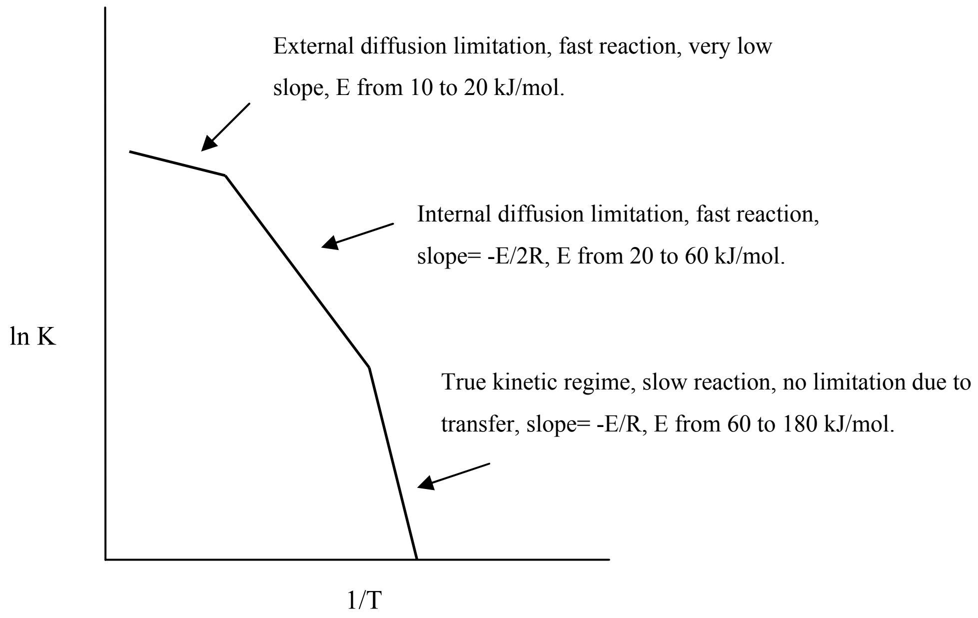


Figure 5.17: Change in apparent rate with temperature. (modified from Trambouze and Euzen, 2004)

Reaction temperature > 500 ^{o}C is considered to be a high temperature (Trambouze and Euzen, 2004). Temperature higher than 500 ^{o}C can affect the choice of reactor and the arrangement required for heat transfer as it may need to be heated by means of gas or fuel burners. High temperature can affect the stability of hydrocarbons and a cause thermal degradation and the formation of coal. The material of construction of the reactor at high temperate can be restricted especially at high pressure.

Operating pressures above 100 bar is considered to be very high pressures (Trambouze and Euzen, 2004). When high pressure is used, the rotating shaft of the CSTR agitator can not be sealed. Therefore reaction should take place in alternative reactors such as a tubular reactor. Furthermore, under high pressure conditions a large diameter CSTR will require a thick wall. Therefore, an alternative can be the PFR, although mixing problems when PFR is used with heterogeneous reactions need to be considered. The

IKBS gives low scores “0” to those reactors which are recommended for high temperature and pressure such as CSTR.

5.3.3 Reaction Rate

The amount of time that molecules spend in the reactor is called the residence time. Fast reactions require smaller residence times than slow ones. Therefore, the type of reactor required is governed by the residence time. This can be seen in the industrial reactors used for fast and slow reactions as tabulated in Table 5.2.

To identify the reaction regime in heterogeneous reactions, the Hatta number can be used. The Hatta number (Ha) is the ratio of the reaction in the liquid surface to the mass transfer into the bulk phase. Therefore, the Hatta number depends on the reaction kinetics. The Hatta number is used for liquid/gas or liquid/liquid reaction. Table 5.4, provides an example of the use of Hatta numbers to classify the gas/liquid reactions based on their speed. It suggests four zones of reactions.

Table 5.4: Use of Hatta number to guide in the selection of gas-liquid reactors. (adapted from Wood, 2007)

Zone	Ha	Speed of reaction	Location of reaction	Controlled by	Reactor
1	<< 0.3	very slow	bulk	reaction kinetics	bubble column; sparged reactor
2	Between 0.3 to 0.6	slow	mostly in bulk	Some mass transfer effects	packed
3	Between 0.6 to 3	intermediate	mostly in film	strong mass transfer effects	trays
4	>3	very fast	surface film	mass transfer	Spray, wetted wall, trickle bed

Based on the practical information from Table 5.2 and 5.4, the IKBS classified reactions into four levels based on the residence time:

1. very fast reaction (residence time ≤ 1 sec),
2. fast reaction (residence time > 1 sec ≤ 1 min) ,
3. slow reaction (residence time > 1 min ≤ 1 hr), and
4. very slow reaction (residence time > 1 hr).

If the reaction is very fast the PFR is highly recommended and therefore is given scores (2 or 3) depending on the heat transfer arrangements. In the other hand, CSTR is not suitable and it is given the score "#".

Reaction rates of gas–solid catalytic reactions are affected by pore diffusion, and the external mass transfer rate of the reactants and the products. At slow diffusion rates in the pores, a reactant concentration profile develops in the interior of the particle, resulting in a different reaction rate at different radial locations inside the catalytic particle. To account for the intra-particle resistance of solid catalysts, the effectiveness factor is used. The effectiveness factor is the ratio of the actual rate to the ideal rate.

The effectiveness factor depends only on the Thiele modulus:

$$\eta = \frac{\tanh \phi}{\phi} \tag{5.6}$$

Where:
ϕ: Thiele modulus.

For small Thiele modulus ϕ or $\phi < 0.4$ the effectiveness factor η is almost equal to 1. Small value of ϕ means either a short poor, slow reaction, or a rapid diffusion (Levenspiel, 1999). For large ϕ or $\phi > 4$ the effectiveness factor $\eta = 1/\phi$. In this case, the reactant concentration drops rapidly to zero and the diffusion strongly influences the reaction rate (Levenspiel, 1999). At $\phi = 1$ the effectiveness factor $\eta = 0.762$ and there is some pore diffusion limitation (Schmidt, 1998). The effectiveness factor plays the same role as the Hatta number for gas-liquid or liquid-liquid reaction systems.

5.3.4 Use of Catalyst, Catalyst Lifetime and Potential Iterations

In commercial operations, the solid catalysts usually lose its effectiveness because of: poisons, sintering, fouling by carbon and coke, and loss of active species via volatilization. The life of a catalyst depends partly on the thermal stability of the support/carrier. Poisoning is minimized by the thermal removal of poisons from the feed stream. Sintering is minimized by controlling the reaction temperature below the maximum allowable temperature. Regeneration of the catalyst can be used to remove the coke and carbon, and active species may be added.

If a catalyst retains its activity for more than one year a fixed bed reactor can be used and the catalyst can be replaced during annual maintenance. Alternatively, if the catalyst life time is between 3 months and one year, two reactors can be used where one is on standby. If the catalyst retains its activity for less than 3 months, fluidized bed, moving bed, or slurry reactors can be used. This is subject to the constraint that catalyst attrition is less than 1% per day (Wood, 2007). If the catalyst attrition is more than 1% per day, it loses its activity in less than 3 months.

Trambouze and Euzen (2004) summarized the criteria of comparison for some available solid catalyst reactor technology as illustrated in Table 5.5. The tabulated information has preliminary use to eliminate some of the reactors under consideration.

The IKBS has the flexibility to add extra reactor selection criteria and the associated selection scores. In the future development of the IKBS, the design rules tabulated in Table 5.5, can be considered to reduce the number of recommended reactors by considering advanced criteria such as the characteristics associated with the catalyst and the technology. For example, important characteristics associated with catalyst stability at different design conditions and the cost of catalyst for different reactor types need to be considered during the selection process of reactors. The capacity, flexibility, simplicity and the design reliability of alternative reactor technologies are also important characteristics in reactor systems evaluation.

Table 5.5: Comparison of solid catalyst reactor technology. (modified from Trambouze and Euzen, 2004)

Criteria of comparison	Implementations of the catalyst	Fixed bed				Moving bed	Catalyst in suspension			
							CSTR	Fluidized bed		Entrained bed
	Heat exchange	Adiabatic		Multitubular		Adiabatic				
	Fluid phases	G or L	G + L	G or L	G + L	G or L	G + L	G or L	G + L	G or L
Characteristics associated with the catalyst grain										
Activity		+	0	+	0	+	++	++	+	++
Selectivity		+	0	+	0	+	++	++	+	++
Stability		+	0	+	0	0	+	+	+	+
Regeneratability		+	+	0	++	++	0	++	++	++
Cost of catalyst		++	++	++	++	-	0	-	-	-
Characteristics associated with the technology										
Concentration gradient		++	+	++	+	++	-	-	-	++
Temperature control		-	-	0	+	-	++	+	++	+
Capacity		++	++	+	+	+	0	+	+	+
Flexibility		+	0	0	-	0	+	-	-	-
Simplicity		++	++	-	-	-	+	0	0	0
Separation of catalyst/product		++	++	++	++	+	-	0	0	-
Replacement of catalyst		-	-	-	-	+	0	+	+	+
Pressure drop		+	0	+	0	+	0	+	0	+
Design reliability		++	++	+	0	0	++	+	0	0

Key: (++) very good; (+) good; (0) average; (-) poor

5.3.5 Reaction Exotherm

In the IKBS, exothermic reactions have been categorized based on King and Hirst (1998) and Wood (2007) into three levels. Highly exothermic, or endothermic reactions have a heat of reaction > 150 kJ/mol or > 3 kJ/g. Oxidation of hydrocarbons is a typical example for a highly exothermic reaction. Exothermic or endothermic reactions have a heat of reaction between 60-150 kJ/mol or 1.2-3 kJ/g such as nitration reactions. Moderately exothermic, or endothermic reactions have a heat of reaction < 60 kJ/mol or < 1.2 kJ/g such as condensation or polymerization reaction of species with molar mass between 20-200 g/mol (Wood, 2007).

5.3.6 Viscosity of Reactants

If reactants are very viscous, a CSTR may not be the best choice as the mixing and the power requirements will not be acceptable. Usually thin film reactors are used for highly viscous materials. For example, the gravity falling film reactor is used for liquid with viscosity < 1.5 Pa s whereas the agitated falling film reactor, is used for liquid viscosity < 2000 Pas (Trambouze and Euzen, 2004; Wood, 2007). All reactors evaluated in the IKBS are suitable for viscosities < 0.1 Pa s.

5.3.7 Sensitivity to Heat

Heat sensitive species can restrict the choice of reactor. It is important to know if thermal degradation is going to take place at the reaction temperature. This can lead to changing the reaction conditions and possibly the type of reactor. It might also lead to exploring the possibility of changing the reaction path or using thermally sensitive solvents. Another approach can involve selecting reactors with good heat transfer, and control, to maintain the reaction temperature below the degradation temperature. Currently, the IKBS only evaluate alternative reactors based on the capability to control the temperature of a reaction with sensitive reactants or products. For example, simple tubular reactors placed in a furnace, adiabatic fixed bed reactors and reactive distillation are not suitable for a reaction involving sensitive species. Reactors with good heat transfer such as spray column, falling and agitated thin film reactors are highly recommended for sensitive species.

5.4 Reaction Kinetics

Quantifying the reaction rate is an important step in analysing a chemical reactor. The rate equation is a function of the properties and the conditions of the reacting material, such as pressure, temperature, concentration and catalyst type. Reaction rate is essentially an algebraic function of concentration. The rate equation can be expressed in variety of forms.

The users are required to provide the rate of reaction equation variables to perform a reliable kinetic study and process optimization. This information may include, activation energy, pre-exponential factor, reaction rate constant and, the number of surface sites and adsorption coefficient if a catalyst is used.

There are five types of reaction in HYSYS: Conversion, Equilibrium, Kinetic, Simple rate and Heterogeneous catalytic reaction. Each of the reaction types require the stoichiometry of all the reactions. The conversion reaction requires the conversion of a base component in the reaction. Conversion reactions are calculated simultaneously. However, sequential reactions can be specified using the ranking feature. In the equilibrium reaction, HYSYS computes the conversion with the provided/calculated reaction equilibrium parameters and stoichiometric constants. The reaction order is calculated based on the stoichiometric coefficients. The equilibrium constant can be calculated as a function of temperature, or determined from the Gibbs free energy.

The three remaining reaction types deal with an expression for the reaction rate. The difference between these three depends on the formulation for the reaction rate expression. The kinetic reaction for equation 5.7 has the simplest form as in equation 5.8. To define the kinetic reaction, it is necessary to specify the Arrhenius parameters and the reaction order for the forward and reverse reactions if applicable.

$$A + B \leftrightarrow C + D \qquad (5.7)$$

$$-r_A = k_f (C_A{}^{\alpha} \cdot C_B{}^{\beta}) - k_r (C_C{}^{\gamma} \cdot C_D{}^{\delta}) \qquad (5.8)$$

Where:

k_f : forward Reaction rate constant

k_r : refers Reaction rate constant

C_A : Species concentration of A

$\alpha,\beta,\gamma,\delta$: The reaction order with respect to each species

The temperature dependence of the reaction rate is given by the Arrhenius equation which varies with temperature as a first approximation:

$$k = A_o\ e^{-E/RT} \tag{5.9}$$

Where:

A_o : pre-exponential factor or frequency factor, (same dimensions as k)

E : activation energy (J/mol)

R : gas constant = 8.314 (J/mol K)

T : absolute temperature (K)

The unit of the rate constant ‘k’ dependents on the order of the reaction. If a reference reaction rate, k_0 at a temperature, T_0 and the activation energy are known, the specific reaction rate, k_T at any other temperature, T can be calculated using a different form of Arrhenius equation:

$$k_T = k_{T_0}\ e^{\frac{E}{R}(\frac{1}{T_0}-\frac{1}{T})} \tag{5.10}$$

The simple reaction is similar to the kinetic reaction; the difference is that the rate expression is derived from equilibrium data as in equation 5.11.

$$-r_A = k(C_A{}^{\alpha} \cdot C_B{}^{\beta}) - \frac{(C_C{}^{\gamma} \cdot C_D{}^{\delta})}{K_{eq}} \tag{5.11}$$

Where:

K_{eq} : Equilibrium constant

For a heterogeneous catalytic reaction, the rate equation considered is based on the surface reaction limited rate law (Froment and Bischoff, 1990 and Trambouze and

Euzen, 2004). The reaction rate equation applies Langmuir's adsorption equilibrium to the rate of catalytic reaction and is called the Langmuir-Hinshelwood equation.

The overall rate is written as:

$$= \frac{\text{(kinetic factor) (driving force group)}}{\text{(adsoption group)}^{\sigma}} \tag{5.12}$$

An example of the use of the above surface reaction controlling rate equation for a reversible catalytic reaction in Equation 5.13 is illustrated here. The rate equation for the disappearance of reactant can be written as:

$$-r_A = k \cdot \frac{K_A K_B (C_A \cdot C_B) - \dfrac{(C_C \cdot C_D)}{K_{eq}}}{\left(1 + C_A K_A + C_B K_B + C_C K_C + C_D K_D\right)^{\sigma}} \tag{5.13}$$

Where:

k : Reaction rate constant

C_A : Species concentration of A

K_{eq} : Equilibrium constant

K_A : Adsorption coefficient of A

σ : Number of active sites

The species concentration can also be expressed as partial pressure or molar fractions. The power law model is one of the general forms that represents the dependence of the reaction rate on the concentration of species. Rate expressions based on the power law model comprise the product of the concentration of individual reacting species raised to the order of reaction with respect to the species. Therefore, the reaction rate expression in Equation (5.13) can be rewritten in the form.

$$r = k \cdot \frac{K_A K_B (C_A{}^{\alpha} \cdot C_B{}^{\beta}) - \dfrac{(C_C{}^{\gamma} \cdot C_D{}^{\delta})}{K_{eq}}}{\left(1 + C_A{}^{\alpha} K_A + C_B{}^{\beta} K_B + C_C{}^{\gamma} K_C + C_D{}^{\delta} K_D\right)^{\sigma}} \qquad (5.14)$$

Where:

α : Reaction partial order with respect to A

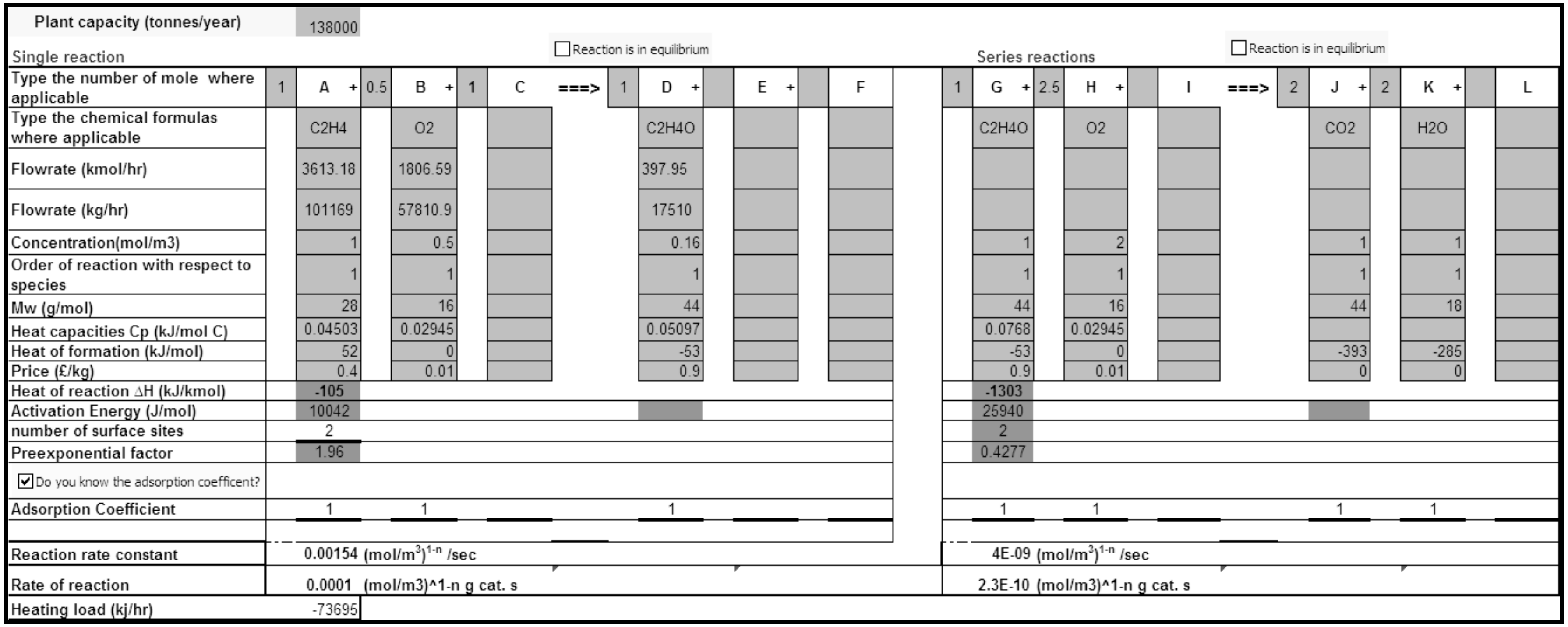
Table 5.6, summaries the groups which form the kinetic equation for heterogeneous and homogeneous catalysed, and non catalytic reactions.

Figure 5.18, illustrates, the IKBS kinetics input information. The user provides the required information based on the chemistry input. The IKBS, only asks for the required information based on the previous inputs. For example, if the reaction is reversible, the IKBS, requires the equilibrium constant and the concentration or pressure of the products/by-products. A further example is that if the reaction is solid catalysed, information on the adsorption coefficient is required. The IKBS, calculates the rate constants and reaction rate based on given data.

These given reaction kinetic parameters can be exported using VBA programming code to Aspen HYSYS for process simulation using the generic flowsheet.

Table 5.6: Groups in kinetic reaction equations.

Reaction	**A** $\leftrightarrow$ C	**A** $\leftrightarrow$ **C+D**	**A+B** $\leftrightarrow$ **C**	**A+B** $\leftrightarrow$ **C+D**
Surface reaction controlling				
Driving force group	$C_A^\alpha - \frac{C_C^\gamma}{K_{eq}}$	$C_A^\alpha - \frac{C_C^\gamma C_D^\delta}{K_{eq}}$	$C_A^\alpha C_B^\beta - \frac{C_C^\gamma}{K_{eq}}$	$C_A^\alpha C_B^\beta - \frac{C_C^\gamma C_D^\delta}{K_{eq}}$
Adsorption group	$(1+K_A C_A^\alpha + K_C C_C^\gamma)$	$(1+K_A C_A^\alpha + K_C C_C^\gamma + K_D C_D^\delta)^2$	$(1+K_A C_A^\alpha + K_B C_B^\beta + K_C C_C^\gamma)^2$	$(1+K_A C_A^\alpha + K_B C_B^\beta + K_C C_C^\gamma + K_D C_D^\delta)^2$
Kinetic group	kK_A	kK_A	$kK_A K_B$	$kK_A K_B$
Homogeneous reaction controlling and non catalytic reactions				
Driving force group	$C_A^\alpha - \frac{C_C^\gamma}{K_{eq}}$	$C_A^\alpha - \frac{C_C^\gamma C_D^\delta}{K_{eq}}$	$C_A^\alpha C_B^\beta - \frac{C_C^\gamma}{K_{eq}}$	$C_A^\alpha C_B^\beta - \frac{C_C^\gamma C_D^\delta}{K_{eq}}$
Adsorption group	1	1	1	1
Kinetic group	k	k	k	k



Plant capacity (tonnes/year) 138000

Single reaction

☐ Reaction is in equilibrium

Type the number of mole where applicable	1	A +	0.5	B +	1	C	===>	1	D +		E +		F
Type the chemical formulas where applicable		C2H4		O2					C2H4O				
Flowrate (kmol/hr)		3613.18		1806.59					397.95				
Flowrate (kg/hr)		101169		57810.9					17510				
Concentration(mol/m3)		1		0.5					0.16				
Order of reaction with respect to species		1		1					1				
Mw (g/mol)		28		16					44				
Heat capacities Cp (kJ/mol C)		0.04503		0.02945					0.05097				
Heat of formation (kJ/mol)		52		0					-53				
Price (£/kg)		0.4		0.01					0.9				
Heat of reaction ΔH (kJ/kmol)		-105											
Activation Energy (J/mol)		10042											
number of surface sites		2											
Preexponential factor		1.96											
☑ Do you know the adsorption coefficent?													
Adsorption Coefficient		1		1					1				
Reaction rate constant		0.00154 $(mol/m^3)^{1-n}$ /sec											
Rate of reaction		0.0001 (mol/m3)^1-n g cat. s											
Heating load (kj/hr)		-73695											

Series reactions

☐ Reaction is in equilibrium

Type the number of mole where applicable	1	G +	2.5	H +		I	===>	2	J +	2	K +		L
Type the chemical formulas where applicable		C2H4O		O2					CO2		H2O		
Flowrate (kmol/hr)													
Flowrate (kg/hr)													
Concentration(mol/m3)		1		2					1		1		
Order of reaction with respect to species		1		1					1		1		
Mw (g/mol)		44		16					44		18		
Heat capacities Cp (kJ/mol C)		0.0768		0.02945									
Heat of formation (kJ/mol)		-53		0					-393		-285		
Price (£/kg)		0.9		0.01					0		0		
Heat of reaction ΔH (kJ/kmol)		-1303											
Activation Energy (J/mol)		25940											
number of surface sites		2											
Preexponential factor		0.4277											
Adsorption Coefficient		1		1					1		1		
Reaction rate constant		4E-09 $(mol/m^3)^{1-n}$ /sec											
Rate of reaction		2.3E-10 (mol/m3)^1-n g cat. s											

Figure 5.18: Kinetic input information.

5.5 Chemical Reactors and Design

In IKBS, there is a wide range of chemical reactor choices available as alternatives. The major types of reactor considered in this work are the Continuous Stirred Tank Reactor (CSTR), Plug Flow Reactor (PFR), Packed Bed Reactor (PBR), Fluidized Bed Reactor (FBR), Bubble Column (BC), Spray Column (SC), Thin Film Reactor (TFR), Monolith Reactor (MR), Gauze Reactor (GR) and Reactive Distillation (RD). These types of reactors are discussed below.

HYSYS can only simulate the ideal CSTR and PFR. The other reactors have to be modelled. gPROMS modeling system can be used to build, validate and execute a unit operation within a flowsheet framework, and non-conventional unit operations can simulated using gPROMS. Design equations for the reactors are discussed below. Modular simulation of fluidized bed reactors for ethylene oxide process has been implemented. Aspen HYSYS extensibility feature can be used to create custom unit operations, property packages and kinetic reactions which become part of the simulation and function as built in objects (Aspen, 2006c).

5.5.1 Continuous Stirred Tank Reactor (CSTR)

A continuous stirred tank reactor is one of the important industrial reactors. In the IKBS, there are different configurations of then CSTR such as: CSTR with Jacket, CSTR with Jacket and internal coil, and CSTR with external heat exchanger on circulation loop. CSTR is recommended for:

- liquid phase reaction
- very slow reactions
- temperatures below 500 ^{o}C
- pressure below 100 bar
- catalytic and non-catalytic reactions
- moderate endothermic and exothermic reaction

CSTR is illustrated in Figure 5.19.

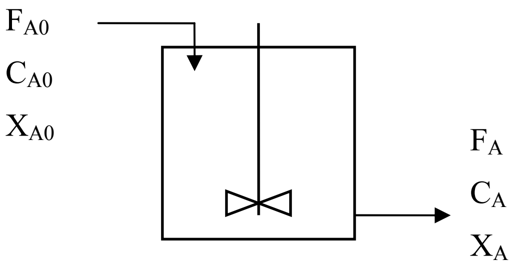


Figure 5.19: Flow of reactant A through a CSTR.

The steady state mole balance is thus:

$$F_{A0} - F_A + r_A V = 0 \tag{5.15}$$

Where:

F_{A0} : molar flow rate of reactant A entering the reactor

F_A : molar flow rate of reactant A leaving the reactor

V : volume of reactant/product mixture contained in the reactor

Rearranging equation (5.15) in terms of the disappearance of reactant A, give:

$$-r_A = \frac{F_{A0} - F_A}{V} \tag{5.16}$$

The space time is the reactor volume divided by volumetric flowrate of the inlet stream measured at the reactor inlet conditions:

$$\tau = \frac{V}{Q_0} \tag{5.17}$$

Rewriting the rate equation (5.15) in term of the space time gives:

$$-r_A = \frac{F_{A0}\, X_A}{Q_0 \tau} = \frac{C_{A0}\, X_A}{\tau} \tag{5.18}$$

Multiple CSTRs can be used either in series or in parallel. CSTRs in series have a higher conversion than CSTRs in parallel. This is because when two CSTRs are in series; the first reactor operates at a higher concentration, which leads to greater reaction rate and conversion. The second reactor in series builds on the conversion from the first reactor. On the other hand, in the parallel CSTRs scheme, the conversion is equal to the first reactor in the series CSTRs scheme.

HYSYS's ideal CSTR model does not support space time option and some different ways of removing, or adding reactor heat are not considered. To start simulating the CSTR, reactor volume, diameter or height and reaction phase needs to be specified. CSTR can be used with HYSYS kinetics, simple and heterogeneous catalytic reactions.

5.5.2 Plug Flow Reactor (PFR)

Reactors in which flow approximates to plug flow are also called tubular reactors. Tubular reactors are widely used in industry. Currently there are three configurations of the non-catalyzed tubular reactor: Simple tubular reactor, Simple tubular reactor with circulation of heat transfer fluid, and Simple tubular reactor placed in a furnace. PFR is recommended for:

- liquid phase reactions
- gas phase reactions
- fast reactions
- temperatures up to 900^{o}C
- pressure up to 3000bar
- highly endothermic and exothermic reaction

Assumptions made to model a plug flow reactor refer to the assumed nature of fluid flow within the tube as described in the following.

- no radial variation in concentration, temperature or flowrate,
- velocity at any radial position is equal to the average velocity of the fluid,
- no mixing along the axial direction between each fluid element.

A differential volume element dV within a pipe through which the reacting fluid is considered as illustrated in Figure 5.20:

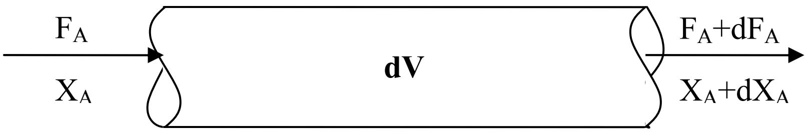


Figure 5.20: Flow of reactant A through a volume element of plug flow reactor.

At steady state, the mole balance on reactant A, over the element gives:

$$F_A = (F_A + dF_A) + (-r_A)dV \qquad (5.19)$$

Therefore, the steady state PFR mole balance equation in terms of the rate of disappearance of a reactant A is:

$$-r_A = F_{A0}\frac{dX_A}{dV} \qquad (5.20)$$

Alternatively, equation (5.20) can be integrated using the conversion to calculate the volume of PFR:

$$V = F_{A0}\int_0^{X_{AE}}\frac{dX_A}{-r_A} \qquad (5.21)$$

Mean residence time is the average amount of time that molecules can spend in the reactor. A higher residence time implies a higher conversion of reactants providing that the equilibrium conversion is not reached.

Equation (5.21) can be written in terms of space time as:

$$\tau = \frac{V}{Q_0} = C_{A0} \int_0^{X_{AE}} \frac{dX_A}{-r_A} \tag{5.22}$$

At constant density, the mean residence time is equal to the space time

$$\tau = \frac{V}{Q_0} = \int_0^V \frac{dV}{Q} = t_m \tag{5.23}$$

The performance of series and parallel combinations of homogeneous PFR under isothermal condition is the same as that of one reactor of the same total volume.

Aspen HYSYS integrates over the length of the PFR by dividing it into a number of sub-volumes like a series of CSTRs. The default sub-volumes is 20. Within each volume, the reaction rate is considered to be uniform. Like the CSTR, the PFR models in Aspen HYSYS can be used with HYSYS kinetics, simple and heterogeneous catalytic reactions. It also does not support space time option and heat of reaction is calculated at 25 ^{o}C.

To start the simulation of the PFR, reaction phase and pressure drop need to be specified. For dimensions specification, two of the three parameters (total volume, diameter and length) need to given. The Aspen HYSYS PFR model can only simulate co-current flow direction of reactants. If no energy stream is provided, HYSYS assumes that the operation is adiabatic. A plot of the reactor performance across the length of the reactor can be obtained

5.5.3 Packed Bed Reactor (PBR)

A wide range of industrial fixed bed reactors are considered in the IKBS reactor systems synthesis such as adiabatic fixed bed reactor, fixed bed with intermediate cooling/heating, and fixed bed with cold/hot shot. Industrial application shows that PFR is recommended for:

- liquid phase reactions
- gas phase reactions
- catalytic and non-catalytic reactions
- fast and slow reactions
- temperatures up to 1000 °C
- pressure up to 3000 bar
- highly endothermic and exothermic reaction

The equation for plug flow and packed bed reactors are very similar. When a catalyst is used, the reaction rate is quoted in terms of catalyst mass.

$$-r_A = F_{A0}\frac{dX_A}{dV} \tag{5.24}$$

$$W = F_{A0}\int_0^{X_{AE}}\frac{dX_A}{-r_A} \tag{5.25}$$

In the HYSYS PFR model, the number of tubes, void volume and catalyst voidage for heterogeneous catalytic reactions need to be specified. This information is used to calculate the pressure drop, reactor heat capacity and the spatial velocity of the fluid travelling down the reactor which impacts on the rate of reaction.

5.5.4 Fluidized Bed Reactors (FBR)

FBR is an important reactor for chemical reaction of fluids in the presence of granular solids. When a solid is a reactant, or a catalyst, which degrades fast, the problem of filling and emptying the reactor becomes dominant. In this case a fluidized bed reactor can be used with advantages over a fixed bed reactor and CSTR. In the IKBS, different fluidization technologies are considered: fluidized bed reactor, moving bed reactor, and riser reactor.

The particle mixing is due to the flow of fluid in the interparticle spaces and the mixing of the entire bed is by particle movement. Therefore, particles are agitated by gravity and fluid flow. Fluid drag in narrow reactors corresponds to the residence time behaviour of a tubular reactor whereas for a wide reactor and low velocity it corresponds to a stirred tank reactor.

Isothermal conditions can be achieved in fluidized beds over a wide range of gas throughputs. Advantages of the use of fluidized bed reactors include: excellent contact between fluids and solid in the bed, good heat and mass transfer between fluids and particles, and high heat transfer coefficients between the bed and the reactor wall. The heat transfer can be up to 10 times higher than in a fixed bed reactor (Vogel, 2005). Therefore, a fluidized bed reactor is advantageous for highly exothermic, or endothermic reactions as the efficient mixing within the bed eliminates the formation of hot spots and facilitates heat transfer to the reactor wall. Furthermore, the FBR has a lower pressure drop compared with the fixed bed reactor.

Catalysts used in fluidized bed reactor must have high mechanical strength to minimize attrition. FBR require solid separation, or gas purification, equipment for solids entrained by fluidized gas. Backmixing of gas might result in lower conversion as a consequence of high solids mixing rate. There is also a broad residence time distribution of solids due to the intense mixing. Erosion of the bed internals is a disadvantage of fluidized bed reactor.

Based on the industrial application, fluidized bed reactors are recommended for:

- liquid phase reactions
- gas phase reactions
- catalytic and non-catalytic reactions
- fast reactions
- temperatures up to 600 ^oC
- pressures up to 50 bar
- highly exothermic reaction
- low attrition of catalyst
- short catalyst lifetime

Most of the significant commercial applications of fluidized bed technology concern gas-solid systems. Applications include Fluid Catalytic Cracking (FCC), and synthesis reactions such as oxidation of naphthalene into phthalic anhydride, Fischer-Tropsch synthesis, ammoxidation of propylene to acrylonitrile, production of cresol and 2,6,-xylenol from phenol and methanol, oxychlorination of ethylene to ethylene dichloride, production of vinyl acetate monomer, methane chlorination, oxidation of n-butane into maleic anhydride and polymerization of olefins.

Fluidized bed reactors are also used in reactions involving solids such as combustion, incineration and gasification of coal, roasting sulphide ores, calcination of alumina chlorination and fluorination of metal oxide, gasification and incineration of solid waste, and reduction of iron oxide (Elvers et al., 1996; Grace et al., 1997; Kunii and Levenspil, 1991). FBR can also be used for applications involving liquid-solid systems such as waste water treatment. Successful applications of the fluidization system lie in the comprehensive understanding of hydrodynamic, heat and mass transfer properties, and mixing.

Bubbling fluidization bed models can be classified into three categories:

2- Models that use constant parameters throughout the bed which are not related to the bubble size,

3- Models that use constant parameters related to the bubble size,

4- Models that use variable parameters through the bed related to the bubble size.

Different models for fluidized bed reactors have been developed. These models mainly analyze the gas-solid contact and the exchange between the phases, and study the effect of gas-solid properties and operating velocity. The objective of a fluidized bed model is to combine the chemistry of the reaction and hydrodynamic parameters mathematically to estimate the degree of conversion and the size of the reactor. Yates (1983); Gupta and Sathiyamoorthy (1999), have presented a number of fluidized bed models and their mass balance equations along with the assumptions made in the development of the models. They further discussed and compared four well known models in fluidization, the two-phase model, Kunii and Levenspiel (K-L) model, Kato and Wen Model, and Partridge and Rowe model. Most of the developed models deal with a gas fluidized bed comprised of a simple cylindrical column.

The two-phase and Kunii and Levenspiel are the two main bubbling bed fluidized bed models which are considered in this study.

5.5.4.1 The Two-phase Model

The simple two-phase model is one of bubbling fluidization which was first introduced by Toomey and Johnston (1952) which states ‘’all gas in excess of that necessary to just fluidize the bed passes through in the form of bubbles” . The simple version of the two-phase model with upflow of emulsion is shown in Figure 5.21. This assumes that all the gas in excess of the minimum fluidizing velocity flows through the bed as bubbles and the emulsion phase is assumed to stay the same as the minimum fluidizing conditions. State equations for the simple two-phase model are given in Table 5.7.

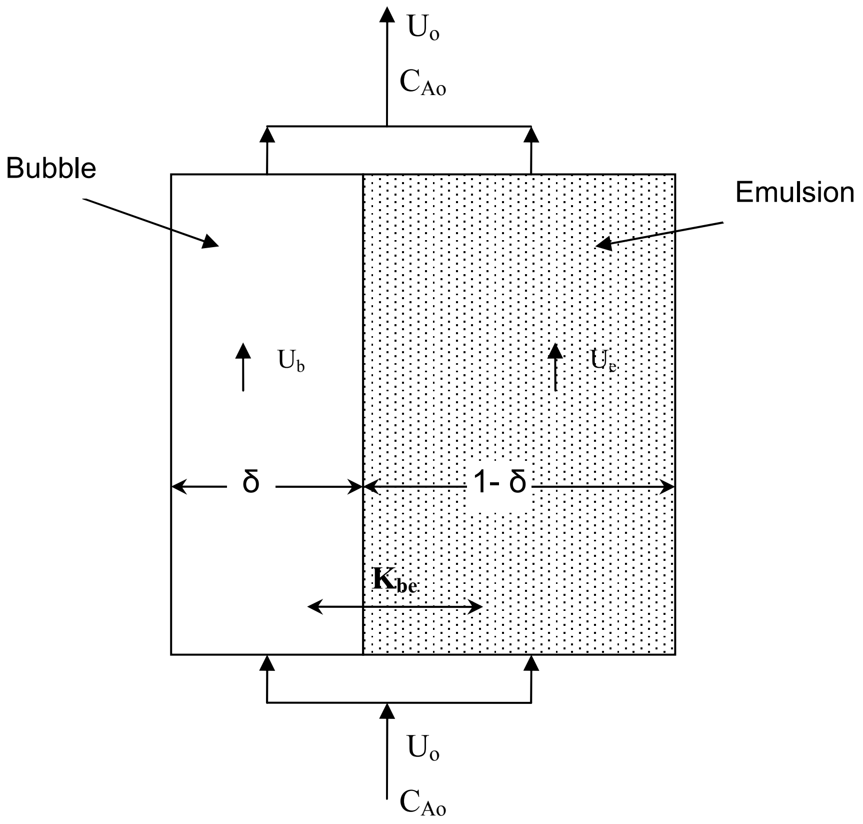


Figure 5.21: Two–phase model with upflow of emulsion. (adapted from Kunii and Levenspiel, 1991)

Table 5.7: State equations for the simple two-phase model.

mole balance for species A in the emulsion phase	$\frac{dC_{Ae}}{dz} = \frac{R_{Ae}(1-\varepsilon_{mf})\rho_p(1-\delta) + K_{be}\delta(C_{Ab} - C_{Ae})}{U_{mf}(1-\delta)}$
mole balance for species A in the bubble phase	$\frac{dC_{Ab}}{dz} = \frac{K_{be}\delta(C_{Ab} - C_{Ae})}{U_b}$
mean concentration of species A	$C_A = \frac{K_{mf}(1-\delta)}{U_o} C_{Ae} + \frac{U_b\delta}{U_o} C_{Ab}$
bubble fraction	$\delta = \frac{U_o - U_{mf}}{U_b - U_{mf}}$
average bed voidage	$\varepsilon = (1-\delta)\varepsilon_{mf} + \delta$

This theory can be applicable for Geldart group B particles (see Table 5.8 and Figure 5.22), but it is an approximation for Geldart group A fluidized at low velocities (Kirk-Othmer, 2005a). Some experimental work shows that the two-phase model does not fit the experimental findings well, as it considerably overestimates the visible bubble flow (Yates, 1983; Kunii and Levenspiel, 1991) and also because of the oversimplified assumptions involved in the model such as neglecting the resistance between the cloud and emulsion interface.

Table 5.8: Properties of powders. (adapted from Kirk-Othmer, 2005a)

Geldart Group	**Powder**	**Average particle size (μm)**	**Particle density (kg/m^3)**	**Sphericity**
A	FCC	60	1400	0.99
B	sand	500	2000	0.92
C	Ion-exchange resin	30	800	0.86
D	TCC beads	3000	1000	1.0

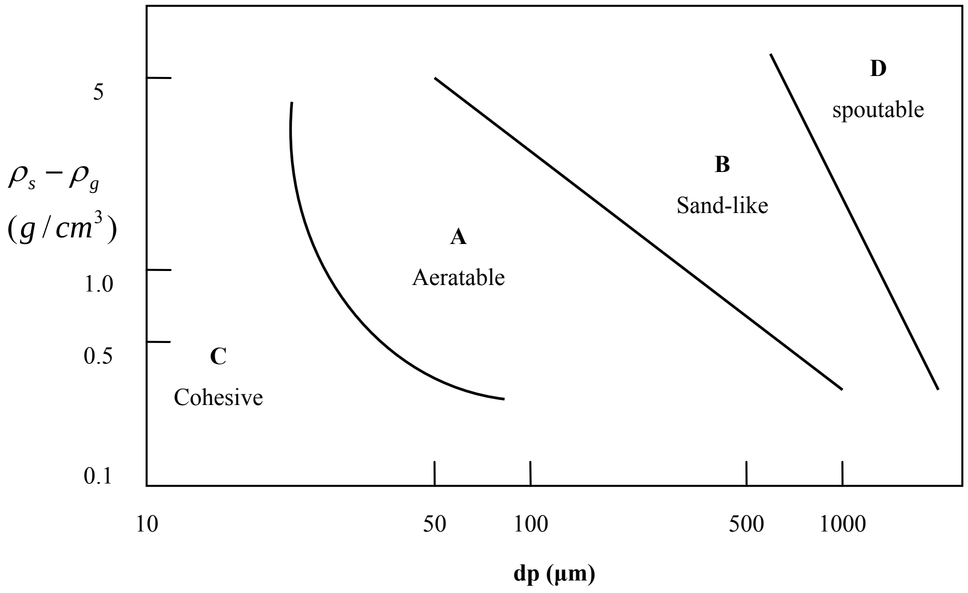


Figure 5.22: Geldart classification of solids in bubbling fluidization bed. (adapted from Levenspiel, 1999)

There have been a large number of models developed based on the two-phase theory of fluidization, but they differ considerably in the assumptions related to the nature of phases, the mode of interphase gas exchange and the degree of gas mixing in the phases. The Davidson-Harrison (D-H) model (Davidson and Harrison, 1963), is one of the well known models employing the two-phase theory. According to the Davidson-Harrison model, the gas in the bubble is continuously being recirculated within the bubble and considered as well mixed.

The Davison-Harrison model assumptions are

1- gas in emulsion phase flows at a superficial velocity at minimum fluidization and is either completely mixed or in plug flow,
2- the bubble size is constant throughout the bed,
3- reaction occurs only in the emulsion with first order kinetics,
4- interphase gas transfer occurs by molecular diffusion and through flow.

The analysis of the mass transfer in the two-phase model by Mostoufi et al, (2001) revealed that at low gas velocities the conversion of reactants occurs mainly in the emulsion phase and in the bubble phase at high gas velocities.

More detailed two-phase schemes have been reported in the developments by, Kato and Wen (1969), Werther (1980), Werther and Hegner (1981), Mostoufi et al, (2001), Kiashemshaki (2006). Two-phase models have also been extended to other flow regimes such as slugging beds by Hovmand et al. (1971), turbulent beds by Chaouki et al. (1999), and fast fluidization by Grace et al. (1997).

5.5.4.2 The Kunii-Levenspiel Three-phase Model

The bubbling bed Kunii-Levenspiel three-phase model (K-L model) was introduced by Kunii and Levenspiel (1968). The K-L model illustrated in Figure 5.23, was developed based on the mass balance of the three phases, bubble, cloud and emulsion (Gupta and Sathiyamoorthy, 1999):

1. gas steam with the dispersed solids moving upward (phase-1)
2. ascending agglomerates (phase-2)
3. descending agglomerates (phase-3) gaining solids from phase-2 and losing solid to phase-1.

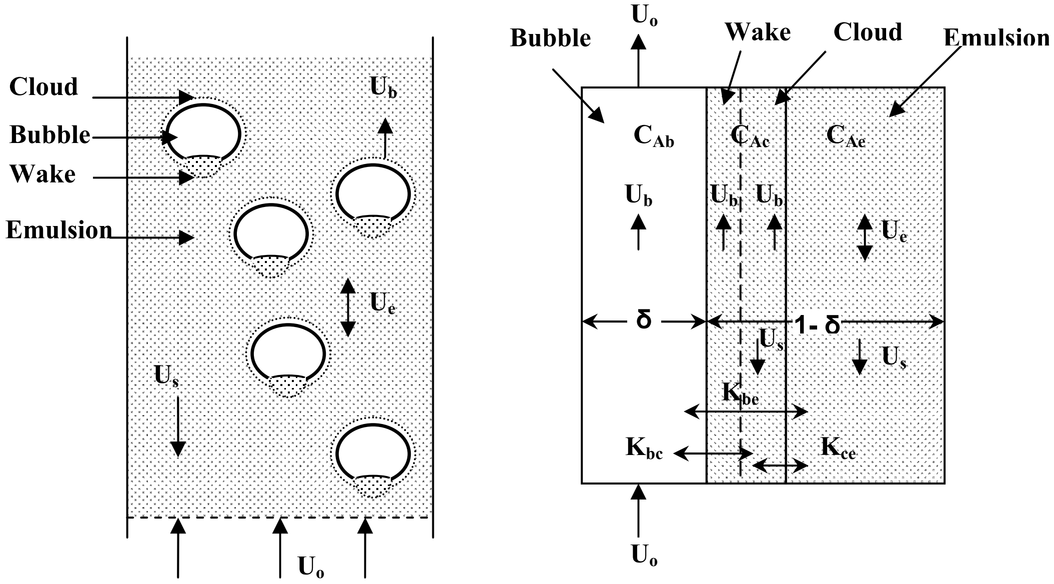


Figure 5.23: The K-L bubbling gas fluidization model. (adapted from Kunii and Levenspiel, 1991; Levenspiel 1999)

Assumption in the K-L Model are (Yates, 1983; Kunii and Levenspiel, 1991):

1. The gas is transported through the bed in uniformly sized bubbles with associated clouds and wakes,
2. Gas flow though the emulsion is negligibly small,
3. The solids in the emulsion phase flow smoothly downward in plug flow,
4. Interphase gas exchange occurs from bubble to cloud and from cloud to emulsion.
5. The emulsion phase exists at minimum fluidization conditions,
6. The concentration of solids in the wake is equal to the concentration of solid in the emulsion phase.

A mass balance for typical bubbling bed model was proposed by Kunii and Levenspiel for the three phases (Yates, 1983; Kunii and Levenspiel, 1991; Levenspiel 1999; Gupta and Sathiyamoorthy, 1999):

Bubble phase:

$$U_b \frac{dC_{Ab}}{dz} = \gamma_b k C_{Ab} + K_{bc}\left(C_{Ab} - C_{Ac}\right) = 0 \tag{5.26}$$

Cloud phase:

$$K_{bc}\left(C_{Ab} - C_{Ac}\right) = \gamma_c k C_{Ac} + K_{ce}\left(C_{Ab} - C_{Ac}\right) \tag{5.27}$$

Emulsion phase:

$$K_c\left(C_{Ac} - C_{Ae}\right) = \gamma_e k C_{Ae} \tag{5.28}$$

The exit fraction of gas (C_{Ae}/C_{Ao}) for 1st order reaction at height h, can be evaluated from Equation 5.26 and 5.27 by eliminating C_{Ae} and C_{Ac}. Thus,

$$\frac{C_{Ae}}{C_{Ao}} = \exp\left[-K\right] \tag{5.29}$$

Where

$$K = H\frac{k}{U_b}\left[\gamma_b + \cfrac{1}{\cfrac{k}{K_{bc}} + \cfrac{1}{\gamma_c + \cfrac{1}{\cfrac{k}{K_{ce}} + \cfrac{1}{\gamma_e}}}}\right] \tag{5.30}$$

The reaction constant (k) considered in the expression for a first order reaction. The transfer occurs from the bubble phase to cloud-wake phase, and then to the emulsion phase. There is no transfer of gas, or reactant, from the emulsion phase to the bubble phase and the reaction takes place only in the emulsion phase in presence of catalyst particles (Gupta and Sathiyamoorthy, 1999).

The relationship between interchange coefficients, or crossflow rates, can be written as:

$$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}} \tag{5.31}$$

K_{be} is the flow of the gas from bubble to emulsion with an equal flow in the opposite direction.

Where for cloud-wake to emulsion interchange coefficient is

$$K_{ce} = 6.77\left(\frac{D_{AB}u_{br}\varepsilon_e}{D_b^3}\right)^{0.5} \tag{5.32}$$

And between cloud-wake and bubble the interchange coefficient

$$K_{bc} = 4.5\left(\frac{U_e}{D_b}\right) + 5.85\left(\frac{D_{AB}^{0.5}g^{0.25}}{D_b^{5/4}}\right) \tag{5.33}$$

The relation governing the solid volume fraction in the three different phases is

$$(\gamma_b + \gamma_b + \gamma_b)\delta = (1 - \varepsilon_{mf})(1 - \delta) \tag{5.34}$$

Where the fraction of the bed in bubbles is:

For slow bubble, $(U_b<U_e)$:

$$\delta = \frac{U_o - U_{mf}}{U_b + 2U_{mf}} \tag{5.35}$$

For intermediate bubble velocity, $U_{mf}/\varepsilon_{mf} < U_b < 5U_{mf}/\varepsilon_{mf}$:

$$\delta = \frac{U_o - U_{mf}}{U_b} \tag{5.36}$$

For intermediate bubble velocity, $U_b > 5U_{mf}/\varepsilon_{mf}$:

$$\delta = \frac{U_o - U_{mf}}{U_b - U_{mf}} \tag{5.37}$$

The distribution of solids in the bubble phase γ_b is very small in the range from 10^{-2} to 10^{-3} (Kunii and Levenspiel, 1991) and can be taken as:

$$\gamma_b = 0.005 \tag{5.38}$$

For cloud-wake the solid distribution is

$$\gamma_c = (1 - \varepsilon_{mf})\left[\frac{3U_{mf}/\varepsilon_{mf}}{0.711(gd_b)^{0.5} - U_{mf}/\varepsilon_{mf}} + \frac{V_w}{V_b}\right] \tag{5.39}$$

The ratio of the volume of bubble and wake, V_w and V_b can be obtained from Figure 5.24.

The value of the ratio of solids dispersed in the emulsion γ_e is found from Equation (5.34) by substitution of γ_c and γ_b.

$$\gamma_e = \frac{(1-\varepsilon_{mf})(1-\delta)}{\delta} - \gamma_b - \gamma_c \tag{5.40}$$

The K-L model gives the best prediction even at low values of interphase exchange.

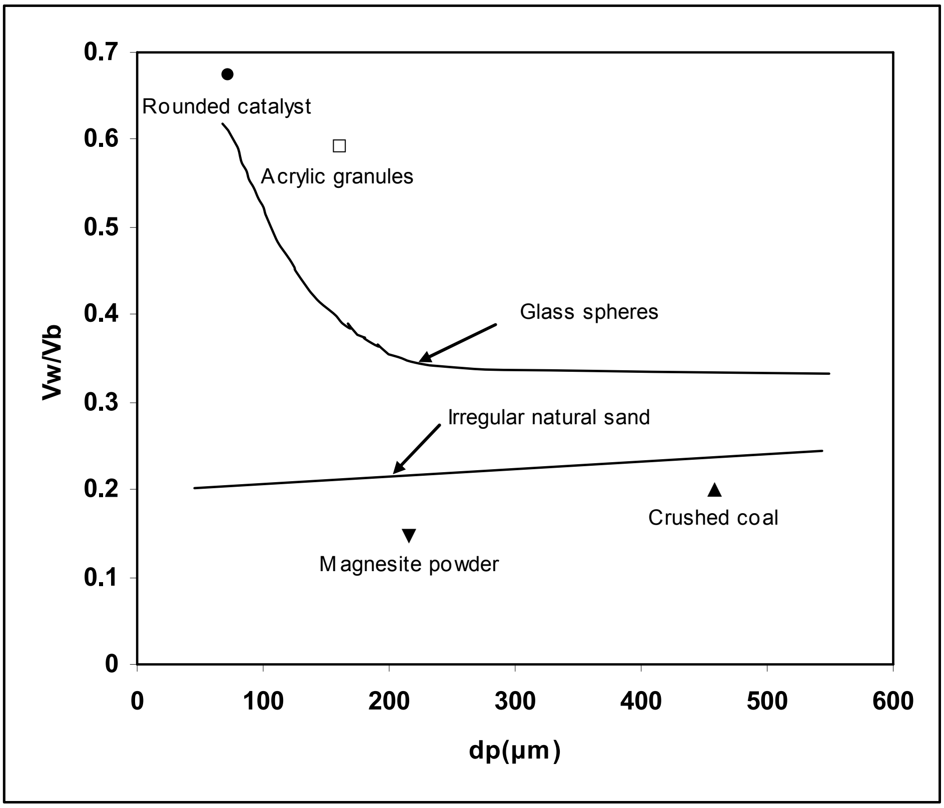


Figure 5.24: Variation of wake fraction with particle size. (reproduced from Kunii and Levenspiel, 1991)

5.5.4.3 Modular Simulation of a Fluidized Bed Reactor

Aspen HYSYS does not simulate fluidized bed reactors as it can not be considered as either a PFR or a CSTR. Previous research by El-Halwagi and El-Refai (1988) and Alizadeh et al. (2004), was conducted to model the non-ideality by a CSTR in series model. This approach ignored the coexistence of bubble and emulsion phases in the reactor. The gas flow through the bubble phase in the fluidized bed can be considered as plug flow (PFR) and the gas flow through the emulsion phase as perfectly mixed (CSTR).

Jafari et al (2004); Karimi-Golpayegani et al. (2005) and Kiashemshaki et al. (2006), have studied the performance of fluidised bed reactors based on the use of a series of CSTRs and PFR. In this work the fluidized bed reactor is divided into several segments in series. In each stage, the flow of gas is considered as plug flow through the bubbles and perfectly mixed through the emulsion phase, as illustrated in Figure 5.25.

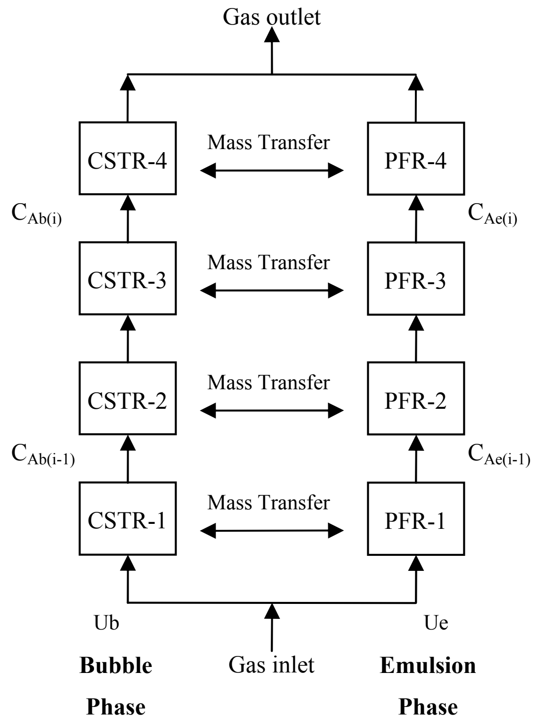


Figure 5.25: The schematic diagram of fluidized bed reactor stages.

The steady state mass balance in any reacting stage for either the bubble or emulsion phases is:

$$\begin{pmatrix}\text{bulk flow}\\ \text{in}\end{pmatrix} - \begin{pmatrix}\text{bulk flow}\\ \text{out}\end{pmatrix} - \begin{pmatrix}\text{disappearance by}\\ \text{chemical reaction}\end{pmatrix} \pm \begin{pmatrix}\text{mass}\\ \text{transfer}\end{pmatrix} = 0 \tag{5.41}$$

Based on equation 5.26, the mass balance in the stage 'i' for bubble phase is given by:

$$C_{Ab(i-1)} U_b A_b - A_b \varepsilon_b \int_{z_i}^{z_i} r_{A(i)} dz - K_{be} (C_{Ab(i)} - C_{Ae(i)}) V_{b(i)} - C_{Ab(i)} U_b A_b = 0 \tag{5.42}$$

And for the emulsion phase is given by:

$$C_{Ae(i-1)} U_e A_e - r_{A(i)} V_{CSTR(i)} + K_{be} (C_{Ab(i)} - C_{Ae(i)}) V_{e(i)} \left(\frac{\delta}{1-\delta} \right) - C_{Ae(i)} U_e A_e = 0 \tag{5.43}$$

The equations employed in the modular simulation of fluidized bed reactor to estimate the bubble size, bubble rising velocity, gas exchange coefficient between bubble and emulsion, the solid exchange coefficient between wake and emulsion, and other parameters that appear in the fluid dynamic model are given in Table 5.9.

Table 5.9: Hydrodynamic and mass transfer equations of the modular simulation of fluidized bed reactor.

Bubble initial diameter	$D_{bo} = 0.8713\left(\frac{A(U_0 - U_{mf})}{N_D}\right)^{0.4}$
Bubble maximum diameter	$D_{bm} = 1.49g^{-0.2}\left(A(U_0 - U_{mf})\right)^{0.4}$
Bubble mean diameter	$D_b = D_{bm} - (D_{bm} - D_{bo})\exp\left(\frac{-0.15h_{mf}}{D_r}\right)$
Bed height at minimum fluidization condition	$h_{mf} = \frac{W}{\rho_p A(1 - \varepsilon_{mf})}$
Minimum fluidization Velocity	$U_{mf} = \frac{\varepsilon_{mf}^3}{150(1 - \varepsilon_{mf})}\frac{(\rho_p \rho_g)(\psi\, d_p)^2 g}{\mu}$
Minimum fluidization voidage	$\varepsilon_{mf} = 0.586\psi^{-0.72}\left(\frac{\mu^2}{\rho_g g(\rho_p - \rho_g)d_p^3}\right)^{0.029}\left(\frac{\rho_g}{\rho_p}\right)^{0.021}$
Cross-sectional area of the reactor	$A = \frac{\pi}{4}D^2$
Rise bubble velocity in a bubbling bed	$U_b = U_0 - U_e + u_{br}$
Single bubble rise velocity	$u_{br} = 0.711\sqrt{gD_b}$
Emulsion gas velocity	$U_e = \frac{U_{mf}}{\varepsilon_{mf}}$
Bubble phase fraction	$\delta = 1 - A_{f(1)} - A_{f(2)}\exp\left(\frac{-(U_0 - U_{mf})}{A_{f(3)}}\right)$
Emulsion phase fraction	$f = 1 - \delta$
Bubble phase voidage	$\varepsilon_b = A_{void-b(1)} - A_{void-b(2)}\exp\left(\frac{-(U_0 - U_{mf})}{A_{void-b(3)}}\right)$
Emulsion phase voidage	$\varepsilon_e = A_{void-e(1)} - A_{void-b(2)}\exp\left(\frac{-(U_0 - U_{mf})}{A_{void-e(3)}}\right)$
Average void fraction of the bed during fluidization	$\varepsilon_g = (1 - \delta)\varepsilon_e + \delta\varepsilon_b$
Terminal velocity of particles	$u_t = \left[\frac{4d_p(\rho_p - \rho_g)g}{3\rho_g CD}\right]^{1/2}$
Reynolds number	$\mathrm{Re} = \frac{\rho_g U_0 d_p}{\mu}$
Bed height	$h = \frac{W}{\rho_p A\varepsilon_g}$
Interphase area per unit volume	$a_i = \frac{6\delta}{D_b}$
Hatta number	$Ha = \frac{(kD_{AB})^{0.5} a_i}{K_{be}}$
Interchange coefficients	$\frac{1}{K_{be}} = \frac{1}{K_{bc}} + \frac{1}{K_{ce}}$
Cloud-wake to emulsion interchange coefficient	$K_{ce} = 6.77\left(\frac{D_{AB} u_{br} \varepsilon_e}{D_b^3}\right)^{0.5}$
Cloud-wake and bubble the interchange coefficient	$K_{bc} = 4.5\left(\frac{U_e}{D_b}\right) + 5.85\left(\frac{D_{AB}^{0.5} g^{0.25}}{D_b^{5/4}}\right)$

Jafari et al. (2004), used a sequential modular approach to model a fluidized bed reactor. The reactor was divided into several segments in series. The number of the segments under different operation conditions can be determined from Table 5.10. Jafari et al, (2004) proposed the number of stages as function of a dimensionless number 'J' as in Equation 5.44.

$$J = Ha\frac{U_0}{U_{mf}} \tag{5.44}$$

Where:

H_a : Hatta number (-)

U_o : superficial gas velocity (m/s)

U_{mf} : minimum fluidization velocity (m/s)

Table 5.10: Number of stages for Fluidized bed reactor simulation. (adapted from Jafari et al, 2004)

J	Number of stages (N)
11.1 < J	1
5.62 < J < 11.1	2
0.63 < J < 5.62	3
J < 0.63	4

According to Jafari et al. (2004), to simulate a fluidized bed reactor with a slower reaction and higher gas velocities a larger number of stages is required. For faster reaction and lower gas velocities the reactor might only require a single stage. For fast reaction or high gas velocity a small number of stages would be needed. High values of Hatta number which reflect a fast reaction and/or very high superficial gas velocity, would give a high value of the dimensionless number 'J'. This would result in a small number of stages required to be employed in the simulation.

5.5.5 Thin-film Reactor

A thin-film reactor is a gas-liquid system where the liquid phase is in form of a thin-film that runs down a vertical wall while the gas flows over the liquid surface countercurrently, or cocurrently. It is possible to exchange heat between the liquid film and the reactor wall. Liquid phase flow can occur along an internal, or exterior, wall of the tube. Figure 5.26, illustrates the principal features of the thin-film reactor. There are two types of thin-film reactor, the simple and the agitated falling film reactor.

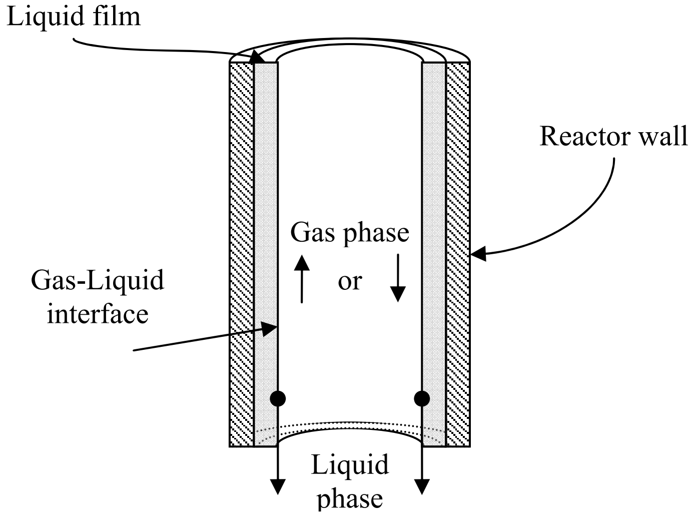


Figure 5.26: Principle features of a thin-film reactor.

In the simple falling film reactor, liquid flow is only as a result of gravity whilst in the agitated film reactor, shear forces caused by blades rotating near the wall are superimposed on gravitational forces. Thin-film reactors are recommended when the reaction is fast, highly exothermic or endothermic and, when the liquid phase where the reaction takes place is viscous.

A falling thin film reactor is recommended for:

- temperature sensitive chemical species
- liquids with viscosity <1.5 Pa s
- mean residence time 5 to 100 s.
- catalytic and non catalytic reaction
- highly endothermic and exothermic reaction
- homogenous liquid phase reactions
- heterogeneous gas-liquid reactions
- heterogeneous gas-liquid-solid reaction

The agitated thin-film reactor is recommended for:

- liquids with viscosity < 2000 Pa s
- mean residence time 5 to 600 s

The capacity of the falling film reactor, liquid holdup, mean residence time, and residence time distribution can be calculated based on the film thickness, the mean flow velocity and the flow velocity profile.

5.5.6 Bubble Column Reactor

In a bubble column reactor (BCR) a gas mixture in the form of bubbles and liquid comes in contact (see Figure 5.27). The liquid may contain inert, or active, particles in suspension. A distributor at the base of the column is used to inject gas in the form of bubbles. The distributor can be a perforated pipe, perforated plates or a sintered metal plate. At the top of the column entrained drops of liquid are collected by a demister.

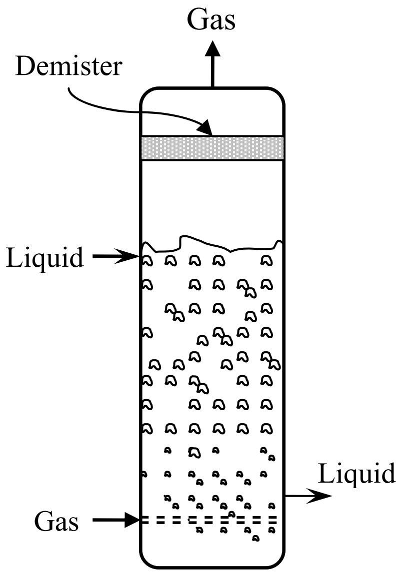


Figure 5.27: Bubble column reactor.

In general, the height to diameter ratio is from 3 to 10 (Trambouze and Euzen, 2004). Heat exchange is performed through the wall, or by using an internal exchanger, or external circuit. This reactor is suitable for non-catalytic reactions, or for homogeneous catalysed reactions where reaction takes place between gaseous and liquid reactants in the presence of a suspended catalyst. The concurrent downflow reactor is mainly used if large liquid streams, with short residence times, are to be contacted with a small gas stream. BCRs offer large interfacial area, which is the area of the bubbles in contact with the liquid. Typical liquid hold-up is more than 70% and between 2-30% gas hold-up (Moulijn et al., 2001). A bubble column has the advantages of high residence time, good heat and, mass transfer, low capital and operating costs. A bubble column reactor is not recommended for highly viscosity liquids.

Important applications of bubble column reactor include the partial oxidation of p-xylene to produce terephthalic acid, the direct chlorination of ethylene and the hydroformylation of propene.

5.5.7 Trickle Bed Reactor

The trickle bed reactor is essentially a three phase fixed bed reactor. The gas and liquid flow (trickle) over porous catalyst pellets. Liquid flows, down over the catalyst while the gas flows either up, or down, in counter-current or co-current flow. Two configurations of a trickle bed reactor are illustrated in Figure 5.28. Counter-current operation is preferred when the gas-liquid mass transfer requires a high driving force. In this case the reactor is limited by flooding. In cases of irreversible heterogeneously catalyzed gas-liquid reactions, co-current down-flow is advantageous. In co-current down-flow operation there is no limit to the gas-liquid throughputs and the pressure drop is lower than that in case of counter-current operation.

The trickle bed reactor is recommended for:

- Gas-liquid phase reaction
- Heterogeneous reaction
- High pressure reaction upto 600 bar
- High temperature up to 800 ^oC
- Fast and slow reactions

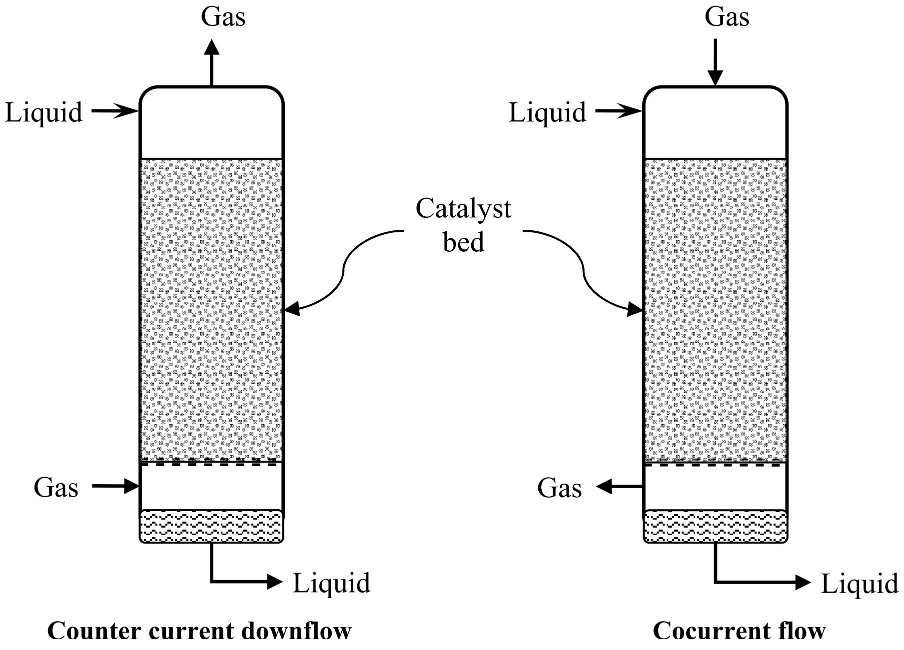


Figure 5.28: Trickle bed reactor with cocurrent and counter current flow.

Reactant conversion, the yield and the selectivity not only depend on reaction kinetics and operating pressure and temperature, but also depend on the hydrodynamics of the bed. According to Westerterp and Wammes (1992), the most important parameters to characterize the flow behaviour is the flow regime in the packed bed. This is because the mass transfer rates are affected differently in each regime. There are four different flow regimes in a trickle bed reactor: trickle flow, spray flow, pulse flow and bubble flow regimes. There are other important parameters which depend on the gas and liquid throughputs, the type of packing, and the physical properties of the gas-liquid-solid phases. These parameters are the liquid hold-up, the pressure drop in the bed, and the dispersion of gaseous and liquid phases.

The height to diameter ratio of the trickle bed reactor is generally between 5 and 25 (Westerterp and Wammes, 1992) and the maximum reactor diameter is limited by the ability to distribute the liquid on the bed.

There is a problem of fluid distribution in a trickle bed reactor, because situations may prevail in which liquid preferentially flows through a certain part of the bed, while the gas flows through another part (Moulijn et al., 2001). The distribution at the reactor inlet needs to be considered.

Trickle bed reactors are often used where it is considered undesirable to heat the liquid feed to turn it into a vapour. Examples of industrial applications of the trickle bed reactor include hydrodesulfurization and catalytic hydrodenitrification of crude oil, oxidative treatment of wastewater, and synthesis of 2-butyne-1,4-diol from acetylene and formaldehyde, butanediol, butenediol, and butynediol (Westerterp and Wammes, 1992).

5.5.8 Multi-tubular Fixed Bed Reactor

In the multi-tubular fixed bed reactor, hundreds of small diameter tubes containing the catalyst particles are surrounded by circulating heat transfer medium to remove, or add, heat to the reaction. Figure 5.29, illustrate the Multi-tubular fixed bed reactor. In a process that imposes special requirements on temperature control such as in case of very highly exothermic, or endothermic, reactions heat transfer must be throughout the reactor. For such reactions the multi-tubular fixed bed reactor is one of the most suitable options. In the IKBS, multi-tubular fixed bed reactor with indirect cooling/heating, and multiple-multi-tubular fixed bed reactor with indirect cooling/heating are evaluated.

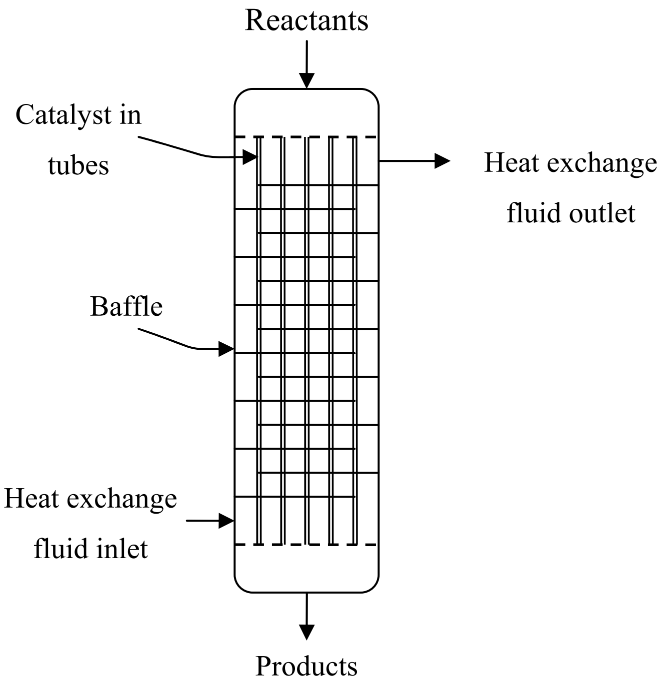


Figure 5.29: Multi-tubular fixed bed reactor.

Multi-tubular fixed bed reactors are recommended for:

- very high exothermic and endothermic reactions
- liquid phase reactions
- gas phase reactions
- catalytic reactions
- fast and slow reactions

- temperatures up to 1000 ^{o}C
- high pressure 100 bar

In case of a very highly exothermic reaction, the flow of the heat transfer medium in the space surrounding the tubes is directed across the tubes by baffles to provide good temperature control to achieve isothermal operation. Usually boiling liquids are used as a heat transfer medium to control highly exothermic reactions. Conversely, endothermic reactions require a large heat input and high temperature, so the tubes are placed in a furnace in which the heat flux is very high. In order to achieve uniform heating the maximum tube diameter should not exceed 10 cm (Moulijn et al., 2001).

Applications are methanol synthesis, Fischer-Tropsch synthesis, the production of ethylene oxidation by partial oxidation of ethylene, steam reforming of methane and naphtha, and the production of maleic anhydride by selective oxidation of butane.

5.5.9 Sparged Stirred Reactor

In a sparged stirred reactor an impeller is used to continuously re-disperse the bubble phase as illustrated in Figure 5.30. Sparged stirred reactors can be used to obtain uniform composition and temperature throughout the reactor rapidly. Therefore it is recommended when there is a thermal effect associated with the reaction, mixing or dissolution. Gas-liquid reactors provide a good transfer between the phases using high shear impellers.

A sparged stirred reactor has similar characteristics to bubble column reactors with respect to mass transfer. Both reactors can have more than 70% liquid holdup. It is common to use a bubble column followed by a sparged stirred reactor. In both reactors the liquids are well mixed. The gas phase in the bubble column shows plug flow behaviour and in the sparged stirred tank is well mixed. A sparged stirred reactor has the following characteristics (Trambouze and Euzen, 2004): high liquid hold-up, excellent gas-liquid mixing, high heat and mass transfer, good temperature control and the ability to process viscous liquids and solutions containing solid catalyst.

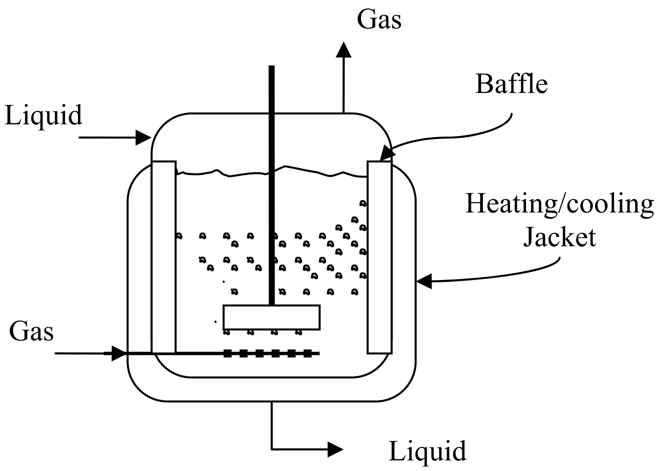


Figure 5.30: Sparged stirred tank.

Sparged stirred reactor is recommended for:

- Gas-liquid phase reaction
- very slow reactions
- temperatures below 500 ^oC
- pressure below 100 bar
- viscous liquids
- catalytic and non-catalytic reactions
- moderate endothermic and exothermic reaction

5.5.10 Spray Column Reactor

In a spray column the liquid falls down a tube with gas introduced at the bottom. The gas is separated from the liquid at the top using a demister. The liquid is withdrawn at the bottom as shown in Figure 5.31. The drop surface area determines the reactant mass transfer and the mass transfer resistance is usually within the liquid drops.

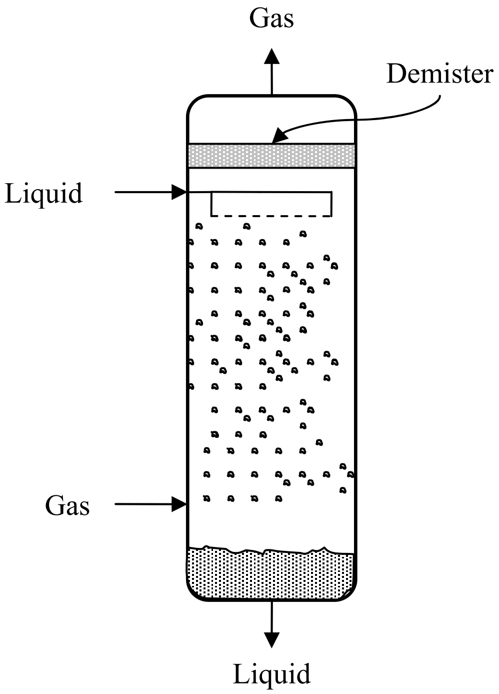


Figure 5.31: Gas-Liquid spray column reactor.

The spray column has low gas phase pressure drop and is suitable for processes requiring large gas throughputs. The spray column is often used for gas treatment and off gas scrubbing such as in the removal of CO_2 and H_2S from gas streams. Other applications of spray column are: the scrubbing of acetaldehyde, the reactor off-gas in the Wacker process, and the scrubbing of acetic acid from the oxidation reactor off-gas in the production of terephtalic acid (Moulijn et al., 2001).

The spray columns are recommended for:

- Gas-liquid phase reaction
- fast reactions
- temperatures below 500 ^{o}C
- pressures below 100 bar
- temperature sensitive chemical species
- homogeneous catalytic and non-catalytic reactions
- highly endothermic and exothermic reaction

A spray column can also be used as a liquid-liquid reactor, which is the simplest form of liquid-liquid contactor. In this type of reactor a continuous phase is circulated and the countercurrent dispersed phase is introduced using a perforated plate or a series of nozzles. The dispersed phase is introduced either from the bottom, or the top, of the column depending on whether it is lighter, or heavier, than the continuous phase as illustrated in Figure 5.32.

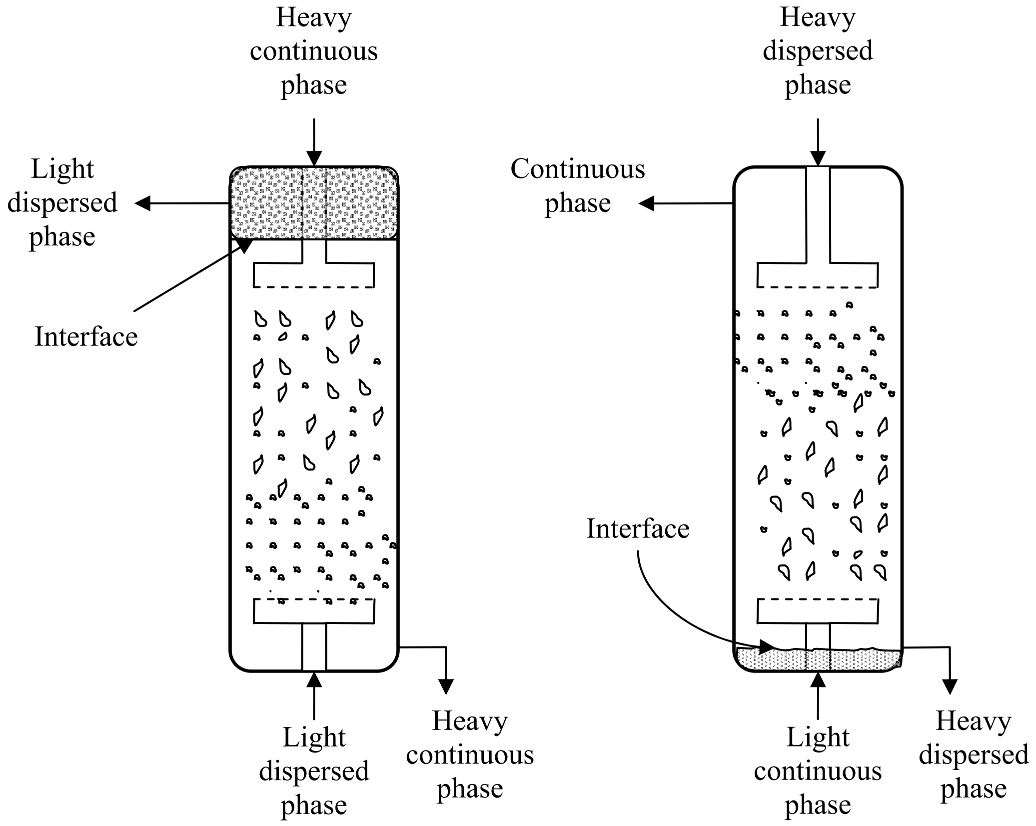


Figure 5.32: Liquid-Liquid spray column reactor.

5.5.11 Monolith Reactor

In a monolith reactor a ceramic and metallic support is coated with a layer of material in which active ingredients are dispersed. Channel walls can be either impermeable or permeable (membrane reactor). Monolith reactors generally consist of several layers of monolithic parallel elements joined in units (see Figure 5.33), containing up to 1000 m^3 of catalyst. The monolith element can have dimensions of 15 cm by 15 cm and a specific area between 400 and 900 m^2/m^3. The length of the element can vary from 30 cm to more than 1 m (Trambouze and Euzen, 2004). The structure of a monolith reactor is illustrated in Figure 5.34.

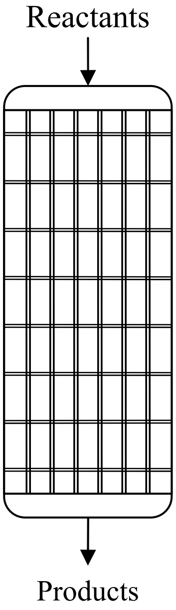
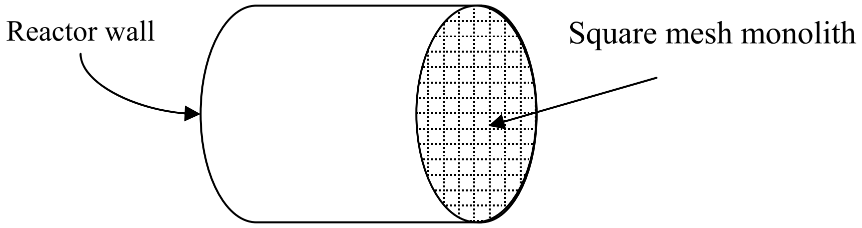


Figure 5.33: Monolith reactor.

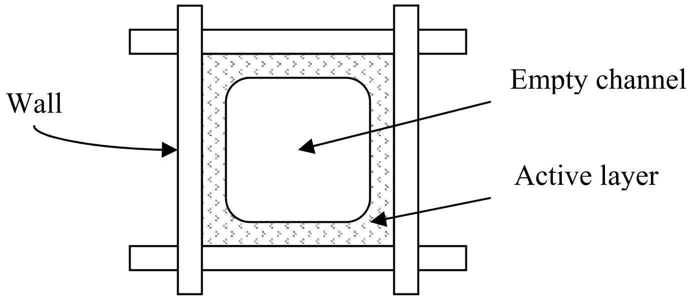
The flow in the channels of a monolith catalyst is most often laminar and the pressure drop is considerably lower compared with fixed bed reactors. This is a result of the flow through straight channels. The external mass and heat transfer in a monolith reactor is much more uniform in comparison with random packing. However, this can be a limiting factor at very high rate of reaction. Monolith reactors also have the advantage of promoting nearly perfect plug flow of the fluids and provide excellent transfer with the wall. Among the disadvantages of monolith reactors is the difficulty of fabrication in comparison with conventional catalyst particles, which makes it more expensive.

Monolith reactor is recommended for:

- Very high exothermic reactions
- Gas phase reactions
- Very fast reactions
- When catalyst is not resistant against attrition



Cross-section of the monolith reactor



Monolith channel

Figure 5.34: Monolith reactor structure. (Adapted from Trambouze and Euzen, 2004)

Monolith reactors were used for applications involving large gas flowrates. It is widely used in combustion reactions such as in the applications in automotive pollution control, or in the incineration of industrial gases. Other processes employing monolith reactors are the catalytic combustion of fuels for gas turbines, the oxidation of sulphur oxide, the oxidation of ammonia, and hydrogenation processes which include gas-liquid systems.

5.6 Conclusion

Chemical reactor systems synthesis can influence the whole process flowsheet structure. This is because the feed preparation, product recovery and recycle structure can be directly affected by the reactor system performance and the design conditions. Unlike other reactor system synthesis approaches, the proposed systematic procedure starts with analysing the process economically and studying the safety and environmental impacts before any reaction paths, or reactor type selection process takes place. Input information to the reactor system can be provided by the user, or from the databases, as well as from the simulated separation systems. A wide range of selection criteria is implemented to account for different reactor characteristics. Information from industrial applications was used for criteria and scoring allocations. To make further improvements in the design decisions, weighting the selection criteria of process units by allocating different values to each criterion is an important future task to account for the fact that some criteria may have a bigger effect on the selection of the reactor-separator-recycle system than others.

Chapter 6

Separation-Recycle Systems Synthesis

6.1 Introduction

Reactor effluents are almost never products that meet the desired purity specifications. Effluents often contain unreacted materials, by-products and feed impurities. Therefore, almost every chemical process that involves a chemical reaction system also involves one, or more, separation systems in addition to one, or more, recycle streams. According to Humphrey and Keller (1997), out of the total cost of chemical plants between 40 to 60% of the capital and operating costs are invested in separation processes. Most of the separation processes are based upon fundamentals such as: the mass transfer due to bulk movement and diffusion. The separation is based on exploiting a fundamental difference that exists between the species.

One of the main separation systems synthesis procedures was proposed by Douglas and co-workers (Douglas, 1985; Douglas et al. 1985; Douglas, 1988; Rajagopal et al., 1992; Douglas, 1995; Douglas and Stephanopoulos, 1995). The original hierarchical decomposition systematic procedure for the synthesis of separation system flowsheets by Douglas was implemented using an expert system called Process Invention Procedure (PIP) by Kirkwood (1987) and Kirkwood et al. (1998). Another implementation is ConceptDesigner by Han (1994) and Han et al. (1996a,b).

Most of Douglas' hierarchical levels have been considered in the proposed integrated approach and its implementation in the IKBS such as, economic potential calculations, and separation selection and design heuristic rules. Douglas restricted the separation process to distillation for liquid streams and absorption for vapour phase feed. He also used flash separation for vapour or mixed reactor effluents. This phase splitting of reactor effluents is considered in the IKBS.

Other important approach to the selection of separation techniques for liquid, and gas mixtures using expert system was proposed by Barnicki and Fair (1990; 1992). Their approach starts with dividing components based on their boiling points then selecting the separation technique. This approach was used by the IKBS in the initial evaluation of reactor output. Barnicki and Fair (1990; 1992) select separation techniques based on the relative volatility, chemical family, thermal sensitivity, product purity, difference in freezing points, difference in polarities, and existence of azeotropes. Most of these selection criteria are considered in the IKBS separation processes evaluation and selection. A systematic procedure for environmentally benign separation process synthesis, which combines the use of algorithmic and heuristic processing of symbolic and numeric data, was developed by Kheawhom and Hirao (2004). Other work involving the synthesis of separation processes using case-based reasoning was proposed by Seuranen et al. (2005). Their method is based on screening feasible separation process sequence alternatives by reusing the existing design cases.

Unlike the proposed integrated systematic procedure which suggest conventional and advanced separation processes, all of previous approaches suggest only conventional separation techniques and no third-party software such as process simulators, flowsheet optimization, sizing and economic evaluation, were used to support the design decision. These approaches do not used databases to provide design input information. Furthermore, most of these approaches synthesise separation systems in isolation from reactor systems.

6.2 Separator-Recycle Systems Synthesis Strategy

The main phases of the general separation system synthesis strategy consist of: the selection of separation systems type and location, the selection of separation sequences and separating agents, and determination of operating conditions. Therefore, the separation system synthesis strategy is a more complex problem than the reactor system synthesis as it may have to deal with a wide range of feed specifications, separation techniques, and recycles. It may also involve the selection of mass separating agents and sequencing of separation processes, or different type of chemical components and separations processes.

The IKBS separation system synthesis procedure illustrated in Figure 6.1 starts with input of information from the reactor system and from the simulated reaction system using Aspen HYSYS process simulator in addition to other specific input information provided by the users. At this stage more information can be obtained from the internal database such as partial pressure, azeotropes, dissociation constants, boiling points and other important physical properties.

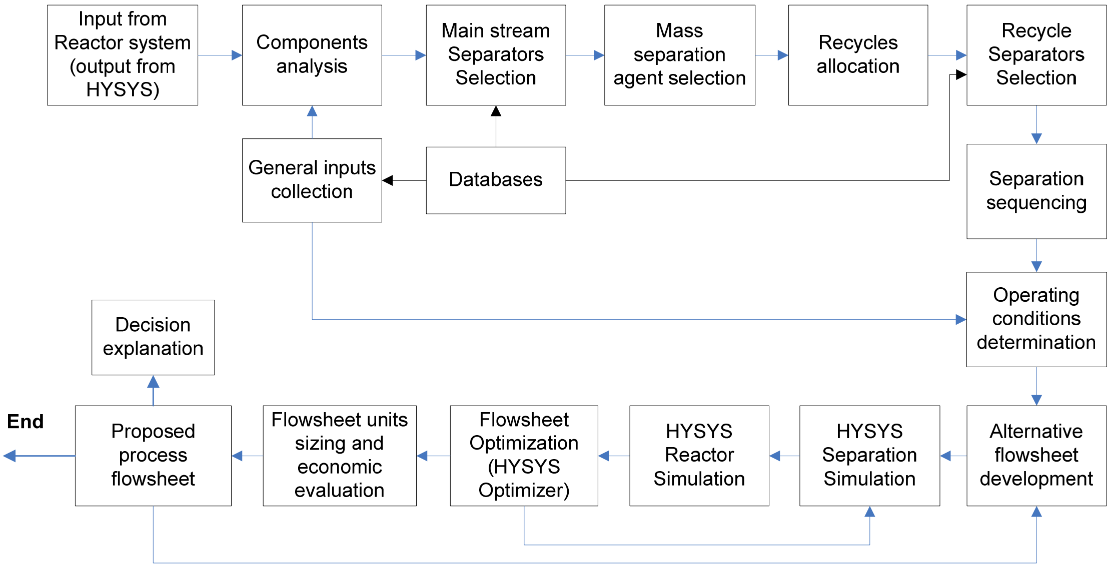
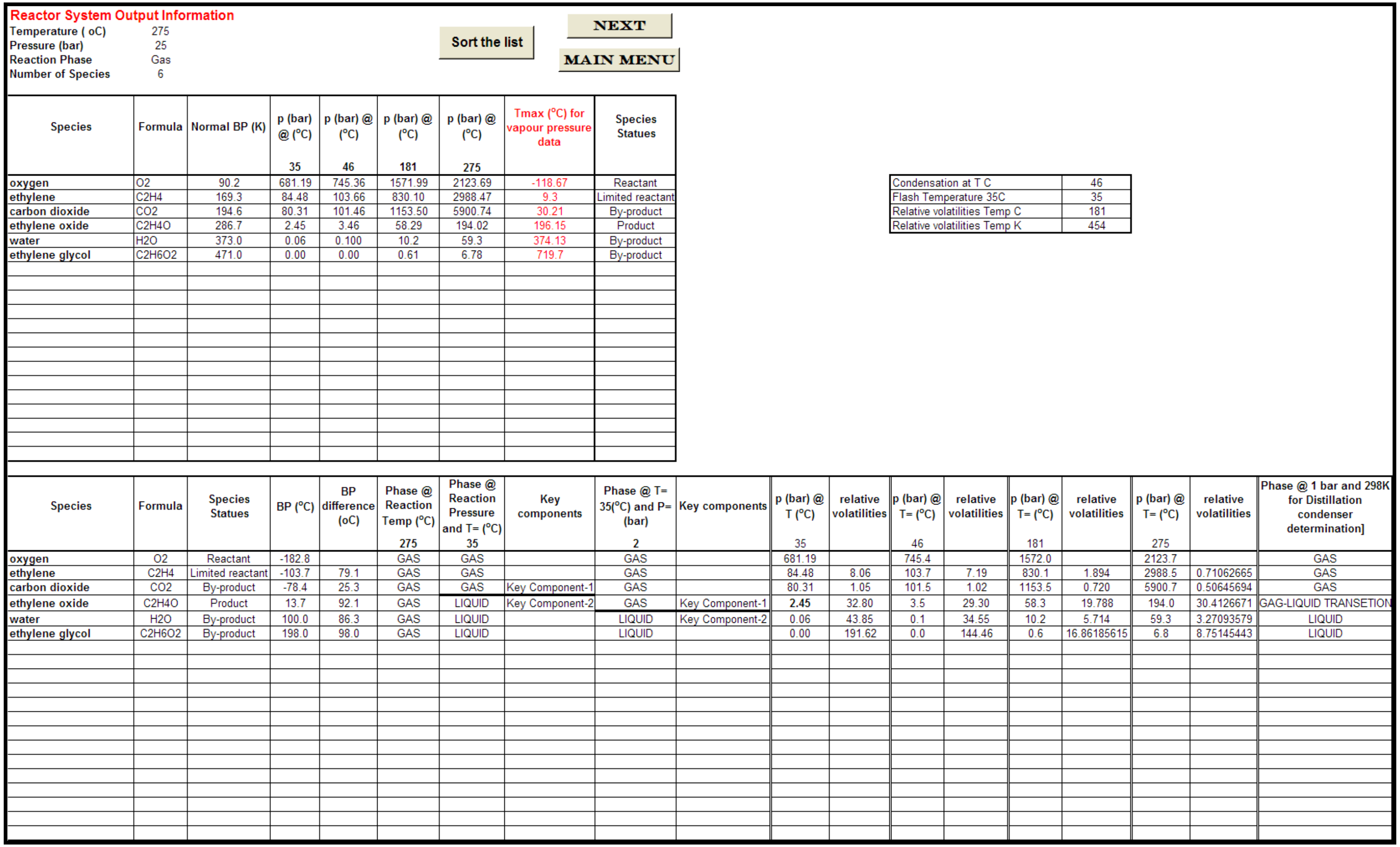


Figure 6.1: Separator system synthesis strategy.

The main stream separator selection involves analyzing the main stream species, exploring the possibility of phase separation of liquid or liquid-vapour streams and identifying the key components in the stream. Once the main separations are determined, Mass Separating Agents (MSA) are selected if required. The IKBS databases contain lists of suggested MSA for different separation processes. Alternative MSA can be analyzed based on the safety and environmental impacts. Information required for this analysis is available from the IKBS safety and environmental impacts databases. The recycle allocation is based on the destination of each species used in the process. The IKBS can identify these destinations and suggest the recycle for the required species. This is followed by the selection of alternative recycled separation processes. Separation sequencing can be achieved by using heuristic rules in order to propose alternative sequences of separation processes. Operating condition of separation processes is the last step before proposing the alternative process flowsheet. More input information is required to achieve this synthesis step.

Developed flowsheets are simulated using the generic flowsheet in Aspen HYSYS. The IKBS is linked to Aspen HYSYS using VBA programming code. Once the flowsheet is simulated, it can be optimized using HYSYS optimizer. The optimized flowsheet is exported to Aspen Icarus process evaluator for sizing and economic evaluations. A proposed flowsheet can be suggested from the list of alternative flowsheets. The IKBS can also explain the decision and the results can be demonstrated to the user. The User can give a feedback on the synthesised flowsheet. The feedback can be used for future improvement of the IKBS design decisions.

Detailed discussion on the proposed strategy for separation systems synthesis and its implementations in the IKBS are discussed here. Figure 6.2, illustrates the input information for the separation system which is the output information from the reactor system. It starts with listing all species in the output stream from the reactor system. The list is sorted automatically based on the boiling points using VBA programming code. The IKBS identifies the states of each species such as product, by-product, reactant, limiting reactant, solvent, inert, catalyst and impurity. This information is important for the interconnectivity of process units and recycles allocation.



Reactor System Output Information

Temperature (oC)	275
Pressure (bar)	25
Reaction Phase	Gas
Number of Species	6

Species	Formula	Normal BP (K)	p (bar) @ (°C) 35	p (bar) @ (°C) 46	p (bar) @ (°C) 181	p (bar) @ (°C) 275	Tmax (°C) for vapour pressure data	Species Statues
oxygen	O2	90.2	681.19	745.36	1571.99	2123.69	-118.67	Reactant
ethylene	C2H4	169.3	84.48	103.66	830.10	2988.47	9.3	Limited reactant
carbon dioxide	CO2	194.6	80.31	101.46	1153.50	5900.74	30.21	By-product
ethylene oxide	C2H4O	286.7	2.45	3.46	58.29	194.02	196.15	Product
water	H2O	373.0	0.06	0.100	10.2	59.3	374.13	By-product
ethylene glycol	C2H6O2	471.0	0.00	0.00	0.61	6.78	719.7	By-product

Condensation at T C	46
Flash Temperature 35C	35
Relative volatilities Temp C	181
Relative volatilities Temp K	454

Species	Formula	Species Statues	BP (°C)	BP difference (oC)	Phase @ Reaction Temp (°C) 275	Phase @ Reaction Pressure and T= (°C) 35	Key components	Phase @ T= 35(°C) and P= (bar) 2	Key components
oxygen	O2	Reactant	-182.8		GAS	GAS		GAS	
ethylene	C2H4	Limited reactant	-103.7	79.1	GAS	GAS		GAS	
carbon dioxide	CO2	By-product	-78.4	25.3	GAS	GAS	Key Component-1	GAS	
ethylene oxide	C2H4O	Product	13.7	92.1	GAS	LIQUID	Key Component-2	GAS	Key Component-1
water	H2O	By-product	100.0	86.3	GAS	LIQUID		LIQUID	Key Component-2
ethylene glycol	C2H6O2	By-product	198.0	98.0	GAS	LIQUID		LIQUID	

Species	p (bar) @ T (°C) 35	relative volatilities	p (bar) @ T= (°C) 46	relative volatilities	p (bar) @ T= (°C) 181	relative volatilities	p (bar) @ T= (°C) 275	relative volatilities	Phase @ 1 bar and 298K for Distillation condenser determination]
oxygen	681.19		745.4		1572.0		2123.7		GAS
ethylene	84.48	8.06	103.7	7.19	830.1	1.894	2988.5	0.71062665	GAS
carbon dioxide	80.31	1.05	101.5	1.02	1153.5	0.720	5900.7	0.50645694	GAS
ethylene oxide	**2.45**	32.80	3.5	29.30	58.3	19.788	194.0	30.4126671	GAG-LIQUID TRANSETION
water	0.06	43.85	0.1	34.55	10.2	5.714	59.3	3.27093579	LIQUID
ethylene glycol	0.00	191.62	0.0	144.46	0.6	16.86185615	6.8	8.75145443	LIQUID

Figure 6.2: Input information to separation system with initial analysis of the reactor output stream.

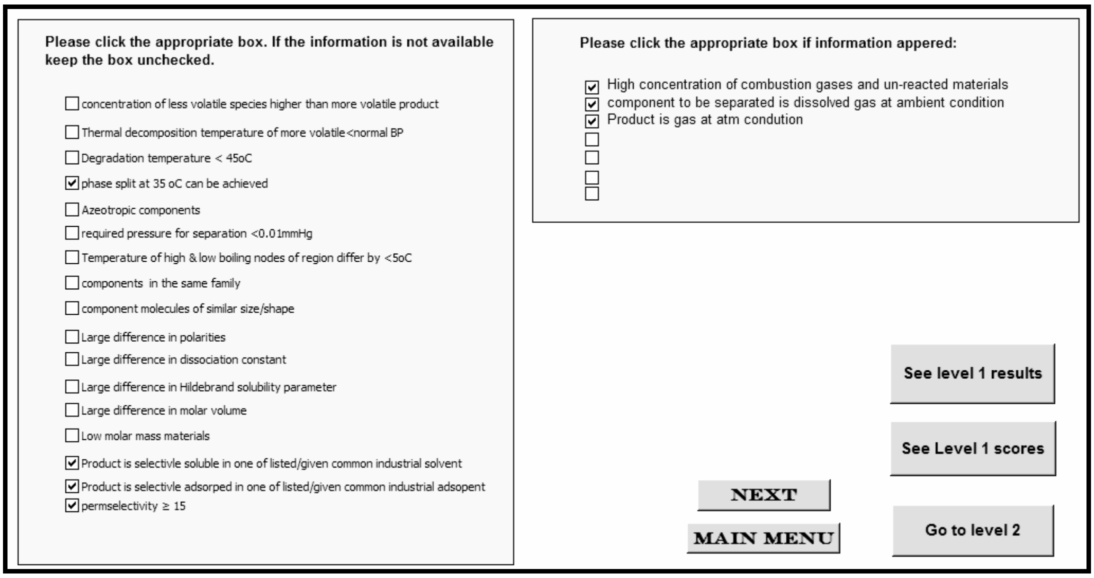
Vapour pressures at different temperatures are imported from the IKBS database. The vapour pressure information is used to calculate the relative volatilities at different temperatures. This approach evaluates reactor effluent to suggest thermal separations as a first choice.

The temperatures used in the calculation of the vapour pressure are selected based on analysing the phase separation: at 35 ^{o}C by using cooling water at 25 ^{o}C, at reactor output temperature, and at different potential thermal separation temperatures. The analysis at 35 ^{o}C explores the possibility of the phase separation of the vapour and mixed stream using cooling water and flash drum. The use of cooling water at 25 ^{o}C is cheaper than using chilled water. However, cooling water at 25 ^{o}C may not be always achievable in a humid area.

The calculation of vapour pressure at the reactor output temperature is another way of exploring the possibility to split the reactor effluent at minimum cost without the need for cooling the stream. Vapour pressure calculations at other potential temperature may include for example, the boiling point temperature of the key components. Complete phase separation may not be achieved. Therefore, the IKBS calculates the partial pressure of the vapour phase output stream from the phase splitter to determine the amount of valuable product which may be recycled to the reactor. For example, in the ethylene oxide process discussed in Chapter 7, if phase separation after the reactor is used, about 10% of the ethylene oxide product will be recycled to the reactor and may be burned. Therefore, the IKBS does not suggest the use of phase separation after the reactor in the ethylene oxide process.

The suitable separation techniques are selected using a scoring system and criteria from industrial experience. The criteria include product purity and the feed stream phase, concentration, degradation temperature, flowrates, relative volatility, chemical family, molar mass, azeotrope, polarities, dissociation constants, solubility, boiling point and, permselectivity. The separation processes selection using these criteria and scoring system used are discussed in the subsequent section. The list of evaluated separation processes include: simple, vacuum, pressure and azeotropic, extractive and pressure swing distillations, absorption, stripping, partial condensation followed by phase separator, flash drum with feed vaporisation, liquid-liquid phase separator, gas-liquid phase separator, wiped film evaporator, adsorption, molecular sieve adsorption, ion exchange, gas permeation, and distillation/pervaporation and distillation/adsorption hybrid systems.

For separation processes to be evaluated and proposed as alternative, there are some key pieces of information that must be provided as illustrated in Figure 6.3. User select form the list illustrated in Figure 6.3, the information applicable to the process under consideration. The list includes information on: feed concentrations, presence of water, need for process stream, thermal decomposition below boiling point, presence of azeotropes, differences in chemical family, polarities and solubility, possibility of adsorption on industrial adsorpents, solubility in common industrial solvents, permeslectivity values etc. Users can obtain the required information for the database.



Please click the appropriate box. If the information is not available keep the box unchecked.

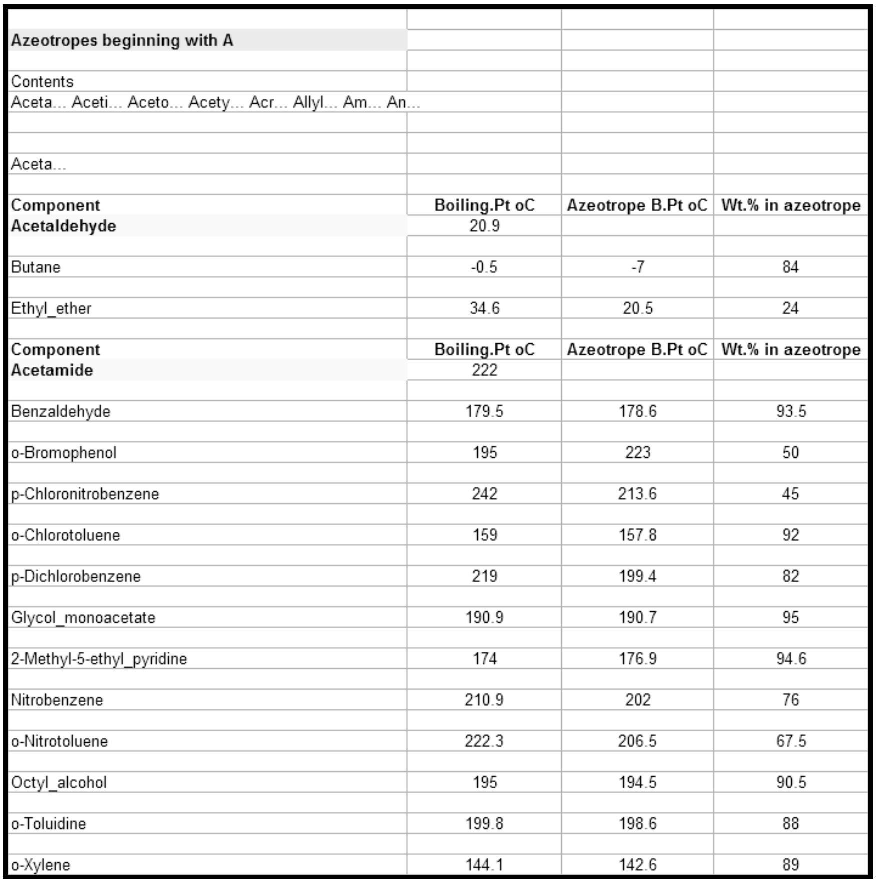
☐ concentration of less volatile species higher than more volatile product
☐ Thermal decomposition temperature of more volatile<normal BP
☐ Degradation temperature < 45oC
☑ phase split at 35 oC can be achieved
☐ Azeotropic components
☐ required pressure for separation <0.01mmHg
☐ Temperature of high & low boiling nodes of region differ by <5oC
☐ components in the same family
☐ component molecules of similar size/shape
☐ Large difference in polarities
☐ Large difference in dissociation constant
☐ Large difference in Hildebrand solubility parameter
☐ Large difference in molar volume
☐ Low molar mass materials
☑ Product is selectivle soluble in one of listed/given common industrial solvent
☑ Product is selectivle adsorped in one of listed/given common industrial adsopent
☑ permselectivity ≥ 15

Please click the appropriate box if information appered:

☑ High concentration of combustion gases and un-reacted materials
☑ component to be separated is dissolved gas at ambient condition
☑ Product is gas at atm condution
☐
☐
☐
☐

Figure 6.3: Separation system synthesis user input information.

For example, the presence of azeotropes can be obtained from the IKBS azeotropes database illustrated in Figure 6.4. If the required information is not available in the databases, or can not be supplied by the users, the related separation processes will not be included in the list of suggested separators by the IKBS. For example, if the dissociation constants information is not provided, ion-exchange will not be evaluated among the other possible separation techniques and a warning statement will inform the user that the separator will not be considered, or separation system type can not be synthesised.



Azeotropes beginning with A			
Contents			
Aceta... Aceti... Aceto... Acety... Acr... Allyl... Am... An...			
Aceta...			
Component	**Boiling.Pt oC**	**Azeotrope B.Pt oC**	**Wt.% in azeotrope**
Acetaldehyde	20.9		
Butane	-0.5	-7	84
Ethyl_ether	34.6	20.5	24
Component	**Boiling.Pt oC**	**Azeotrope B.Pt oC**	**Wt.% in azeotrope**
Acetamide	222		
Benzaldehyde	179.5	178.6	93.5
o-Bromophenol	195	223	50
p-Chloronitrobenzene	242	213.6	45
o-Chlorotoluene	159	157.8	92
p-Dichlorobenzene	219	199.4	82
Glycol_monoacetate	190.9	190.7	95
2-Methyl-5-ethyl_pyridine	174	176.9	94.6
Nitrobenzene	210.9	202	76
o-Nitrotoluene	222.3	206.5	67.5
Octyl_alcohol	195	194.5	90.5
o-Toluidine	199.8	198.6	88
o-Xylene	144.1	142.6	89

Figure 6.4: the IKBS azeotropes database.

Alternative reactors and separators are shown in the IKBS in the form of the block diagram illustrated in Figure 6.5. These alternatives are sorted and listed in the block diagram by using a VBA programming code illustrated in Appendix C. The block diagram is the simplest form of the generic flowsheet used in the IKBS. It contains a reactor (RS) system, two phase separation systems (PSS-1 and PSS-2), vapour separation systems (VSS-1 and VSS-2) and liquid separation systems (LSS-1 and LSS-2). Recycle gas can be separated in two recycle separation systems (RSS-1 and RSS-2).

If the phase of the reactor (RS) effluent is liquid, it will be sent directly to the liquid separation systems (LSS-1). If it is vapour, it may be sent tot the phase separation system (PSS-1) depending on the possibility of the phase separation using and the potential loss of valuable product in the gas recycle. If the phase separation of the vapour reactor effluent is not visible, it is sent directly to the vapour separation system. Recycled gas can be separated in two recycle separation systems. There are interactions between the generic superstructure systems in many possible ways of design connectivity. For example, the liquid stream from the vapour separation system (VSS-1) is connected to the liquid separation system (LSS-1). Recycle gas from the vapour separation system (VSS-1) is connected to recycle separation systems (RSS-1). The reactor (RS) system, vapour separation systems (VSS-1 and VSS-2), liquid separation systems (LSS-1 and LSS-2) and recycle separation systems (RSS-1 and RSS-2) are connected by mixing and splitting units to direct the flow based on the IKBS decisions, and the control of the direction of the streams is governed by an Excel expert system matrix. Users can view the alternatives using the drop-down list. Users can chose one of the alternatives for further analysis. Detailed discussion of the proposed generic superstructure has already been illustrated in Chapter 4.

There are some alternatives which when selected will remove other alternative in the other blocks. For example, in the gas recycle separation of the ethylene oxide process in Chapter 7, there are several alternatives. One of the alternatives is to use absorption in (RSS-1) followed by stripping in (RSS-2). Another alternative is to include adsorption and membrane separation in the recycle separation system (RSS-1). If adsorption is selected in (RSS-1), stripping in (RSS-2) will disappear as it is not required.

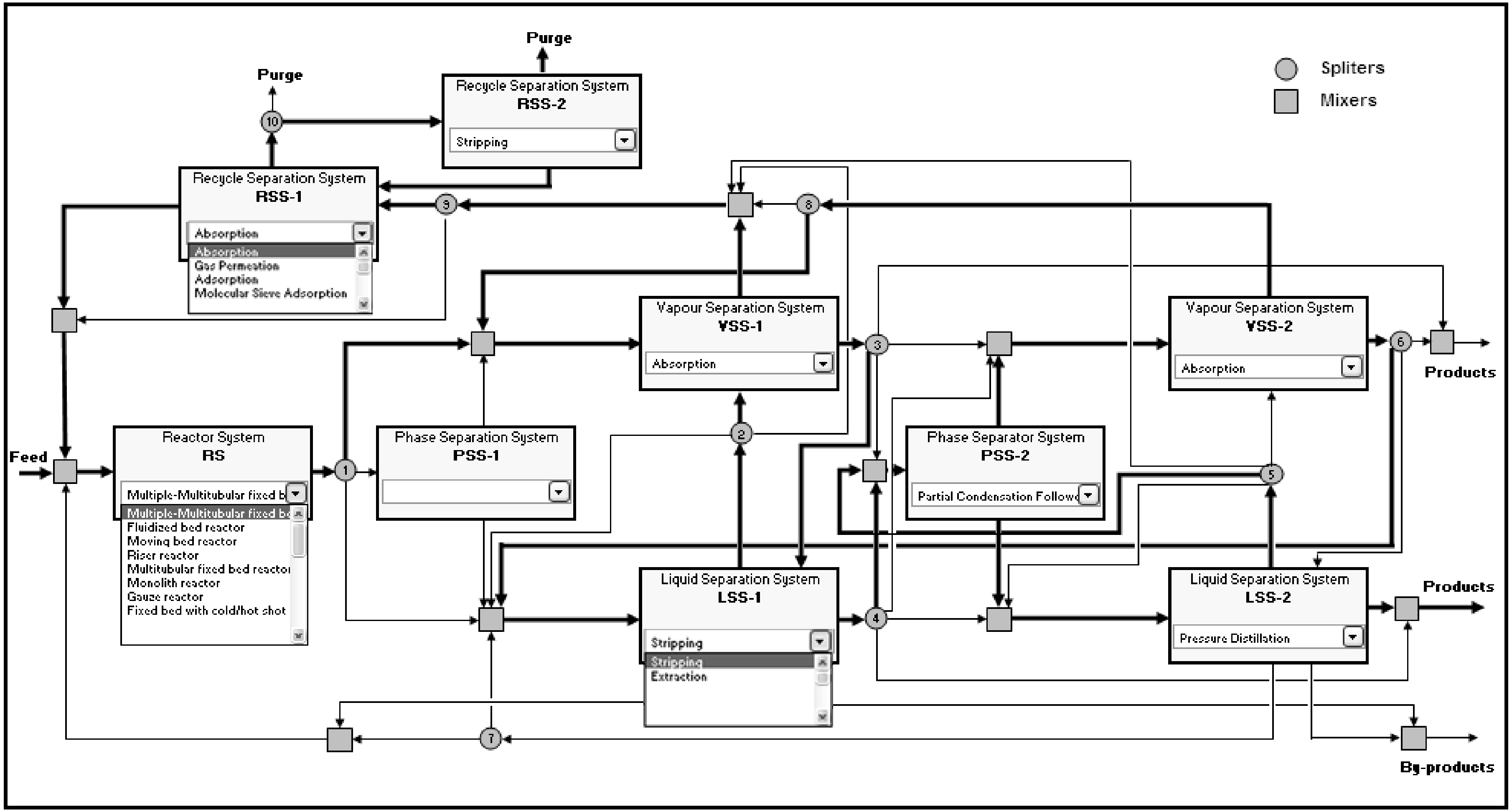
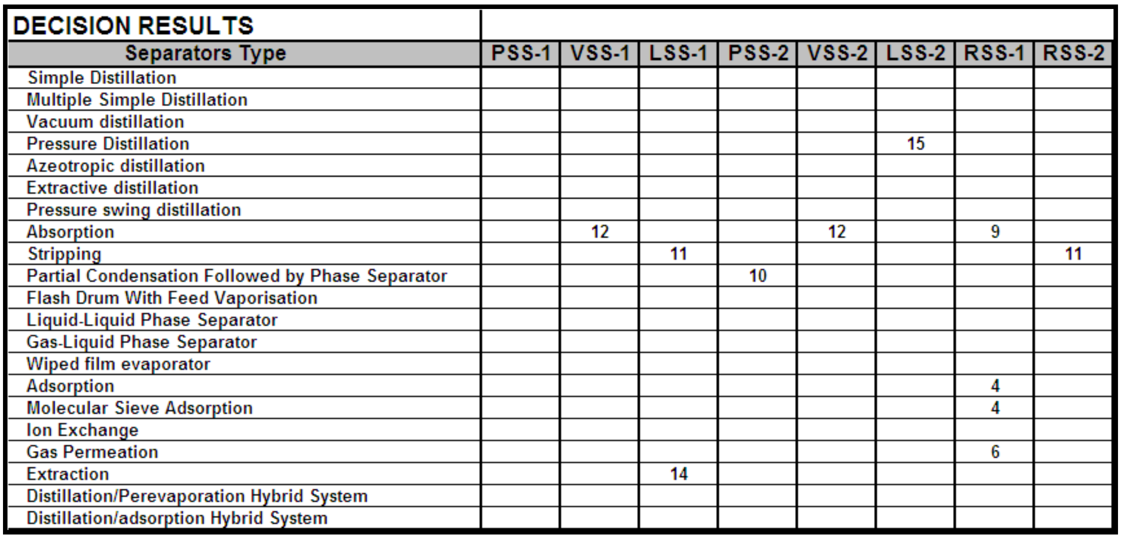


Figure 6.5: Ethylene oxide synthesis results illustrated in the generic superstructure.

The alternatives in each block are listed in order of increasing scores where the first has the highest score and last has the lowest score. The scores for each suitable separation process is tabulated in the decision results illustrated in Figure 6.6. The allocated scores to separators are the sum of all criterion scores. The same separation system may have more than one alternative such as recycle gas separation system can be an absorber followed by striping, or adsorption, or gas permeation. The scoring system is discussed in the subsequent section.



DECISION RESULTS

Separators Type	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Simple Distillation								
Multiple Simple Distillation								
Vacuum distillation								
Pressure Distillation						15		
Azeotropic distillation								
Extractive distillation								
Pressure swing distillation								
Absorption		12			12		9	
Stripping			11					11
Partial Condensation Followed by Phase Separator				10				
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption							4	
Molecular Sieve Adsorption							4	
Ion Exchange								
Gas Permeation							6	
Extraction			14					
Distillation/Perevaporation Hybrid System								
Distillation/adsorption Hybrid System								

Figure 6.6: The IKBS separation synthesis decision results.

The mass separation agent is selected from the available database, or the user can supply this information. Table 6.1, shows an example of the mass separating agents used by the IKBS for absorption processes. Other available databases in the IKBS include adsorption solid agents, and liquid extraction solvents. Users can view the database and select the required MSA. Users can also view the safety and environmental impacts of the selected MSA based on the safety and environmental database information.

After selecting the required mass separation agent, recycle allocation takes place based on the composition and the phase of the stream. For example, if the stream contains mainly feed impurities it should be treated as a by-product stream and if the stream contains mainly condensable gas or liquid reactants, it should be recycled to the reactor. This is followed by the selection of suitable recycle separation techniques.

Table 6.1: Absorption mass separating agents database used by the IKBS.

Solute/ Species	in	Agent
H2S	Hydrocarbons	Triethanolmine, Sodium vanadate
H2S/Air	Air	Triethanolmine, Sodium vanadate
CO2; H2S		Monoethanolmine, hot potassium carbonate, diglycolamine, sulfinol, selexol, tributylphosate, methanol
NH3	Air	water
HCL		water
NO2		water
SO3		dilute sulphuric acid
H2O	Air	sulphuric acid; diethylene glycol, Lithium chloride in water
Ethylene	CH4	lean oil C4+
H2		lean oil C4+
CO2		Triethanolmine (TEA), hot potassium carbonate, diglycolamine (DGA), sodium hydroxide, propylene carbonate, glycerol triacetate
Ethylene oxide		Water

There are three types of recycle in the generic flowsheet: internal recycle within the reactor systems, internal recycle between separation processes, liquid recycle from separation system to reactor system and vapour recycle from the separation system to the reaction systems. The last may pass through the recycle recovery system. Recycle structure starts with calculating the number of output streams by following four steps (Dimian and Bildea, 2008):

1. Examining reactor outlet mixture composition
2. Ordering the components based on boiling points
3. Assigning a destination code to each component as tabulated in Table 6.2
4. Grouping neighbouring components with the same destination

The number of all groups minus the recycle streams gives the number of the outlet streams. However, the presence of azeotropes, or solid components, may change the above rules. Table 6.2 can be used to construct the connectivity within the reactor-separator recycle systems based on the destination of each stream.

If the process involves light reactants and light feed impurities, or a light by-product, then it is more likely that a gas recycle and purge are needed. According to Douglas (1988), light components are those that boil below the propylene boiling point. The boiling point of propylene is -48 ^{o}C. If the boiling point of a component is lower than -48 ^{o}C, it will not be condensed above ambient pressure using cooling water. Using cooling water is more economical than using a refrigeration system which is one of the most expensive processing operations.

Table 6.2: Classification of process component and destination codes.

Component classification	Destination code
Reactant (liquid)	Liquid recycle
Reactant (solid)	Recycle or waste
Reactant (gas)	Gas recycle, purge, vent
By-product (gas)	Fuel or flare
By-product (reversible reaction)	Recycle or exit
Reaction intermediate	Recycle
Product	Product storage
Valuable by-product	By-product storage
Fuel by-product	Fuel supply
Waste by-products (aqueous waste)	Biological treatment
Waste by-products (solid waste)	Incinerator
Feed impurity	Same as by-product
Homogeneous catalyst	Recycle
Homogeneous catalyst activator	Recycle
Reactor or product solvent	Recycle

The sequencing of separation is one of the important steps of separation system synthesis. This is due to the high cost of energy and investment in separation processes. Therefore, it is important in the future development of the IKBS to use heuristic rules for exploring all possible structures of separation and selecting the best one. King (1980); Douglas (1988); Biegler et al. (1997); Doherty and Malone (2001); Wankat (2007) suggest heuristic rules for separation sequences such as:

1. remove dangerous, corrosive and reactive components first to minimize the safety concerns and reduce the cost of material of construction in later columns.
2. remove components which require either very high or very low temperatures or pressure first to eliminate the need for tall columns.
3. do easy splits first to keep the cost down as the easy split requires short columns and low reflux ratio.
4. the next splits should remove the most volatile component to reduces the flowrate as early as possible.
5. do the most difficult separations as a binary separation to remove the difficult to condense materials and allow for operating the column at lower pressure. Removing most volatiles early could reduce the cost of energy required for condensation in the subsequent columns
6. favour 50:50 splits to balance separation columns and the flowrates do not change significantly.
7. when a mass separating agent is used, remove it in the separation immediately and recycle to accounts for the early recovery of a mass separating agent which should reduce the size of the subsequent columns.
8. if possible, final product withdrawals should be as a distillate products as it may results in purer products
9. consider side stream withdrawals for sloppy separations to look for additional effective sequences for sloppy separation in which all components are distributed between overhead and bottom at minimum reflux
10. consider thermally coupled multi-effect columns if energy is very expensive.

Some of the heuristic rules may conflict with each other. Therefore, it is necessary to examine several different sequences to see which of these heuristics are dominant. The number of sequences to be evaluated grows progressively with the number of alternative separations techniques. Furthermore, after selecting the separation techniques, the number of sequences is still considerable as illustrated in Table 6.3. The examined logical alternative sequences need to be reduced as the large number of alternatives may not be favoured by many heuristics.

Table 6.3: The number of possible sequences versus the number of products in distillation columns.

Number of products	Number of separators	Number of sequences
2	1	1
3	2	2
4	3	5
5	4	14
6	5	42
7	6	132
8	7	429
9	8	1430

There can be five possible alternative sequences for a four component mixture ABCD, each of three columns, as shown in Table 6.4 (Dimian, 2003). In case of the direct sequence, all the components are separated in order of their volatilities.

Table 6.4: Sequences type for separating four component mixtures. (adapted from Dimian, 2003)

Type	First split	Second split	Third split
Direct	A/BCD	B/CD	C/D
Equal split	AB/CD	A/B	C/D
Indirect	ABC/D	AB/C	A/B
Direct/indirect	A/BCD	BC/D	B/C
Indirect/direct	ABC/D	A/BC	B/C

In the indirect sequence, all components are obtained as bottoms except the lightest component. In the equal split sequence, A and C are obtained as overheads and B and D as bottoms. The mixed sequences depend on the second split, whereas the third split is the same.

Before the development of alternative flowsheets, the operating conditions have to be determined. The main variables in the operating condition are the pressure, temperature and the flowrate of each stream in the separation processes. Other difficulties come from dealing with a wide range of separation processes with different concepts of separation phenomena. Therefore, the determination of separation process operating conditions is complex. The complexity comes mainly from diversity in the properties of the components to be separated. An example of the operating condition is the mode of operation of distillation column condenser, as illustrated in Table 6.5 (Dimian, 2003; Barnicki and Fair, 1990).

Table 6.5: Mode of operation of distillation column condenser.

Component group	Boiling point range (^oC)	Distillation pressure range (bar)	Condenser type
Gas	$T < -20$	$P > 25$	Refrigeration
Gas-Liquid	$-20 < T < 0$ $0 < T < 50$	$15 < P > 25$ $P < 15$	Partial Total
Liquid	$T > 50$	$P < 15$	Total

There are cases when the operating condition of the separation processes are affected by the reactor system condition, which restricts the condition of the separation. For example, in the ethylene oxide process illustrated in the Chapter 7, the absorption of ethylene oxide product using water takes place at a pressure close to the reactor pressure. This is required as the unreacted ethylene can be recycled at a pressure close to the reaction condition with low operating cost of the recycle gas compressor. If low pressure is used in the absorber, ethylene oxide will not be in the gas phase at absorption temperature. Absorption of ethylene oxide releases heat therefore, water and reactor effluent should be kept at low temperature. This will keep the required flowrate of water as small as possible and the subsequent separation processes as small as possible. This example shows how complex the determination of separation process operating conditions which is requiring further work in the future development of the IKBS.

The next step is the flowsheets simulation for mass and energy balances. The calculation following the generic flowsheet illustrated in Figure 6.7. The separation part of the generic flowsheet currently contains: two adsorption columns, a re-boiled stripping column, three distillation columns, and an extraction column connected to two other distillation columns for solvent recovery and regeneration. In the recycle separation HYSYS component splitter is used for simplicity. The generic flowsheet also contains heat exchangers at different locations to bring the process streams to the desired temperature. There are also pumps and compressors for fluids transports and bring the pressure to required levels. Expansion valves are also used to reduce the streams pressure when required. The flowsheet systems are connected with a set of mixing and splitting units. A matrix of splitters ratio is used in Excel to specify the direction and magnitude of streams between the reactors and separators.

This generic flowsheet has been compared with several existing petrochemical processes such as methanol, formaldehyde, ammonia, acetic acid, maleic anhydride, isopropanol, ethylbenzene, styrene and aniline using published data from Chauvel and Lefebvre, (1989); Matar and Hatch (2001); Moulijn, et al. (2001); Meyers (2005). The generic flowsheet found to cover the required units connectivity used.

Results from the simulation are imported to the Excel interface in the IKBS using VBA programming. Users can modify the process variables and then new variables are exported to Aspen HSYSY for simulation as illustrated in Figure 6.8. This arrangement can be useful to simulate alternative process flowsheets and examine the effect of different variables on the process performance. If any process unit in the generic flowsheet is not used, it will be disappear in the Excel interface by VBA programming illustrated in Appendix D.

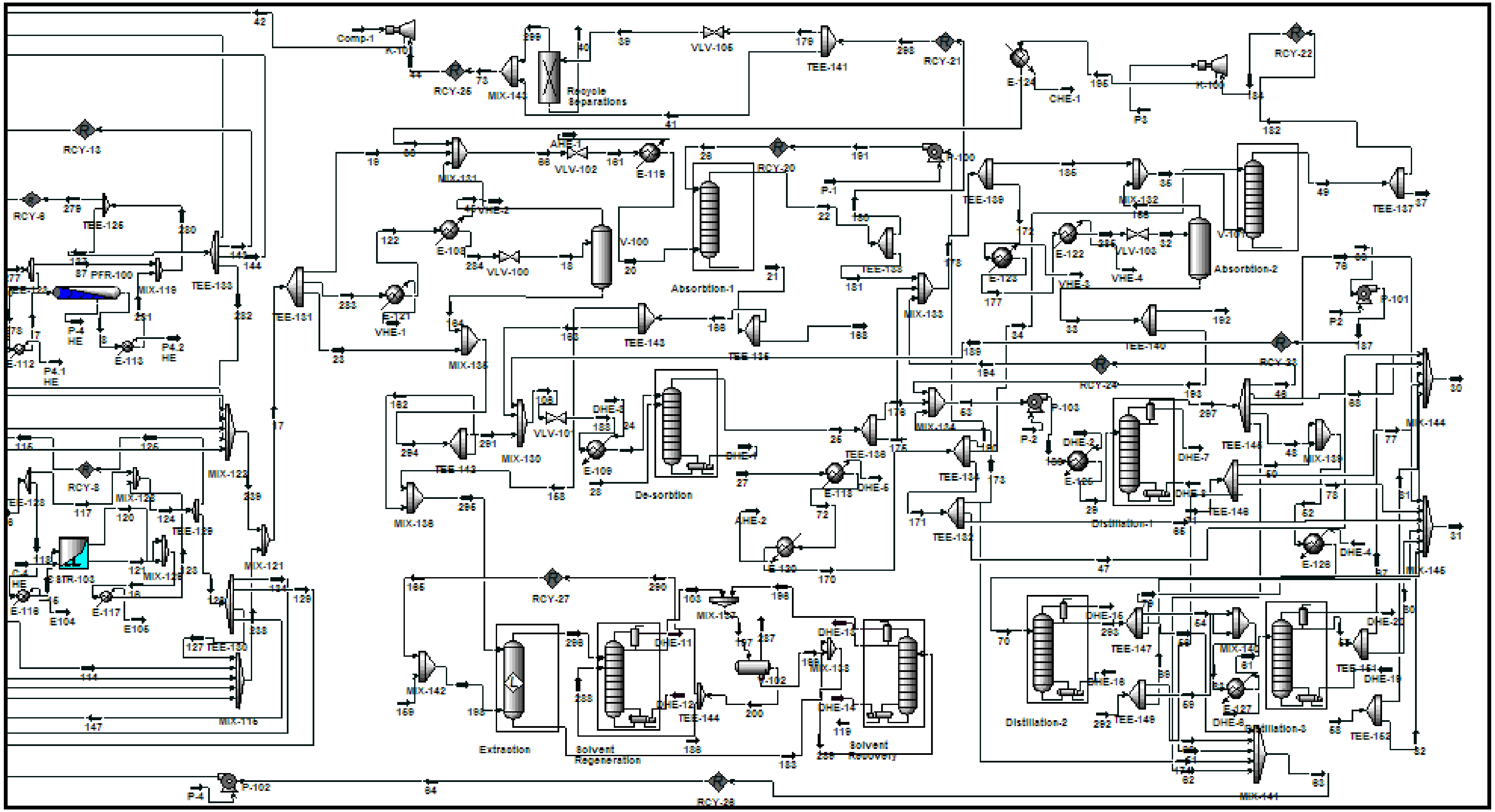
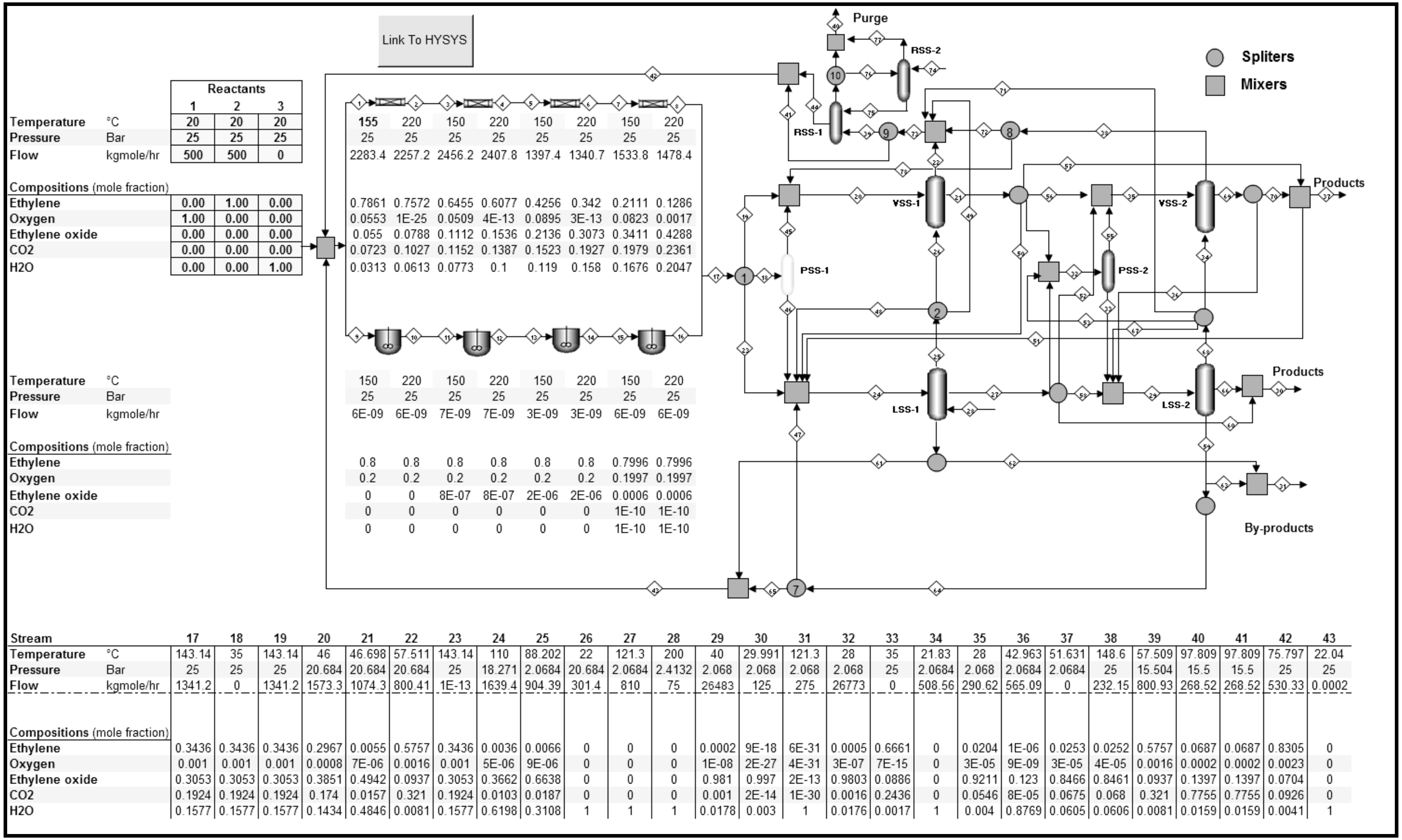


Figure 6.7: Separation system of the generic process flowsheet.



		Reactants		
		1	2	3
Temperature	°C	20	20	20
Pressure	Bar	25	25	25
Flow	kgmole/hr	500	500	0
Compositions (mole fraction)				
Ethylene		0.00	1.00	0.00
Oxygen		1.00	0.00	0.00
Ethylene oxide		0.00	0.00	0.00
CO2		0.00	0.00	0.00
H2O		0.00	0.00	1.00

155	220	150	220	150	220	150	220
25	25	25	25	25	25	25	25
2283.4	2257.2	2456.2	2407.8	1397.4	1340.7	1533.8	1478.4
0.7861	0.7572	0.6455	0.6077	0.4256	0.342	0.2111	0.1286
0.0553	1E-25	0.0509	4E-13	0.0895	3E-13	0.0823	0.0017
0.055	0.0788	0.1112	0.1536	0.2136	0.3073	0.3411	0.4288
0.0723	0.1027	0.1152	0.1387	0.1523	0.1927	0.1979	0.2361
0.0313	0.0613	0.0773	0.1	0.119	0.158	0.1676	0.2047

Temperature	°C	150	220	150	220	150	220	150	220
Pressure	Bar	25	25	25	25	25	25	25	25
Flow	kgmole/hr	6E-09	6E-09	7E-09	7E-09	3E-09	3E-09	6E-09	6E-09
Compositions (mole fraction)									
Ethylene		0.8	0.8	0.8	0.8	0.8	0.8	0.7996	0.7996
Oxygen		0.2	0.2	0.2	0.2	0.2	0.2	0.1997	0.1997
Ethylene oxide		0	0	8E-07	8E-07	2E-06	2E-06	0.0006	0.0006
CO2		0	0	0	0	0	0	1E-10	1E-10
H2O		0	0	0	0	0	0	1E-10	1E-10

Stream		**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Temperature	°C	143.14	35	143.14	46	46.698	57.511	143.14	110	88.202	22	121.3	200	40	29.991
Pressure	Bar	25	25	25	20.684	20.684	20.684	25	18.271	2.0684	20.684	2.0684	2.4132	2.068	2.068
Flow	kgmole/hr	1341.2	0	1341.2	1573.3	1074.3	800.41	1E-13	1639.4	904.39	301.4	810	75	26483	125
Compositions (mole fraction)															
Ethylene		0.3436	0.3436	0.3436	0.2967	0.0055	0.5757	0.3436	0.0036	0.0066	0	0	0	0.0002	9E-18
Oxygen		0.001	0.001	0.001	0.0008	7E-06	0.0016	0.001	5E-06	9E-06	0	0	0	1E-08	2E-27
Ethylene oxide		0.3053	0.3053	0.3053	0.3851	0.4942	0.0937	0.3053	0.3662	0.6638	0	0	0	0.981	0.997
CO2		0.1924	0.1924	0.1924	0.174	0.0157	0.321	0.1924	0.0103	0.0187	0	0	0	0.001	2E-14
H2O		0.1577	0.1577	0.1577	0.1434	0.4846	0.0081	0.1577	0.6198	0.3108	1	1	1	0.0178	0.003

Stream		**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**	**41**	**42**	**43**
Temperature	°C	121.3	28	35	21.83	28	42.963	51.631	148.6	57.509	97.809	97.809	75.797	22.04
Pressure	Bar	2.068	2.068	25	2.0684	2.068	2.0684	2.0684	25	15.504	15.5	15.5	25	25
Flow	kgmole/hr	275	26773	0	508.56	290.62	565.09	0	232.15	800.93	268.52	268.52	530.33	0.0002
Compositions (mole fraction)														
Ethylene		6E-31	0.0005	0.6661	0	0.0204	1E-06	0.0253	0.0252	0.5757	0.0687	0.0687	0.8305	0
Oxygen		4E-31	3E-07	7E-15	0	3E-05	9E-09	3E-05	4E-05	0.0016	0.0002	0.0002	0.0023	0
Ethylene oxide		2E-13	0.9803	0.0886	0	0.9211	0.123	0.8466	0.8461	0.0937	0.1397	0.1397	0.0704	0
CO2		1E-30	0.0016	0.2436	0	0.0546	8E-05	0.0675	0.068	0.321	0.7755	0.7755	0.0926	0
H2O		1	0.0176	0.0017	1	0.004	0.8769	0.0605	0.0606	0.0081	0.0159	0.0159	0.0041	1

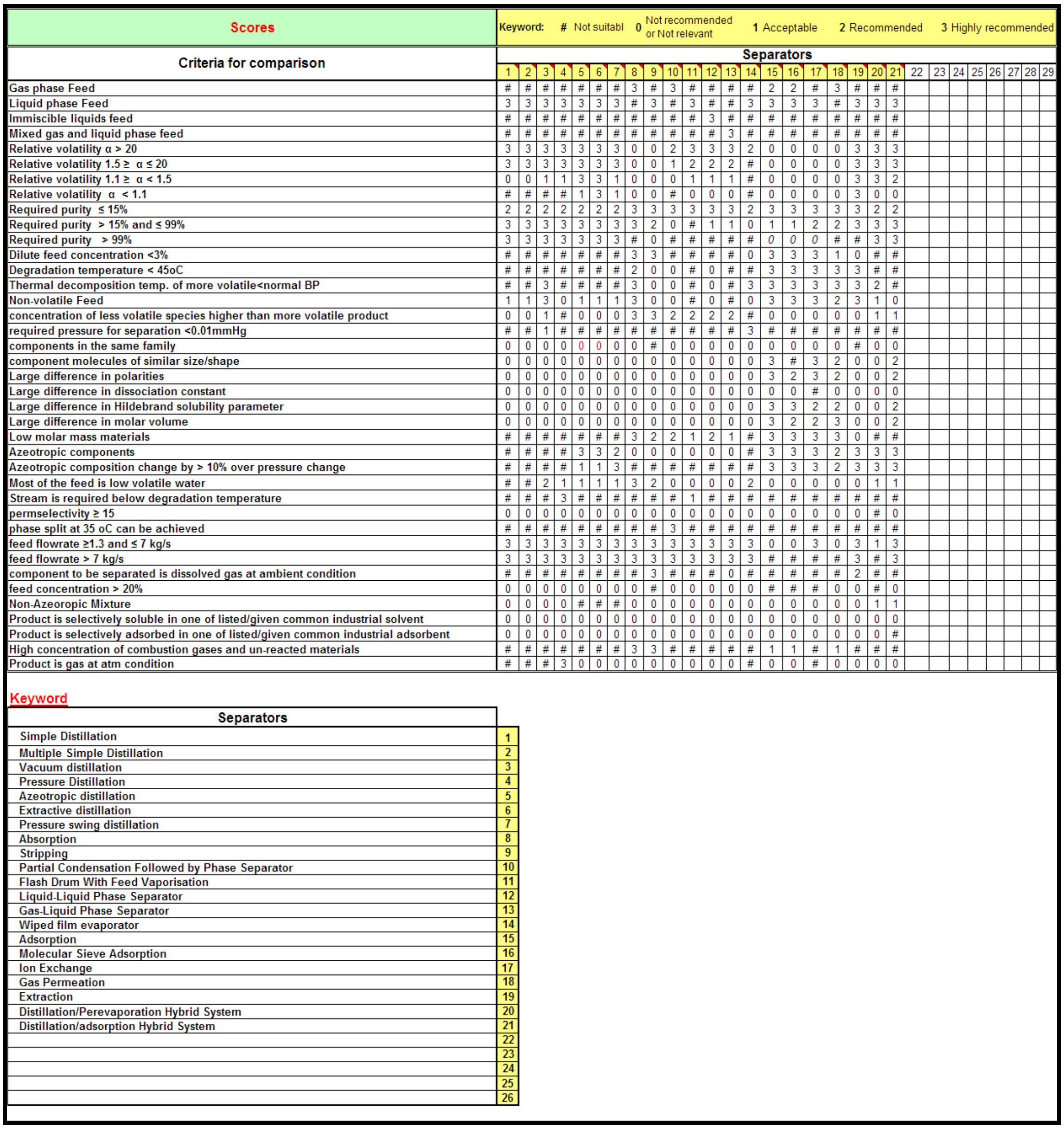
Figure 6.8: Linking the IKBS with the simulated reactor-separator-recycle systems by Aspen HYSYS.

6.3 Separation Selection Criteria

Separator systems synthesis is to find the type, sequences and operating conditions of separation processes which meet design requirements and constraints. The general factors that affect the selection of separation processes are discussed here.

Separator systems selection criteria in the IKBS start with reactor effluents analysis and screening based on the boiling points and the vapour pressure. This initial reactor output stream analysis is being used by the IKBS to determine the suggested suitable separators for further design considerations such as sequencing and operation conditions determination in the future development of the software. The states of all feed stream species are identified in order to determine their destination in the process flowsheet. Subsequent analyses are based on a set of criteria. Figure 6.9, illustrates the key information that the IKBS uses to select the suitable separation processes. Figure 6.9 also illustrates the IKBS criteria for reactor selection and associated scores. The main selection criteria are:

- phase of feed stream
- relative volatilities
- required purities
- feed concentration
- boiling points
- thermal decomposition
- chemical family
- differences in disassociation constants
- differences in polarity
- differences in solubility
- presence of azeotropes
- presence of water
- permselectivity
- feed flowrate
- presence of combustion gases



Scores

Keyword: # Not suitabl 0 Not recommended or Not relevant 1 Acceptable 2 Recommended 3 Highly recommended

Criteria for comparison	Separators																												
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Gas phase Feed	#	#	#	#	#	#	#	3	#	3	#	#	#	#	2	2	#	3	#	#	#								
Liquid phase Feed	3	3	3	3	3	3	3	#	3	#	3	#	#	3	3	3	3	#	3	3	3								
Immiscible liquids feed	#	#	#	#	#	#	#	#	#	#	#	3	#	#	#	#	#	#	#	#	#								
Mixed gas and liquid phase feed	#	#	#	#	#	#	#	#	#	#	#	#	3	#	#	#	#	#	#	#	#								
Relative volatility α > 20	3	3	3	3	3	3	3	0	0	2	3	3	3	2	0	0	0	0	3	3	3								
Relative volatility 1.5 ≥ α ≤ 20	3	3	3	3	3	3	3	0	0	1	2	2	2	#	0	0	0	0	3	3	3								
Relative volatility 1.1 ≥ α < 1.5	0	0	1	1	3	3	1	0	0	0	1	1	1	#	0	0	0	0	3	3	2								
Relative volatility α < 1.1	#	#	#	#	1	3	1	0	0	#	0	0	0	#	0	0	0	0	3	0	0								
Required purity ≤ 15%	2	2	2	2	2	2	2	3	3	3	3	3	3	2	3	3	3	3	3	2	2								
Required purity > 15% and ≤ 99%	3	3	3	3	3	3	3	3	2	0	#	1	1	0	1	1	2	2	3	3	3								
Required purity > 99%	3	3	3	3	3	3	3	#	0	#	#	#	#	#	*0*	*0*	*0*	#	#	3	3								
Dilute feed concentration <3%	#	#	#	#	#	#	#	3	3	#	#	#	#	0	3	3	3	1	0	#	#								
Degradation temperature < 45oC	#	#	#	#	#	#	#	2	0	0	#	0	#	#	3	3	3	3	3	#	#								
Thermal decomposition temp. of more volatile<normal BP	#	#	3	#	#	#	#	3	0	0	#	0	#	3	3	3	3	3	3	2	#								
Non-volatile Feed	1	1	3	0	1	1	1	3	0	0	#	0	#	0	3	3	3	2	3	1	0								
concentration of less volatile species higher than more volatile product	0	0	1	#	0	0	0	3	3	2	2	2	2	#	0	0	0	0	0	1	1								
required pressure for separation <0.01mmHg	#	#	1	#	#	#	#	#	#	#	#	#	#	3	#	#	#	#	#	#	#								
components in the same family	0	0	0	0	0	0	0	0	#	0	0	0	0	0	0	0	0	0	#	0	0								
component molecules of similar size/shape	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	#	3	2	0	0	2								
Large difference in polarities	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	2	3	2	0	0	2								
Large difference in dissociation constant	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	0	0								
Large difference in Hildebrand solubility parameter	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	3	2	2	0	0	2								
Large difference in molar volume	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	2	2	3	0	0	2								
Low molar mass materials	#	#	#	#	#	#	#	3	2	2	1	2	1	#	3	3	3	3	0	#	#								
Azeotropic components	#	#	#	#	3	3	2	0	0	0	0	0	0	#	3	3	3	2	3	3	3								
Azeotropic composition change by > 10% over pressure change	#	#	#	#	1	1	3	#	#	#	#	#	#	#	3	3	3	2	3	3	3								
Most of the feed is low volatile water	#	#	2	1	1	1	1	3	2	0	0	0	0	2	0	0	0	0	0	1	1								
Stream is required below degradation temperature	#	#	#	3	#	#	#	#	#	#	1	#	#	#	#	#	#	#	#	#	#								
permselectivity ≥ 15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0								
phase split at 35 oC can be achieved	#	#	#	#	#	#	#	#	#	3	#	#	#	#	#	#	#	#	#	#	#								
feed flowrate ≥1.3 and ≤ 7 kg/s	3	3	3	3	3	3	3	3	3	3	3	3	3	3	0	0	3	0	3	1	3								
feed flowrate > 7 kg/s	3	3	3	3	3	3	3	3	3	3	3	3	3	3	#	#	#	#	3	#	3								
component to be separated is dissolved gas at ambient condition	#	#	#	#	#	#	#	#	3	#	#	#	0	#	#	#	#	#	2	#	#								
feed concentration > 20%	0	0	0	0	0	0	0	0	#	0	0	0	0	0	#	#	#	0	0	#	0								
Non-Azeoropic Mixture	0	0	0	0	#	#	#	0	0	0	0	0	0	0	0	0	0	0	0	1	1								
Product is selectively soluble in one of listed/given common industrial solvent	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0								
Product is selectively adsorbed in one of listed/given common industrial adsorbent	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#								
High concentration of combustion gases and un-reacted materials	#	#	#	#	#	#	#	3	3	#	#	#	#	#	1	1	#	1	#	#	#								
Product is gas at atm condition	#	#	#	3	0	0	0	0	0	0	0	0	0	#	0	0	#	0	0	0	0								

Keyword

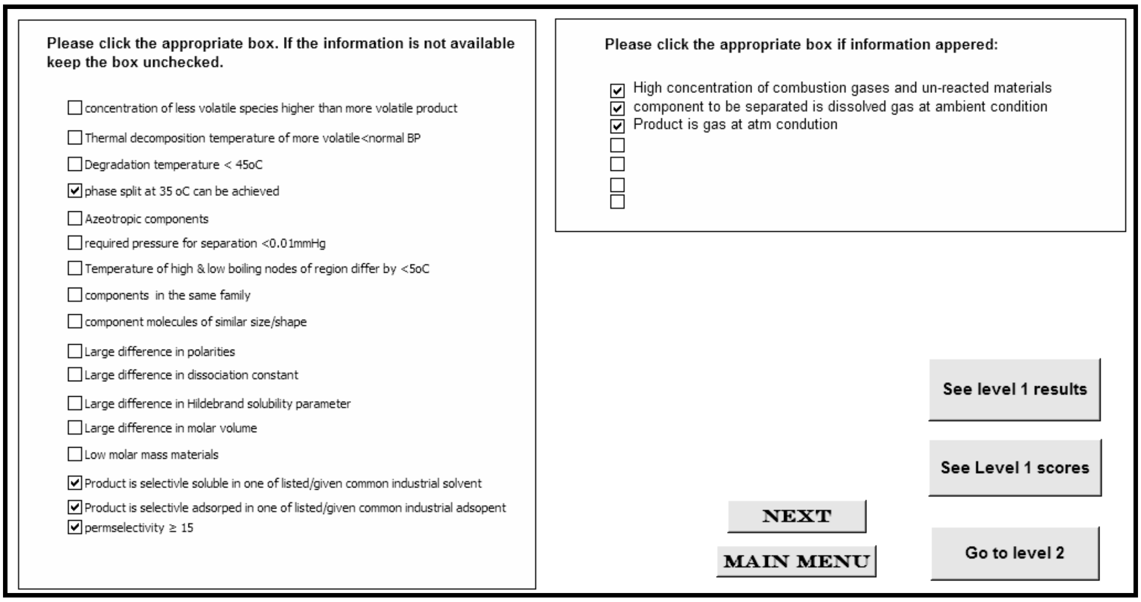
Separators	
Simple Distillation	1
Multiple Simple Distillation	2
Vacuum distillation	3
Pressure Distillation	4
Azeotropic distillation	5
Extractive distillation	6
Pressure swing distillation	7
Absorption	8
Stripping	9
Partial Condensation Followed by Phase Separator	10
Flash Drum With Feed Vaporisation	11
Liquid-Liquid Phase Separator	12
Gas-Liquid Phase Separator	13
Wiped film evaporator	14
Adsorption	15
Molecular Sieve Adsorption	16
Ion Exchange	17
Gas Permeation	18
Extraction	19
Distillation/Perevaporation Hybrid System	20
Distillation/adsorption Hybrid System	21
	22
	23
	24
	25
	26

Figure 6.9: Separation selection criteria and scores

The reactor selection scoring worksheet contains 39 selection criteria and 21 separators and separation processes configuration. Figure 6.9, illustrates that the IKBS has the flexibility to add more criteria, reactors, and scores. More separators and criteria can be added to the separation systems evaluation and selection.

The scoring system used for the separation systems selection is similar to the scoring system for the reactor systems selection. As illustrated in Figure 6.9, the scoring system used in the selection process ranges from “not suitable” which is given the sign (#), this will immediately eliminate the choice of separator. For example, absorption column is not suitable for liquid phase feed separation. Therefore, it is given the score “#” which eliminates it. For suitable separators, the selection scores range from 0 to 3 where 0 can be given to “not recommended”, or “not relevant”, 1 “acceptable”, 2 “recommended” and 3 “highly recommended”. The highly recommended score is given to selection criteria, which have been implemented in many existing commercial processes using the same separator type.

By selecting the appropriate box in the separation input information worksheet illustrated in Figure 6.10, information is transferred to the separations processes selection worksheet illustrated in Figure 6.11 in form of answers “YES” or “NO”. If the answer is “YES” then the sore in Figure 6.9 is considered and the criterion is accounted for in the selection of the reactor. If the answer is “NO”, the score in Figure 6.9 is ignored.



Please click the appropriate box. If the information is not available keep the box unchecked.

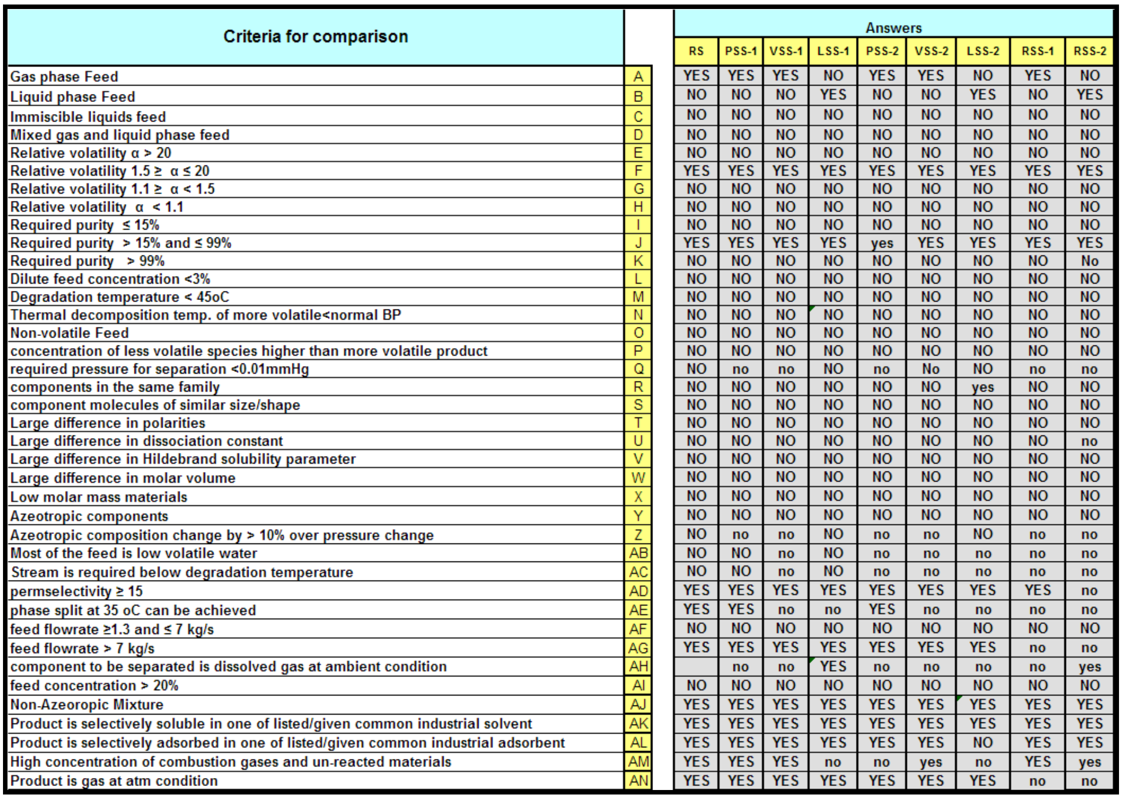
☐ concentration of less volatile species higher than more volatile product
☐ Thermal decomposition temperature of more volatile<normal BP
☐ Degradation temperature < 45oC
☑ phase split at 35 oC can be achieved
☐ Azeotropic components
☐ required pressure for separation <0.01mmHg
☐ Temperature of high & low boiling nodes of region differ by <5oC
☐ components in the same family
☐ component molecules of similar size/shape
☐ Large difference in polarities
☐ Large difference in dissociation constant
☐ Large difference in Hildebrand solubility parameter
☐ Large difference in molar volume
☐ Low molar mass materials
☑ Product is selectivle soluble in one of listed/given common industrial solvent
☑ Product is selectivle adsorped in one of listed/given common industrial adsopent
☑ permselectivity ≥ 15

Please click the appropriate box if information appered:

☑ High concentration of combustion gases and un-reacted materials
☑ component to be separated is dissolved gas at ambient condition
☑ Product is gas at atm condution
☐
☐
☐
☐

Figure 6.10: Separation system synthesis user input information.

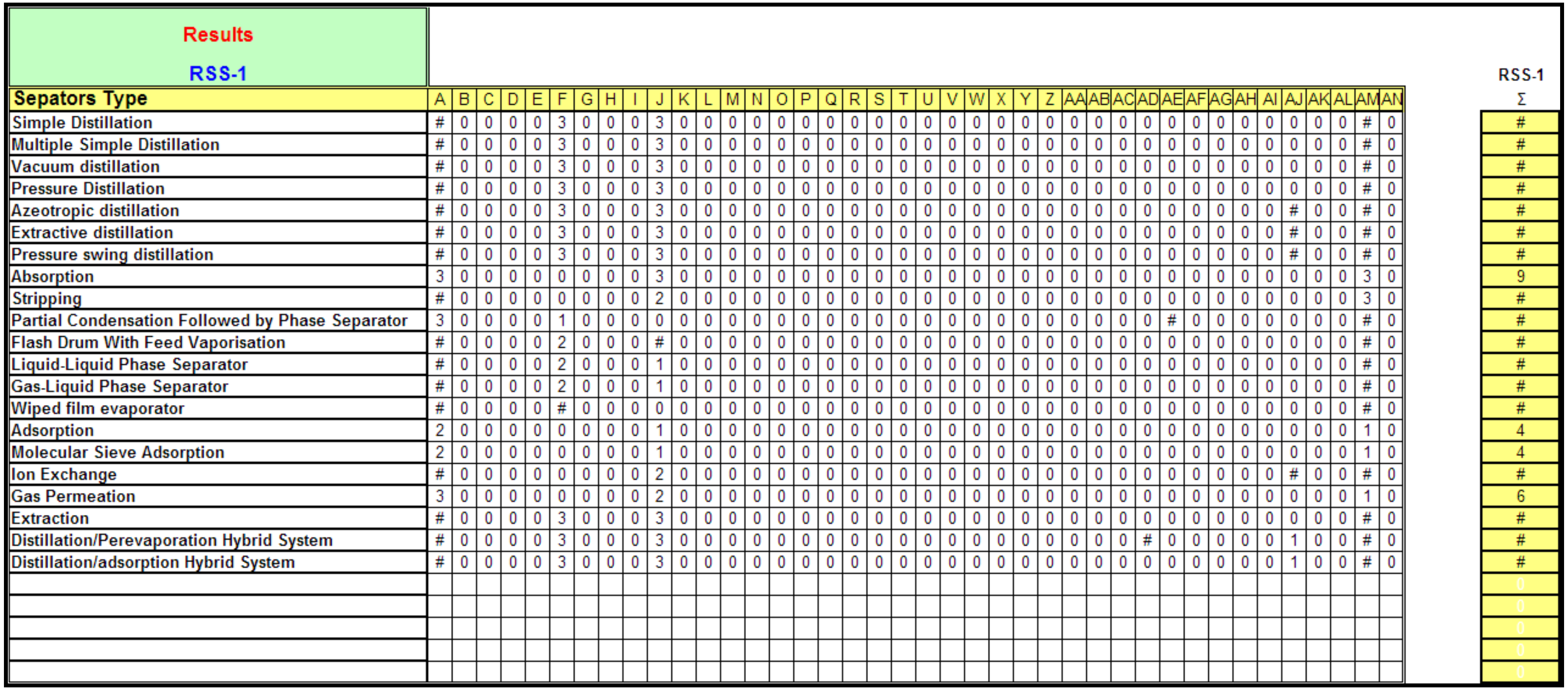
To select the required box users can use information from the IKBS databases. For example user can check the IKBS database for the potential azeotropes, solvent, solubility in common industrial solvents. Some information can be provided based on the previous initial analysis of the reactor effluents. For example, the possibility of achieving phase splitting of the stream at 35 ^oC is calculated and determined in the reactor output analysis step.



Criteria for comparison		Answers								
		RS	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Gas phase Feed	A	YES	YES	YES	NO	YES	YES	NO	YES	NO
Liquid phase Feed	B	NO	NO	NO	YES	NO	NO	YES	NO	YES
Immiscible liquids feed	C	NO	NO	NO	NO	NO	NO	NO	NO	NO
Mixed gas and liquid phase feed	D	NO	NO	NO	NO	NO	NO	NO	NO	NO
Relative volatility α > 20	E	NO	NO	NO	NO	NO	NO	NO	NO	NO
Relative volatility 1.5 ≥ α ≤ 20	F	YES	YES	YES	YES	YES	YES	YES	YES	YES
Relative volatility 1.1 ≥ α < 1.5	G	NO	NO	NO	NO	NO	NO	NO	NO	NO
Relative volatility α < 1.1	H	NO	NO	NO	NO	NO	NO	NO	NO	NO
Required purity ≤ 15%	I	NO	NO	NO	NO	NO	NO	NO	NO	NO
Required purity > 15% and ≤ 99%	J	YES	YES	YES	YES	yes	YES	YES	YES	YES
Required purity > 99%	K	NO	NO	NO	NO	NO	NO	NO	NO	No
Dilute feed concentration <3%	L	NO	NO	NO	NO	NO	NO	NO	NO	NO
Degradation temperature < 45oC	M	NO	NO	NO	NO	NO	NO	NO	NO	NO
Thermal decomposition temp. of more volatile<normal BP	N	NO	NO	NO	NO	NO	NO	NO	NO	NO
Non-volatile Feed	O	NO	NO	NO	NO	NO	NO	NO	NO	NO
concentration of less volatile species higher than more volatile product	P	NO	NO	NO	NO	NO	NO	NO	NO	NO
required pressure for separation <0.01mmHg	Q	NO	no	no	NO	no	No	NO	no	no
components in the same family	R	NO	NO	NO	NO	NO	NO	yes	NO	NO
component molecules of similar size/shape	S	NO	NO	NO	NO	NO	NO	NO	NO	NO
Large difference in polarities	T	NO	NO	NO	NO	NO	NO	NO	NO	NO
Large difference in dissociation constant	U	NO	NO	NO	NO	NO	NO	NO	NO	no
Large difference in Hildebrand solubility parameter	V	NO	NO	NO	NO	NO	NO	NO	NO	NO
Large difference in molar volume	W	NO	NO	NO	NO	NO	NO	NO	NO	NO
Low molar mass materials	X	NO	NO	NO	NO	NO	NO	NO	NO	NO
Azeotropic components	Y	NO	NO	NO	NO	NO	NO	NO	NO	NO
Azeotropic composition change by > 10% over pressure change	Z	NO	no	no	NO	no	no	NO	no	no
Most of the feed is low volatile water	AB	NO	NO	no	NO	no	no	no	no	no
Stream is required below degradation temperature	AC	NO	NO	no	NO	no	no	no	no	no
permselectivity ≥ 15	AD	YES	YES	YES	YES	YES	YES	YES	YES	no
phase split at 35 oC can be achieved	AE	YES	YES	no	no	YES	no	no	no	no
feed flowrate ≥1.3 and ≤ 7 kg/s	AF	NO	NO	NO	NO	NO	NO	NO	NO	NO
feed flowrate > 7 kg/s	AG	YES	YES	YES	YES	YES	YES	YES	no	no
component to be separated is dissolved gas at ambient condition	AH		no	no	YES	no	no	no	no	yes
feed concentration > 20%	AI	NO	NO	NO	NO	NO	NO	NO	NO	NO
Non-Azeoropic Mixture	AJ	YES	YES	YES	YES	YES	YES	YES	YES	YES
Product is selectively soluble in one of listed/given common industrial solvent	AK	YES	YES	YES	YES	YES	YES	YES	YES	YES
Product is selectively adsorbed in one of listed/given common industrial adsorbent	AL	YES	YES	YES	YES	YES	YES	NO	YES	YES
High concentration of combustion gases and un-reacted materials	AM	YES	YES	YES	no	no	yes	no	YES	yes
Product is gas at atm condition	AN	YES	YES	YES	YES	YES	YES	YES	no	no

Figure 6.11: Input information answers in the IKBS for separators selection.

The sum of all applicable criteria scores is given to each suitable separator for RSS-1 as illustrated in Figure 6.12. For example, when absorber is examined for the recovery of recycled gas with concentration between 15 – 99% and the stream contains combustion gases, the IKBS gives the score "3" for each of the three criteria: feed phase and concentration, and the presence of combustion gasses. This gives the total score of "9".



Results

RSS-1

Sepators Type	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	AA	AB	AC	AD	AE	AF	AG	AH	AI	AJ	AK	AL	AM	AN	RSS-1 Σ
Simple Distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Multiple Simple Distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Vacuum distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Pressure Distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Azeotropic distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	#	0	#
Extractive distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	#	0	#
Pressure swing distillation	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	#	0	#
Absorption	3	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	9
Stripping	#	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	#
Partial Condensation Followed by Phase Separator	3	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	0	0	0	0	0	#	0	#
Flash Drum With Feed Vaporisation	#	0	0	0	0	2	0	0	0	#	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Liquid-Liquid Phase Separator	#	0	0	0	0	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Gas-Liquid Phase Separator	#	0	0	0	0	2	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Wiped film evaporator	#	0	0	0	0	#	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Adsorption	2	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	4
Molecular Sieve Adsorption	2	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	4
Ion Exchange	#	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	#	0	#
Gas Permeation	3	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	6
Extraction	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	#
Distillation/Perevaporation Hybrid System	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	#	0	0	0	0	0	1	0	0	#	0	#
Distillation/adsorption Hybrid System	#	0	0	0	0	3	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	#	0	#
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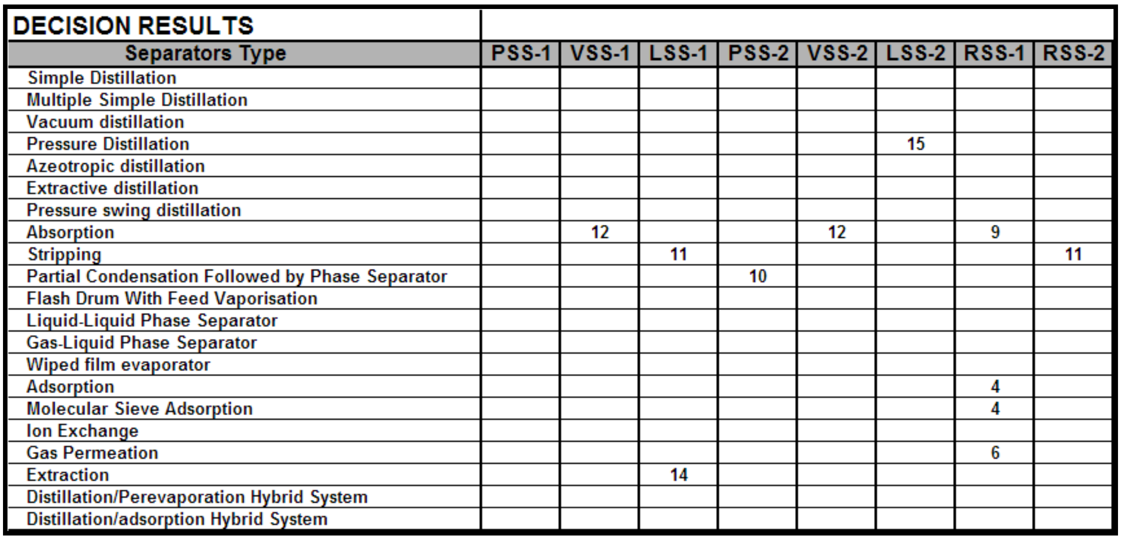
Figure 6.12: The IKBS separators scores calculation for RSS-1



DECISION RESULTS								
Separators Type	**PSS-1**	**VSS-1**	**LSS-1**	**PSS-2**	**VSS-2**	**LSS-2**	**RSS-1**	**RSS-2**
Simple Distillation								
Multiple Simple Distillation								
Vacuum distillation								
Pressure Distillation						15		
Azeotropic distillation								
Extractive distillation								
Pressure swing distillation								
Absorption		12			12		9	
Stripping			11					11
Partial Condensation Followed by Phase Separator				10				
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption							4	
Molecular Sieve Adsorption							4	
Ion Exchange								
Gas Permeation							6	
Extraction			14					
Distillation/Perevaporation Hybrid System								
Distillation/adsorption Hybrid System								

Figure 6.13: The IKBS separator selection decision results.

Figure 6.12, illustrates the scores for all required separation process for ethylene oxide presses. Detailed description of this alternative separation processes is illustrated in Chapter 7.

In Figure 6.12, most of the separators are given "#" as a sum of scores. This means the separator is not suitable because at least on of the selection criteria was given the sign "#" which reflects that the separator is not meeting the requirement. If any of the scores in Figure 6.12 for the evaluated separator is given "#", the separators decision results table illustrated in Figure 6.13 show "not suitable" even of all other criteria shows that the separator is suitable. The suitable separators are given the sum of the criteria scores.

Weighting the selection criteria of separation processes can be achieved by allocating different values to each criterion. This can improve the design decision. The implementation of weighting the selection criteria can be an important future task to account for the fact that some criteria may have a bigger effect on the selection of the reactor-separator-recycle system than others.

The main selection criteria used in the IKBS for the separation system synthesis are discussed here.

6.3.1 Feed Phase

Currently, the IKBS deals with four classes of feed phase: gas, liquid, immiscible liquids, and mixed gas and liquid. The phase of feed determines the general type of separation process because some separation techniques are restricted to a particular feed phase. For example, absorption can only be used for vapour phase feed. The IKBS gives the vapour phase feed the score "3" as it is highly recommended. Absorption is not suitable for the liquid phase feed stream; therefore the score given by the IKBS is "#" which will eliminate absorption columns. Other separation techniques can be used for more than one feed phase such as adsorption which can be used for gas or liquid phase feed.

6.3.2 Relative Volatility

One of the most important criteria of selecting thermal separation techniques is the relative volatility (α). The bigger the relative volatility, the easer the separation and wider range of thermal separation techniques can be suggested. For example if the relative volatility is grater than $\alpha > 20$, distillation and evaporation are highly recommended. This is subject to the feed concentration and desired product purity in case of evaporation. Distillation can be considered when $\alpha > 1.5$ and is not recommended if $\alpha < 1.1$. Alternatively, when $\alpha < 1.1$, liquid-liquid extraction is recommended (Seader and Henley, 2006).

6.3.3 Product Purity

The required purity of product may require a long column or train of columns. Very high purity separation (>99%) can only be achieved by using a limited number of separation processes such as distillation, and hybrid separation systems such as distillation-pervaporation. These separation processes are given the highest score "3". Other separation techniques may achieve high purity if the feed concentration, flow rate and separation factor are within ideal levels. An example is the use of liquid extraction with solvent recovery and regeneration. Another example is adsorption.

6.3.4 Feed Concentration

The feed concentration can make some separation processes ineffective either because of the economics, such as evaporating most of the feed to purify the high boiling point product, or due to the over loading of the separation unit when a highly concentrated stream needs to be purified. Even when the feed in not very concentrated, high feed flowrates might cause over loading the separation unit. For example, ion-exchange separation can be used when the feed concentration is between 0.5% and 2% w/w, and the flowrate up to 15 kg/s. If both feed flowrate and concentration are very high, the ion-exchange media will be over loaded quickly and separation may not be feasible.

If the concentration of less volatile species is higher than that the more volatile product, then thermal separation techniques requires higher energy consumption and the IKBS gives the thermal separation techniques low score such as ‘’0” for normal distillation and “#” (not suitable) for pressure distillation,. Another case of feed concentration constraints is when most of the feed is as water; the energy cost of using thermal separation is also high due to the high heat capacity and latent heat of vaporization of water. In this case, vacuum separation or non-thermal separations are recommended and high scores are given such as “2” for vacuum distillation.

6.3.5 Phase Splitting

The IKBS analyses the reactor effluents and determines if a gas feed stream phase split can be achieved using cooling water at 35 ^{o}C and suggest the use of phase splitting. The use of cooling water is cheaper than refrigeration. However, if the splitter vapour phase stream contains big amounts of valuable product which is going to be recycled to the reactor, phase splitting is not recommended at the beginning of the separation process. It may still be used after separating the product from the unreacted material and by-products. If the phase separation can not be achieved, the IKBS give the score “#” to the flash drum with feed vaporisation technique.

6.3.6 Thermal Decomposition

As in the reaction system criteria, the possibility of material decomposition with temperature should be considered. These criteria may eliminate a wide range of separations processes such as the thermal separation techniques. Low degradation temperature is considered to be < 45^{o}C (Koolen, 2001). The user is asked at an early stage of the separation system synthesis, if any of the species are subject to degradation below 45^{o}C. In this case all thermal separation are given the score “#” which will eliminate them form any further consideration of separation alternatives.

The user is also asked if the thermal decomposition temperature of more volatile components is less than the normal boiling point. If this is the case, then normal and pressure distillation, or evaporation are not recommended. Alternatively vacuum distillation and non-thermal separation can be proposed. This criteria implementation can be seen in the ethylene glycol process illustrated in Chapter 7, where vacuum distillation is used for the purification of ethylene glycol from the higher glycols. Ethylene glycol, di-ethylene glycol and tri-ethylene glycol start degradation below the normal boiling points.

6.3.7 Permeabilities

The ease of separating two gaseous components by membrane permeation is characterized by the ratio of their permeabilities in the membrane. According to Barnicki and Fair (1992), for a membrane process to be commercially feasible the permselectivity has to be ≥ 15. Moreover, permeate purity is relatively unaffected by a permselectivity when it is more than 20. The score “3” is given by the IKBS to membrane permeation if the permselectivity has to be ≥ 15. Flux, economics and the permeability of membrane are important factor that need to be considered in the future development of the software.

6.3.8 Presence of Combustion Gases

When the reactor effluent stream contains a high concentration of combustion gases and un-reacted materials, then recycle and purge are required. The IKBS uses this heuristic design rule to analyse the process and predict the need for gas recycle separation system and purge for the separation of the combustion gasses from the unreacted materials.

6.3.9 Presence of Azeotropes

In an azeotropic system, the vapour and liquid composition are identical. Thus all separation constant K-values are equal to 1 and there will be no separation of species. Azeotropes can limit the separation achieved if normal distillation. The presence of azeotropic components in the mixture requires a specific way of separation to break the azeotrope, or move it away from the region of separation. If an azeotrope is present, normal distillation is given the score “#” (not suitable).

Another way to overcome this separation problem is by not using separation techniques that can form the azeotrope. This can be achieved by introducing an entrainer such as in extractive distillation, changing the operating conditions such as in pressure swing distillation, or by using non-thermal separation techniques such as liquid-liquid extraction or membrane separation. Theses separation processes are given the high score “3” if azeotrope is presence in the feed. The user can identify the presence of azeotrope by using the available azeotropic database in the IKBS.

6.3.10 Component Molecular Characteristics

The size and shape characteristic of molecules is being used as one of the criteria to examine the possibility of using molecular sieve adsorption. To select molecular sieve adsorption as one of the potential separation techniques, the molecules of the component to be separated should not have similar size and shape as the rest of the components in the mixture. This information needs to be provided by the user. If the user is not able to provide this information, molecular sieve adsorption will be ignored by the IKBS.

6.3.11 Chemical Family

Selective physical solvents for the mass separating agent (MSA) based separation processes will achieve separation only for chemically dissimilar components. If the mixture has similar size and isomers in the same chemical family it can not be separated by physical solvents, or entrainer methods such as azeotropic/extractive distillation, liquid-liquid extraction. Generally, components with close molecular weight and shape in the same chemical family tend to have similar physical properties and thus similar selectivity and solubility in solvents (Barnicki and Fair, 1992). If the species in the feed stream are from the same chemical family, stripping and extraction will be illuminated.

6.3.12 Polarity

Adsorbents can be divided into polar and non-polar. Polar adsorbents such silica gel, activated alumina, and zeolites more strongly bind the polar compounds in a mixture. Less polar materials from a mixture of more polar compounds are removed by non-polar adsorbents, such as activated carbon. Higher selectivity is achieved when there is a large difference in polarity between the desired adsorbates and the unadsorbed liquid. However, adsorption may still be a viable option if polarities are similar when size and structural differences are large (Barnicki and Fair, 1992).

6.4 Separation Processes

Chemical separation considered in the IKBS include: distillation, vacuum distillation, pressure distillation, azeotropic distillation, extractive distillation, pressure swing distillation, absorption, adsorption, stripping, phase separation, wiped film evaporator, ion-exchange, gas permeation, membrane separation, extraction, and distillation/pervaporation and distillation/adsorption hybrid systems. Table 6.6, illustrates the common industrial separation methods used by the IKBS. Brief discussion on these separation techniques and the most import features and criteria that the IKBS makes the selection are discussed here.

Table 6.6: Separation methods used in the IKBS. (adapted from Seider et al., 2003)

Separation methods	Phase of feed	Separation agent	Developed or added phase	Separation principle
Flash	Liquid and/or vapour	Pressure reduction or heat transfer	Liquid or vapour	Difference in volatility
Distillation	Liquid and/or vapour	Heat transfer	Liquid or vapour	Difference in volatility
Evaporation	Liquid	Heat transfer	Liquid and vapour	Difference in volatility
Condensation	Vapour	Heat transfer	Liquid and vapour	Difference in volatility
Gas absorption	vapour	liquid absorbent	Liquid	Difference in volatility
Stripping	liquid	Vapour stripping agent	Vapour	Difference in volatility
Extractive distillation	Liquid and/or vapour	Liquid solvent	Liquid and vapour	Difference in volatility
Azeotropic distillation	Liquid and/or vapour	Liquid solvent and heat transfer	Liquid and vapour	Difference in volatility
Liquid-liquid extraction	liquid	Liquid entrainer and heat transfer	Second liquid	Difference in solubility
Gas adsorption	vapour	Solid adsorbent	Solid	Difference in adsorbability
Liquid adsorption	liquid	Solid adsorbent	Solid	Difference in adsorbability
Membrane	Liquid or vapour	Membrane	Membrane	Difference permeability and/or solubility
Supercritical extraction	Liquid or vapour	Supercritical solvent	Supercritical fluid	Difference in solubility

Table 6.7, illustrates the comparison of selected separation methods based on the feed concentration, the presence of azeotropes and thermal sensitively. Mainly the criteria in Table 6.7 with “YES” are given the score “3” in the IKBS separation selection scoring system. Not suitable separations are given the score “#” in the IKBS. In this case weighting the selection criteria can usefully account for those criteria which may have a bigger effect on the selection of the separation processes than others.

Table 6.7: Key distillation methods comparison. (adapted from Dimian and Bildea, 2008)

Distillation method	Dilute separation	Bulk separation	Azeotropic mixtures	Temperature sensitivity
Simple distillation	Yes	Yes	No	No
Complex distillation	Yes	Yes	No	No
Vacuum distillation	Yes	Yes	No	Yes
Extractive distillation	No	Yes	Yes	No
Azeotropic distillation	No	No	Yes	No
Absorption	Yes	Yes	Yes	Yes
Stripping	Yes	Yes	No	Yes
Liquid-liquid extraction	Yes	Yes	Yes	Yes
Adsorption	Yes	Yes	Yes	Yes
Membrane permeation	Yes	No	Yes	Yes

6.4.1 Phase Separation

Reactor effluents can be liquid, vapour or mixed liquid and vapour. In a chemical process when the reactants and feed impurities, or by-products, boil at a temperature lower than propylene (-48 ^{o}C), a recycle and purge are required. This heuristic is based on the fact that propylene can be condensed with cooling water at high pressure. Therefore, any material less volatile than propylene can be recovered by a liquid recovery system. The heuristics for phase separation selection is illustrated in Figure 6.14. In addition to the phases separations in Figure 6.14, Rajagopal et al. (1992) have accounted for the presence of solids in the stream.

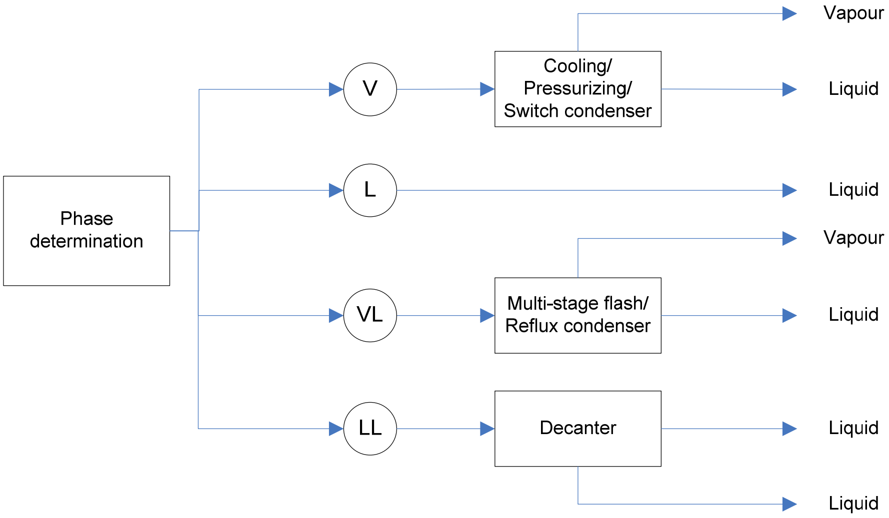


Figure 6.14: Heuristics for phase separation system selection

If a reactor effluent stream is liquid it is sent directly to liquid recovery system. If a reactor effluent stream is mixed liquid and vapour, the reactor can be used as phase splitter, or the phase separation can take place in a flash drum located after the reactor. The vapour stream can be cooled to 35 ^{o}C using cooling water to phase-split the stream in the flash drum. If the low temperature flash liquid obtained is mostly reactants, it should be recycled to the reactor and if it contains mostly products it has to be sent to the liquid recovery system. The flash vapour is sent to the vapour recovery system.

If the reactor effluent contains only a small amount of vapour it can be sent directly to the liquid recovery system. If the reactant effluent is only vapour, it can be cooled to 35 ^{o}C to achieve a phase spilt, or for complete condensation. If this does not occur, the stream can be pressurised and cooled using refrigeration. If no phase split occurs, the vapour should be sent to the vapour recovery system. If the phase splitting causes the recycle of valuable product back to the reactor it should be avoided. This analysis is performed by the IKBS at the initial stage of separation systems synthesis. For example, the IKBS, calculates the vapour pressure of the reactor effluent at 35^{o}C to explore the possibilities of separating the key components using cooling water and flash drum. If the separation is not feasible, phase splitting will be given the score “#” and eliminated.

6.4.2 Distillation

Distillation separates a mixture of components based on the difference in composition between a boiling liquid mixture and the formed vapour. The composition difference is due to differing effective vapour pressures, or volatilities, of the components of the liquid mixture.

Normal distillation is recommended for:

- homogenous liquid systems
- wide range of feed concentrations
- > 99 product purity
- High flowrate (>7 kg.s)

Distillation is not suitable for:

- Heat sensitive species
- Low relative volatility (<1.1)
- azeotropic mixtures

In the chemical industry, there are different types of distillation: simple distillation, complex distillation, azeotropic distillation, extractive distillation, pressure swing distillation, vacuum distillation, pressure distillation, cryogenic distillation.

Azeotropic distillation deals with the separation of mixtures involving one or more azeotropes. The more structurally the similar chemical components are, the less likely that the separation will be improved by azeotropic distillation. The selection of suitable MSA is critical in azeotropic distillation. The IKBS, provides a list of suggested MSA which can be used in the azeotropic distillation. The synthesis of separation processes involving azeotropes is complicated. However, systematic methods based on the representation in Residue Curve Maps (RCM) can be used (Dimian, 2003). Attempts to use complicated implementation of RCM for a mixture of water, acetic acid, *iso*-amyl alcohol and *iso*-amyle acetate, have been explored by Alqahtani (2004) and Alqahtani et al. (2005). The results were used to investigate the feasibility of the separation in a reactive distillation experimental column to recover dilute acetic acid by esterification reaction with *iso*-amyl alcohol. In the future development of the software, the IKBS may make use of third party software to investigate the visibility of the alternative separation processes.

Extractive distillation is based on the ability of an entrainer to increase the selectivity of the components. Extractive distillation is usually not recommended for separating components that show similar liquid-phase behaviour such as isomers. Components to be separated should have different functional groups for the MSA to affect liquid-phase behaviour differently. Pressure swing distillation is used for azeotropic mixture separation. Azeotrope composition must change at least from 5 to 10% for the process to be economical (Barnicki and Siirola, 1997). If this change in the composition is possible the IKBS can suggest pressure swing distillation for azeotropic mixtures. In case of the presence of azeotropic mixture in the feed stream, the IKBS will only evaluate those azeotropic and non thermal separators.

6.4.3 Absorption and Stripping

Absorption and stripping are two chemical process operations that are normally used together in order to remove a low concentration solute from vapour phase feed, and then recover that same component in a more concentrated form. A carefully selected solvent, in which the solute is selectively soluble, is fed to the absorber and the rich solvent is then fed to the stripper, where the solute is recovered. Strippers can also be used alone for separating a minor component from a liquid mixture.

Absorption is recommended for:

- gas feed
- concentration of targeted solute is in the range from 0.1 to 20%
- a possible purity is up to 98% (Wood, 1997)
- Flowrate > 7 kg/s

Stripping is recommended for:

- Liquid feed
- Dilute feed
- Flowrate > 7 kg/s

6.4.4 Liquid Extraction

If a mixture cannot be easily separated using a direct separation such as evaporation or distillation, alternative indirect separation processes are considered. Extraction is an indirect separation that relies on the ease of separating a chemical from a solvent compared to that from its original feed.

Supercritical extraction is a modern separation technique. Supercritical extraction uses the dramatic increase in solubility of some solutes in supercritical fluids. Examples of applications are in the recovery of ethanol by supercritical carbon dioxide.

Liquid-liquid extraction is often used for:

- Low relative volatilities (<1.1)
- Feed concentration from 0.3 to 95% w/w (Wood, 2007).
- Azeotropic mixtures
- Heat sensitive species
- Species not from the same chemical family

6.4.5 Adsorption

Adsorption is a surface phenomenon. For a multi-component fluid mixture, certain components of the mixture called adsorbates are preferentially concentrated i.e. selectively adsorbed at the solid surface called the adsorbent due to differences in the fluid–solid forces of attraction between the components. Users can check the IKBS database for suitable solid adsorption agents. If the user is not able to find a suitable solid adsorption agent and the information is not available in the IKBS databases, adsorption will not be considered as one of the alternative separation processes.

The recovery of adsorbate and regeneration of the adsorbent can be performed using: thermal swing adsorption, pressure swing adsorption, inert-purge swing, or displacement desorption (Dimian, 2003).

Gas adsorption is suitable for:

- liquid feed
- gas feed concentration of the more volatile species in the range 0.15 to 10%
- separation factor more than 2 (Wood, 2007).
- thermal sensitive chemical species
- azeotropic mixtures
- low feed flowrate (< 1.3 kg/s)

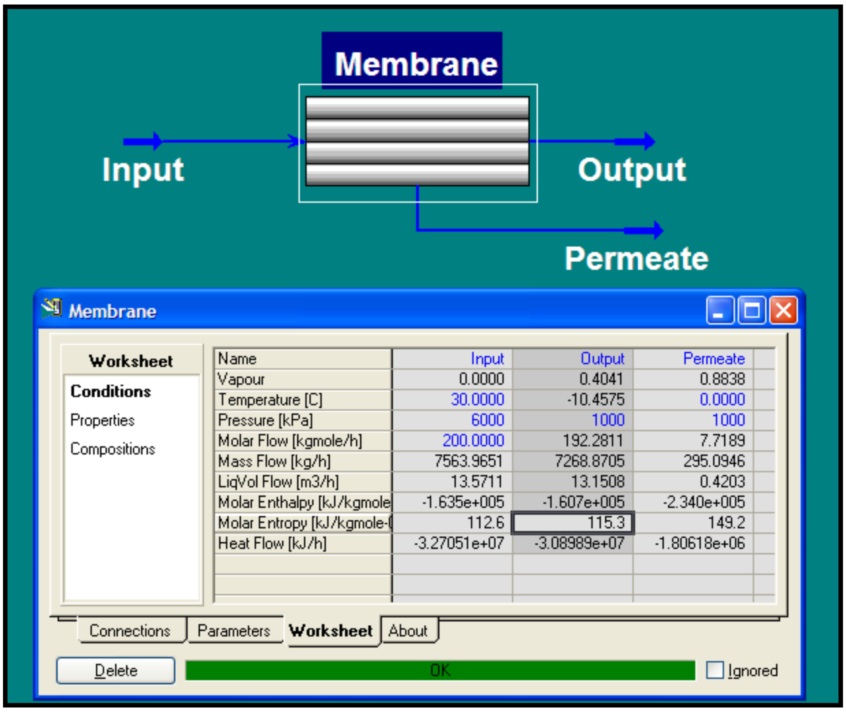
6.4.6 Membrane Separation

The separation of gas and liquid mixtures by membranes is an important separation technique. Examples include: gas permeation, pervaporation, reverse osmosis, dialysis and electrodialysis. Membranes can be classified into porous and non-porous materials. Gas permeation is an interesting technique for large scale applications such as the separation of carbon dioxide, hydrogen, and air separation in oxygen and nitrogen rich gases.

Gas permeation is suitable for:

- permselectivity has to be ≥ 15.
- feed concentration between 5 and 75% w/w and
- gas purity from 75 to 90% (Wood, 2007).
- thermal sensitive chemical species
- azeotropic mixtures

Gas permeation can be simulated by the customization of Aspen HYSYS. Aspen HYSY has an extensibility method to for the creation of custom unit operations. Gas permeation was simulated in Aspen HYSYS as illustrated in Figure 6.15. The input information required for the simulation includes: gas input stream temperature, pressure, flowrate and composition in addition to the permeate pressure and temperature. It is also required to provide the permeability values for species in the feed stream.



Name	Input	Output	Permeate
Vapour	0.0000	0.4041	0.8838
Temperature [C]	30.0000	-10.4575	0.0000
Pressure [kPa]	6000	1000	1000
Molar Flow [kgmole/h]	200.0000	192.2811	7.7189
Mass Flow [kg/h]	7563.9651	7268.8705	295.0946
LiqVol Flow [m3/h]	13.5711	13.1508	0.4203
Molar Enthalpy [kJ/kgmole	-1.635e+005	-1.607e+005	-2.340e+005
Molar Entropy [kJ/kgmole-(	112.6	115.3	149.2
Heat Flow [kJ/h]	-3.27051e+07	-3.08989e+07	-1.80618e+06

Figure 6.15: Gas permeation simulation in Aspen HYSYS.

6.4.7 Hybrid Separation Systems

Hybrid separation, such as combined distillation with other separation methods e.g. liquid-liquid extraction, adsorption, and membrane may be used. Hybrid separation is mainly employed when use of only distillation is unfeasible, very costly or due to the presence of azeotropes between the key components.

In the IKBS, there are two hybrid separations: distillation-pervaporation and distillation-adsorption hybrid systems. The combination of distillation with membrane permeation or adsorption, allows the breaking of an azeotrope without the need of introducing contaminating solvents.

6.5 Conclusion

Separation-recycle systems synthesis is a complex task as it involves: the selection of a wide range of separation processes, sequencing of separation columns and the construction of recycle systems. Furthermore, it also deals with a variety of species with different properties that can affect the choice of the separation-recycle systems. In the proposed systematic procedure, the separation systems are not synthesised in isolation from the reactor systems. The IKBS starts the separation-recycle system synthesis by input information from the reactor system in addition to information provided by the user and from the database.

If the user provides all of the required information, more alternative separation processes can be suggested. If the minimum required information is not provided, separation-recycle systems may not be fully investigated. However, the availability of the database in the IKBS and the possibility to incorporate other databases can provide enough input information for the IKBS. The analysis of the mixture to be separated examines the possibility of phase splitting and then the separation on the liquid and vapour mixtures in two liquid and two vapour separation systems.

Work on the operating conditions selection and separation sequencing is needed in further software development. As in the reactor systems synthesis, weighting the selection criteria of process units by allocating different values to each criterion is an important future software development task.

Chapter 7

Case Studies

7.1 Introduction

The proposed integrated approach to chemical process flowsheet synthesis and its implementation in the knowledge based system are illustrated in four case studies. The first case study is related to one of the latest technologies for producing acetic acid by the oxidation of ethane. The second case study is the alkylation of benzene by propylene for the synthesis of Cumene. The third and fourth case studies are the ethylene glycol and its intermediate ethylene oxide. The selection of the case studies was based on the diversity of reactions and separations. For example, ethylene oxide is a gas phase catalytic reaction whereas ethylene glycol is a liquid phase non-catalytic reaction. Furthermore, the product in the ethylene oxide process is gas at ambient conditions and liquid within the ethylene glycol process suggesting different types of reactor-separator-recycle systems. The main purpose of the ethylene oxide and ethylene glycol case studies is to further validate the reactor-separator-recycle systems selection decisions used in the first two case studies.

As illustrated in Figure 7.1, the case studies demonstrate most of the integrated knowledge based system capabilities in: chemistry analysis, preliminary economic evaluation, safety and environmental impact, and the reactor-separator-recycle systems selection. The ethylene oxide case study demonstrates the use of process simulation based on using the proposed generic flowsheet.

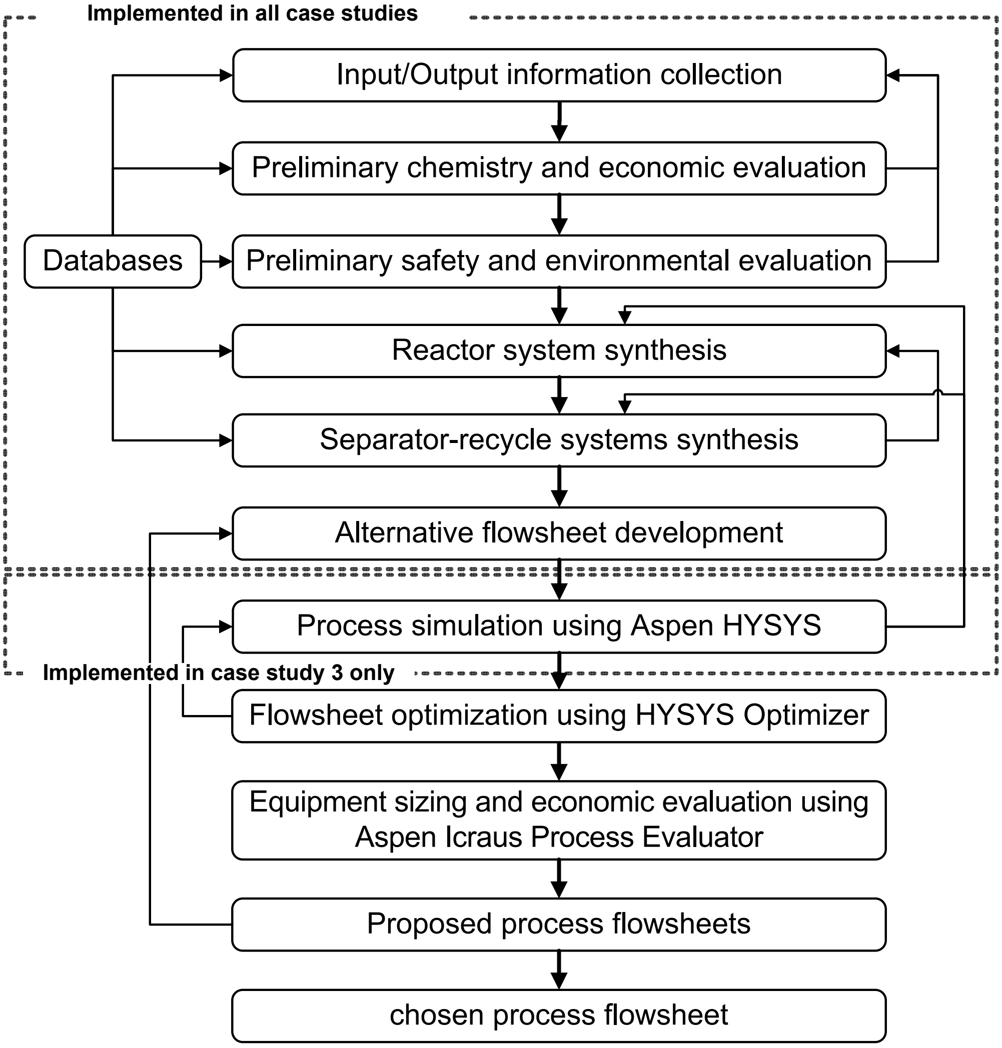


Figure 7.1: Flowchart of the proposed systematic procedure highlighting the tasks implemented in each case study.

The case studies do not demonstrate the last three tasks of integrated approach to chemical process flowsheet synthesis as they are not implemented in the current phase of IKBS development. The tasks are: the flowsheet optimization, sizing and economic evaluation.

7.2 Case Study 1: Acetic Acid Process Synthesis

Acetic acid is one of the most important commodity chemicals in the petrochemical industry. It is an important raw material used for the production of vinyl acetate monomer, production of acetic anhydride for the use in producing cellulose acetate esters, and polymer grade terephthalic acid (PET). There are several methods of producing acetic aid, such as methanol carbonylation, oxidation of acetaldehyde, direct oxidation of ethylene. The carbonylation of methanol is the world leading process. However, synthesis via the carbonylation of methanol takes place at a pressure of up to 40 bar. One of the latest technologies of producing acetic acid is by using catalytic gas phase direct oxidation of ethane to acetic acid. The main advantage of direct oxidation of ethane to acetic acid is the high selectivity to acetic acid which is close to 90%, and low temperature (250^{o}C) and pressure (15 bar) operations (Chem Systems, 2001).

The equation for the direct oxidation reaction is:

$$C_2H_6 + 1.5O_2 \rightarrow CH_3COOH + H_2O \tag{7.1}$$

Side reaction form ethylene and water:

$$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O \tag{7.2}$$

Carbon dioxide, carbon monoxide and water are formed as by-products from the complete combustion of ethane:

$$C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O \tag{7.3}$$

$$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \tag{7.4}$$

The reaction network for ethane oxidative dehydrogenation is illustrated in Figure 7.2.

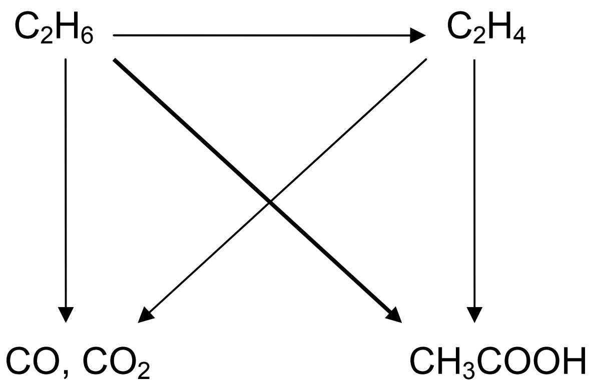
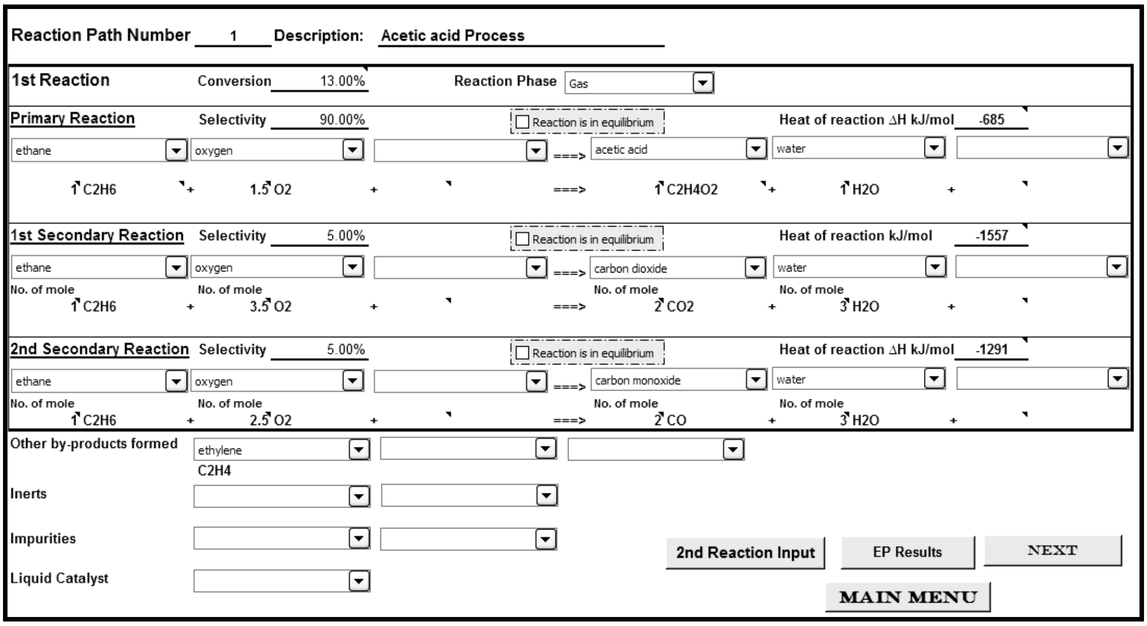


Figure 7.2: The reaction network for ethane oxidative dehydrogenation.

Recently, ethane oxidation reaction kinetics were studied by several researcher groups: Fakeeha et al., 2000; Linke et al, 2002a,b,c and Karim et al., 2003. These studies were used to provide input information to the IKBS for the synthesis of the reaction system. Key information include: reaction operating conditions, residence time, selectivity, conversion, and the kinetic model parameters. Chemistry input information for acetic acid is illustrated in Figure 7.3.


Reaction Path Number 1 Description: Acetic acid Process

1st Reaction Conversion 13.00% Reaction Phase Gas

Primary Reaction Selectivity 90.00% ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol -685

ethane oxygen ===> acetic acid water

1 C2H6 + 1.5 O2 + ===> 1 C2H4O2 + 1 H2O +

1st Secondary Reaction Selectivity 5.00% ☐ Reaction is in equilibrium Heat of reaction kJ/mol -1557

ethane oxygen ===> carbon dioxide water

No. of mole 1 C2H6 + No. of mole 3.5 O2 + ===> No. of mole 2 CO2 + No. of mole 3 H2O +

2nd Secondary Reaction Selectivity 5.00% ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol -1291

ethane oxygen ===> carbon monoxide water

No. of mole 1 C2H6 + No. of mole 2.5 O2 + ===> No. of mole 2 CO + No. of mole 3 H2O +

Other by-products formed ethylene C2H4

Inerts

Impurities

Liquid Catalyst

Figure 7.3: Chemistry input information on the ethane oxidation to acetic acid.

Preliminary economic potential shows that the process is economically viable. The flammability analysis shows that, oxygen concentration must be limited for safety reasons. Therefore, ethane conversion is limited per pass to about 10%. The octanol/water partition coefficient for acetic acid is -0.17 which indicates that the solubility of acetic acid in octanol is less than in water.

Results for the reactor alternatives illustrated in Table 7.1, shows that fixed bed reactor with hot shot and multi-tubular fixed bed reactors are recommended because of the highly exothermic reactions. Multiple multi-tubular reactors are currently used in industry (Chem Systems, 2001). A fluidized bed is recommended to improve the heat transfer. This suggested reactor by the IKBS is also recommended by industrial research (Benkalowycz et al., 1994). Monolith and Gauze reactors are novel reactors for this process. The suggested reactors are similar to those for ethylene oxidation in the previous section. This is because the nature of reaction and the operating conditions in both processes are similar.

Table 7.1: List of alternative reactors for acetic acid process.

Reactors Type	Scores
Continuous Stirred Tank Reactor (CSTR) with Jacket	
CSTR with Jacket and internal coil	
CSTR with external heat exchanger on circulation loop	
Sparged CSTR	
Simple tubular reactor	
Simple tubular reactor with circulation of heat transfer fluid	
Simple tubular reactor placed in a furnace	
Adiabatic fixed bed reactor	
Fixed bed with intermediate cooling/heating	
Fixed bed with cold/hot shot	11
Multitubular fixed bed reactor with indirect cooling/heating	12
Multiple-Multitubular fixed bed reactor with indirect cooling/heating	14
Trickle-bed reactor	
Fluidized bed reactor	15
Moving bed reactor	15
Riser reactor	15
Bubble column	
Spray column reactor	
Falling thin-film reactor	
Agitated thin-film reactor	
Monolith reactor	14
Gauze reactor	14
Reactive distillation	

The results from the separation-recycle systems are illustrated in Table 7.2 and Figure 7.4. Reactor effluents can be separated using the phase separator system (PSS-1) as splitting the stream into two phases is possible using cooling water at 35 ^{o}C and acetic acid is only 0.25 % of the splitter vapour phase. The unseparated acetic acid is sent along with the unreacted oxygen and ethane, and combustion gasses to the absorber (VSS-1) for further recovery. The gas stream from the vapour separation system (VSS-1) is sent to the recycle separation system to separate the combustion gasses using absorber-desorber, membrane separation, or adsorption.

The Liquid stream from the phase splitter (PSS-1) contains acetic acid and water. Liquid streams from the phase separator system (PSS-1) and vapour separation system (VSS-1) are sent to the liquid separation system (LSS-1). Alternative separation processes in the liquid separation system (LSS-1) include: extraction with solvent recovery and regeneration, azeotropic and extractive distillation, and hybrid pervaporation-distillation systems. These types of separation processes are suggested by the IKBS mainly due to the low relative volatility between the water and acetic acid (about 1.4). As reported by Van Brunt (2005), the secondary bonding effects in the liquid phase and the nonideal chemical effects in the vapour phase reduce the relative volatility of the water to acetic acid to approximately 1.1. Therefore, normal distillation was not suggested by the IKBS.

Table 7.2: List of alternative separators for acetic acid process.

Separators Type	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Simple Distillation						9		
Multiple Distillation						10		
Vacuum distillation						10		
Pressure Distillation								
Azeotropic distillation			15					
Extractive distillation			15					
Pressure swing distillation								
Absorption		6					15	
Stripping								9
Partial Condensation Followed by Phase Separator	9							
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption							13	
Molecular Sieve Adsorption							12	
Ion Exchange								
Gas Permeation							11	
Extraction			18					
Distillation/Pervaporation Hybrid System			14					
Distillation/adsorption Hybrid System								

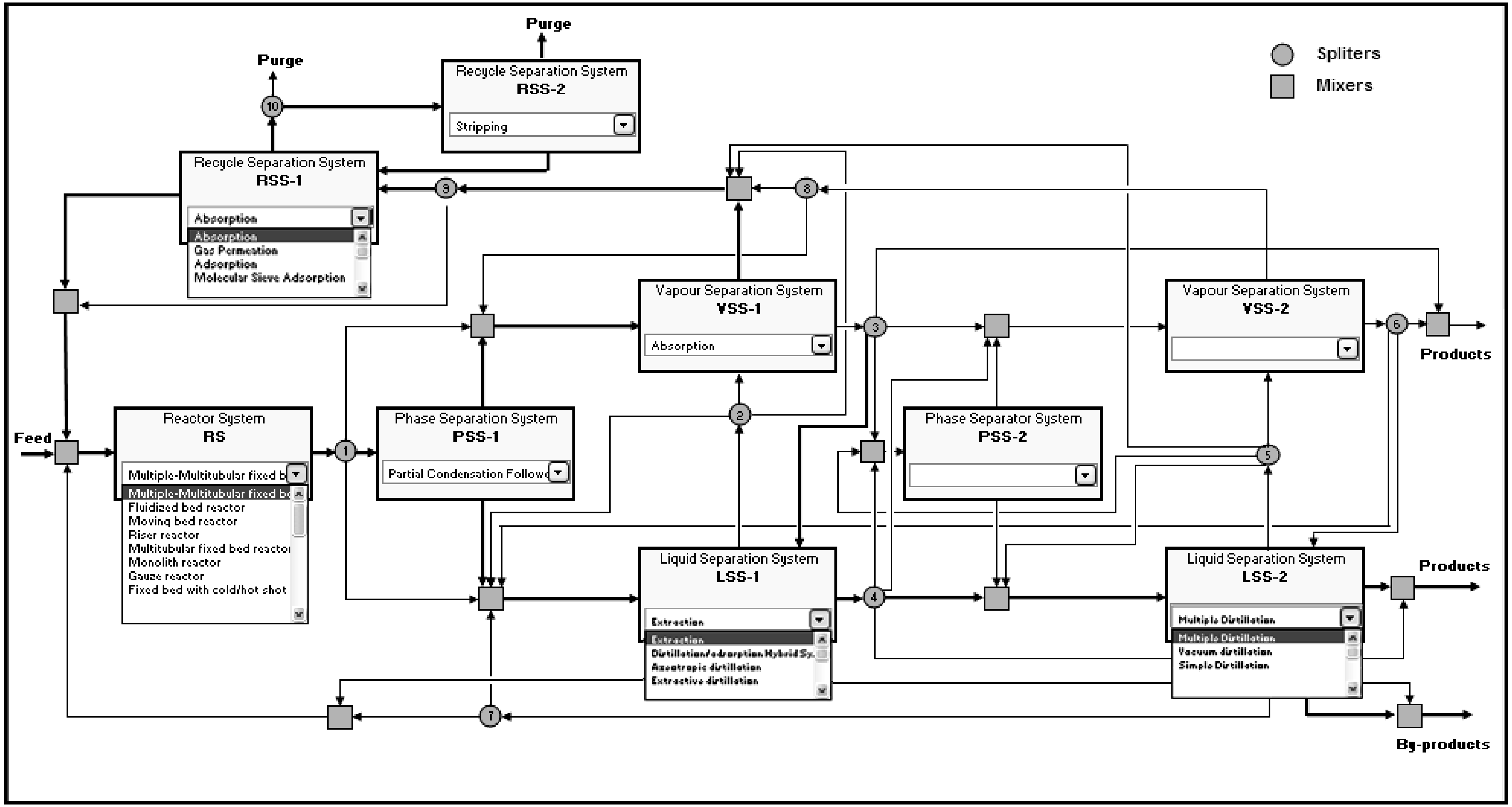


Figure 7.4: Acetic aced synthesis results illustrated in the generic superstructure.

Unlike the process analysis and design decisions by the IKBS, Linke and co-workers suggest separation processes which do not account for the nature of the mixture to be separated in the acetic acid process. Examples include the work by Montolio-Rodriguez et al. (2007), which only suggest the use of normal distillation for the separation of acetic acid from the water. If simple distillation is used, the recovery of acetic acid from water requires the evaporation of all the water as a distillate, and the distillation column will have a high reflux ratio and large diameter. This can increase the operating and capital costs for the distillation.

In order to meet the required specification for glacial acetic acid, acetic acid is redistilled in the liquid separation system (LSS-2) by normal distillation, or vacuum distillation to remove any impurities as overhead and bottom products, whereas acetic acid is removed as a side stream product.

7.3 Case Study 2: Cumene Process Synthesis

Cumene is mainly used for the production of phenol and acetone. The main process for producing cumene is by the alkylation of benzene with propylene. The alkylation reaction can be either a liquid or gas phase process. In the liquid phase process, propylene is dissolved in a large excess of benzene at sufficiently high pressure that ensures only one liquid phase at the reaction condition temperature, which is between 160 and 240 ^{o}C exists (Dimian and Bildea, 2008). In the gas phase process, the reaction temperature and pressure are higher.

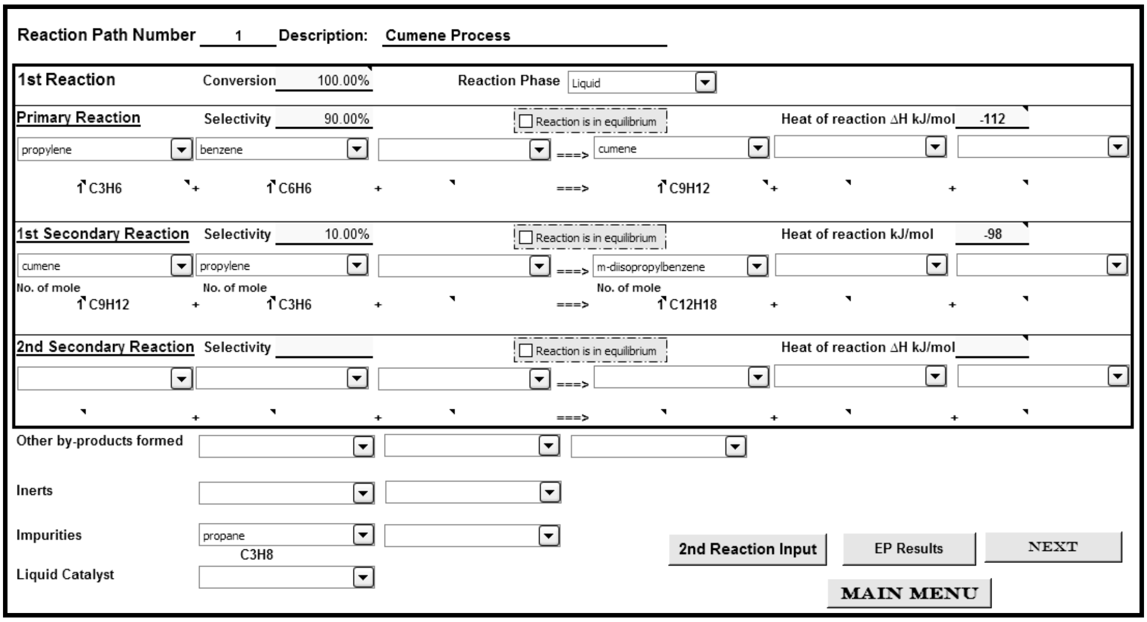
The alkylation catalytic reaction:

$$C_3H_6 + C_6H_6 \rightarrow C_9H_{12} \quad (7.5)$$

The main undesirable reaction is the reaction of cumene with propylene to make disiopropylbenzene:

$$C_9H_{12} + C_3H_6 \rightarrow C_{12}H_{18} \quad (7.6)$$

A Langmuir-Hinshelwood type kinetic model was proposed by Han et al., (2001) based on experimental results. The selectivity of the main reaction is about 90% and the complete conversion of propylene can be achieved (Chauvel and Lefebvre, 1989; Matar and Hatch, 2001; Meyers, 2005). Figure 7.5, illustrates the initial chemistry input information. It shows the primary and secondary reaction in addition to propane as an impurity.


Reaction Path Number 1 Description: Cumene Process

1st Reaction Conversion 100.00% Reaction Phase Liquid

Primary Reaction Selectivity 90.00% ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol -112

propylene + benzene ===> cumene

C3H6 + C6H6 ===> C9H12

1st Secondary Reaction Selectivity 10.00% ☐ Reaction is in equilibrium Heat of reaction kJ/mol -98

cumene + propylene ===> m-diisopropylbenzene

No. of mole C9H12 + No. of mole C3H6 ===> No. of mole C12H18

2nd Secondary Reaction Selectivity ☐ Reaction is in equilibrium Heat of reaction ΔH kJ/mol

Other by-products formed

Inerts

Impurities propane C3H8

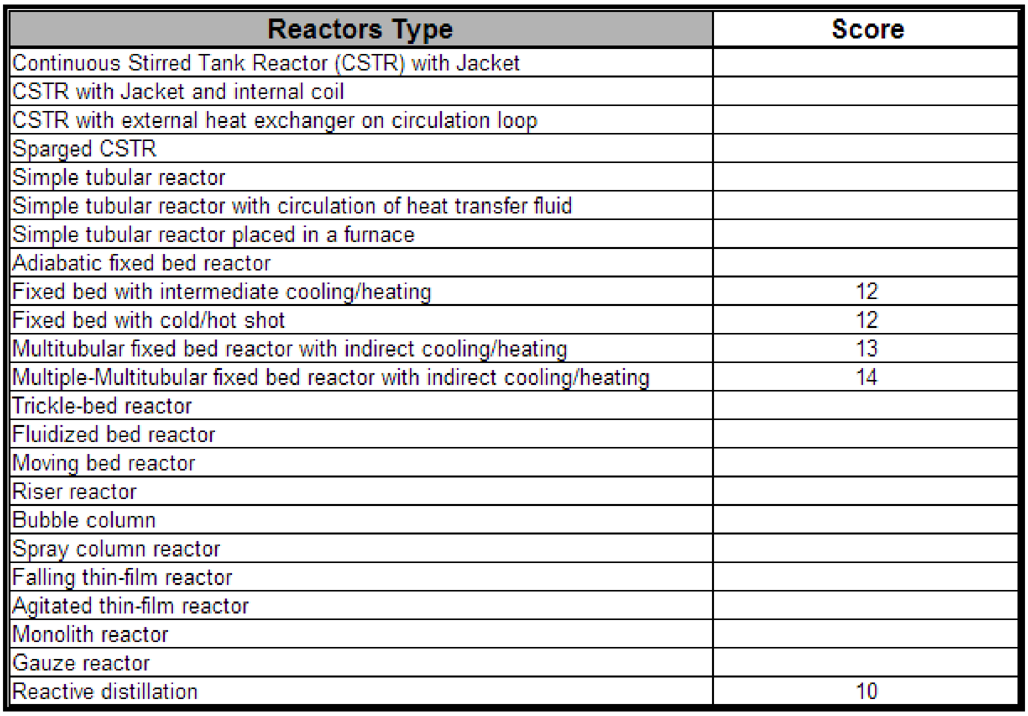
Liquid Catalyst

Figure 7.5: Chemistry input information on the alkylation of benzene by propylene to cumene.

The IKBS system analyzes the process based on further kinetics and economic, environmental information and proposes alternative configurations of fixed bed reactors in addition to reactive distillation as illustrated in Table 7.3. The fixed bed reactors are proposed based on several key criteria such as: the phase of reaction, use of catalyst, reaction exotherm, and the rate of reaction. The alternative fixed bed reactors suggest different methods of controlling the heat of the exothermic reactions by increasing the area of heat transfer, or by introducing cold shot of reactants. The multi fixed bed with cold shot is currently implemented in the commercial cumene processes. Other arrangements of fixed bed reactors are novel reactors for this process.

Reactive distillation is another alternative to the fixed bed reactor. It combines reaction and fractionation in a single unit operation. The use of reactive distillation can allow for operating the process isothermally and at low temperature. Reaction products are continuously removed from the reaction zones by distillation which can provide high selectivity to cumene. This can limit the formation of by-products formed by Equation 7.6. The use of reactive distillation for the cumene process is available technology from CDTECH (Meyers, 2005).

Table 7.3: List of alternative reactors for cumene process.



Reactors Type	Score
Continuous Stirred Tank Reactor (CSTR) with Jacket	
CSTR with Jacket and internal coil	
CSTR with external heat exchanger on circulation loop	
Sparged CSTR	
Simple tubular reactor	
Simple tubular reactor with circulation of heat transfer fluid	
Simple tubular reactor placed in a furnace	
Adiabatic fixed bed reactor	
Fixed bed with intermediate cooling/heating	12
Fixed bed with cold/hot shot	12
Multitubular fixed bed reactor with indirect cooling/heating	13
Multiple-Multitubular fixed bed reactor with indirect cooling/heating	14
Trickle-bed reactor	
Fluidized bed reactor	
Moving bed reactor	
Riser reactor	
Bubble column	
Spray column reactor	
Falling thin-film reactor	
Agitated thin-film reactor	
Monolith reactor	
Gauze reactor	
Reactive distillation	10

The separation-recycle system selection results are tabulated in Table 7.4 and Figure 7.6. The IKBS starts analysing the reactor effluent by listing the species in order of increasing boiling point and then calculates the relative volatilities and identifies the state of each species in order to construct the recycle systems. The first separation process is the removal of the propane in a pressure distillation column (LSS-1). Propylene contains 8% w/w propane as an impurity. The IKBS analysis shows that propane is difficult to separate from the fresh propylene feed as the boiling point difference between propylene and propane is 5.8 ^{o}C and the relative volatility is around 1.2.

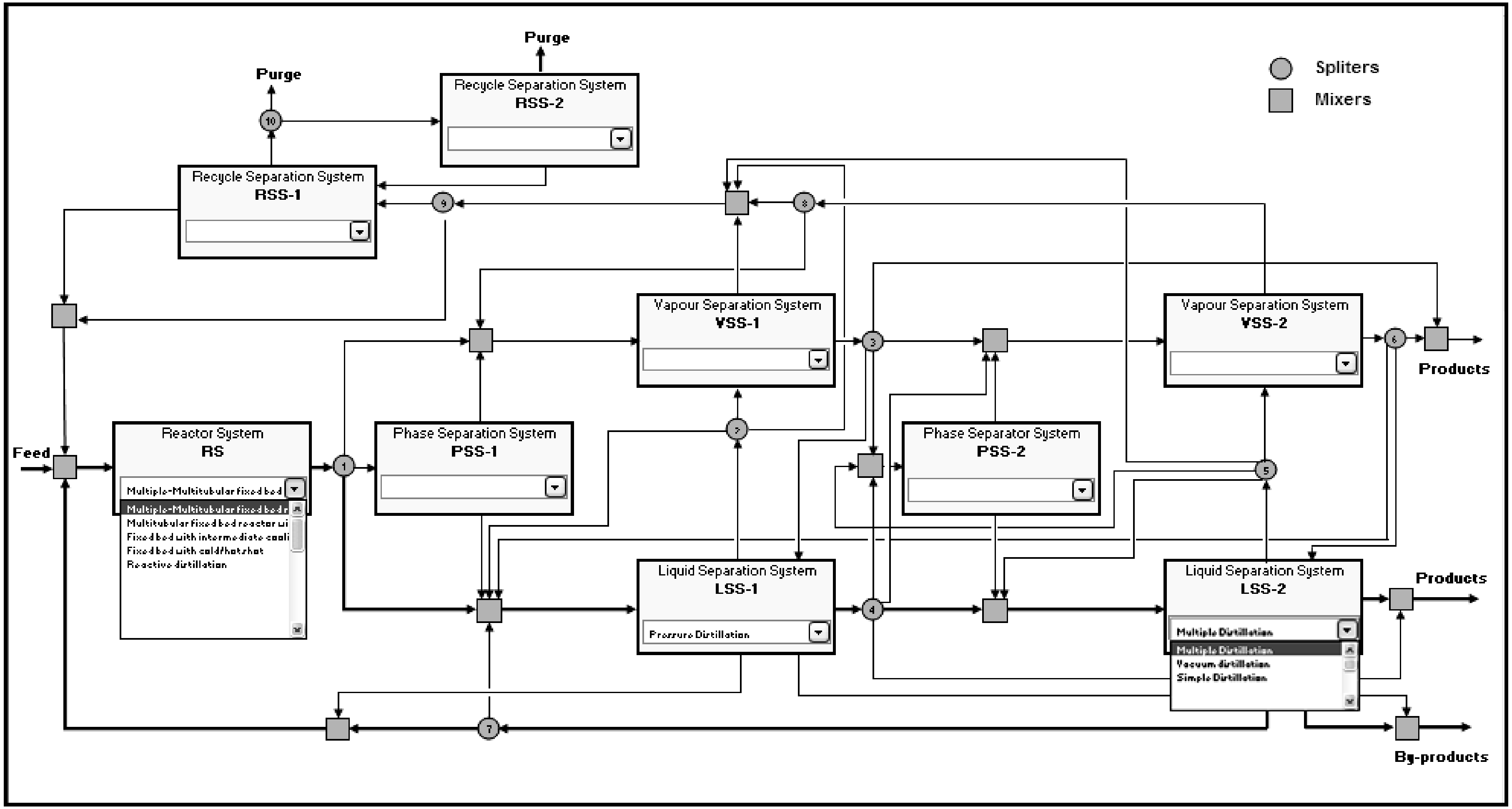
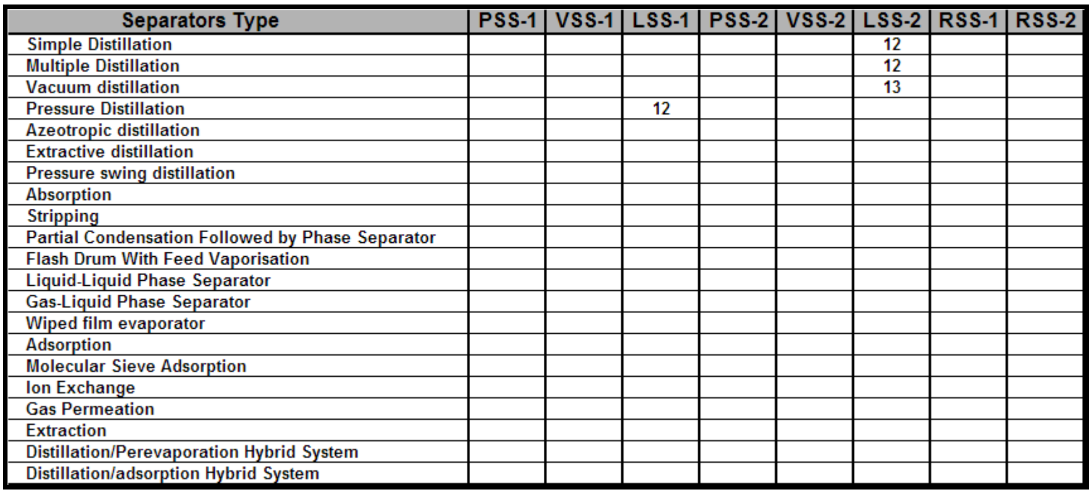


Figure 7.6: Cumene synthesis results illustrated in the generic superstructure.

The complete conversion of propylene using zeolite catalyst can make propane separation from the reactor effluent easer in the early stages of the separation process. The boiling point difference between the key components in the reactor effluent is 112.3 ^{o}C and the relative volatility is around 60. After removing the propane as top product, the mixture contains benzene, cumene and by-product disiopropylbenzene.

Table 7.4: List of alternative separators for cumene process.



Separators Type	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Simple Distillation						12		
Multiple Distillation						12		
Vacuum distillation						13		
Pressure Distillation			12					
Azeotropic distillation								
Extractive distillation								
Pressure swing distillation								
Absorption								
Stripping								
Partial Condensation Followed by Phase Separator								
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption								
Molecular Sieve Adsorption								
Ion Exchange								
Gas Permeation								
Extraction								
Distillation/Perevaporation Hybrid System								
Distillation/adsorption Hybrid System								

The benzene is separated as a distillate in LSS-2 and recycled to the reactor, whereas the cumene is separated in another distillation column as a distillate from the by-product which is separated as a bottom product. The benzene, cumene and disiopropylbenzene separation can be achieved in the liquid separation system (LSS-2). The main separation is between benzene and cumene with a boiling point difference of 72.4 ^{o}C and the relative volatility is around 6. Finally, the cumene is recovered from the disiopropylbenzene as distillate in a distillation column. The boiling point difference is 50.5 ^{o}C and the relative volatility is around 10. The IKBS suggests the use of simple distillation for benzene separation followed by vacuum distillation for the cumene-disiopropylbenzene separation. Alternatively a train of two normal distillation columns can be used. The use of combination of normal distillation column for benzene recovery and vacuum distillation column for cumene purification is a better option due to the high boiling point of the cumene-disiopropylbenzene mixture. This combination of normal and vacuum distillation columns is the widely used separation in current commercial processes.

7.4 Case Studies 3 & 4: Ethylene Oxide and Ethylene Glycol Processes Synthesis

Ethylene glycol is an important basic industrial petrochemical. It is a feedstock for the production of polyester fibres and resins including polyethylene terephthalate (PET), which is used to produce films, packaging and bottles. Other formulations of ethylene glycol are used as antifreeze and deicing solutions. Ethylene glycol is also used as a general purpose solvent in paints and the plastic industries.

There are many different reaction routes to synthesise ethylene glycol such as (1) hydration of ethylene oxide, (2) ethylene oxide via ethylene carbonate, (3) synthesis gas, (4) formaldehyde via glycolaldehyde, (5) directly from ethylene etc. (Kirk-Othmer, 2005). Some of these reaction routes are being evaluated for primary economic potential, and safety and environmental impacts. This case study illustrates the reactor-separator-recycle systems synthesis for ethylene oxidation to ethylene oxide and the subsequent hydration to ethylene glycol.

Ethylene oxide is produced commercially by vapour phase direct oxidation of ethylene over a silver based catalyst. Reaction typically takes place at 200-300 ^{o}C and 15-25 bar. The selectivity of modern catalyst to ethylene oxide can be up to 90% (Ullmans 2005).

The main reaction is the partial oxidation of ethylene:

$$C_2H_4 + 0.5O_2 \rightarrow C_2H_4O \tag{7.7}$$

Carbon dioxide and water are formed as by-products from the complete combustion of ethylene:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \tag{7.8}$$

Or by further oxidation of ethylene oxide:

$$C_2H_4O + 2.5O_2 \rightarrow 2CO_2 + 2H_2O \tag{7.9}$$

The reaction network for ethylene oxidation is illustrated in Figure 7.7.

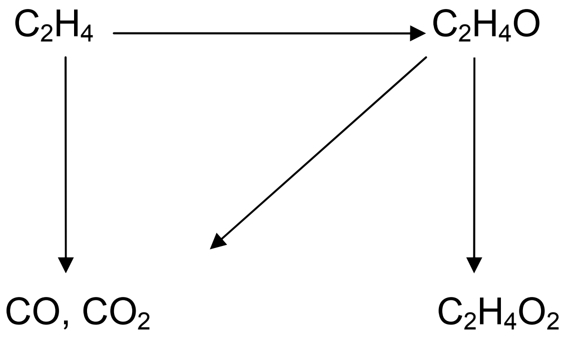


Figure 7.7: The reaction network for ethylene oxidation.

Ethylene glycol is commercially produced by liquid phase non-catalytic hydrolysis of ethylene oxide:

$$C_2H_4O + H_2O \rightarrow C_2H_6O_2 \tag{7.10}$$

A large excess of water is used to minimize to formation of higher glycol by-products such as diethylene glycol and triethylene glycol:

$$C_2H_6O_2 + C_2H_4O \rightarrow C_4H_{10}O_3 \tag{7.11}$$

$$C_4H_{10}O_3 + C_2H_4O \rightarrow C_6H_{14}O_4 \tag{7.12}$$

The reaction network for ethylene glycol reactions is illustrated in Figure 7.8.

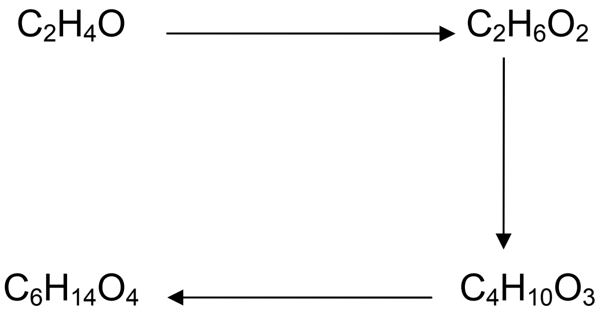


Figure 7.8: The reaction network for ethylene glycol reactions.

The rate of reaction for ethylene oxide based on a Langmuir-Hinshelwood model is (Schouten et al., 1996):

$$r_i = \frac{k_r^i K_E^i K_O^i P_E P_O}{\left(1 + K_E^i P_E + K_O^i P_O + K_C^i P_C + K_W^i P_W + K_{EO}^i P_{EO}\right)^2} \tag{7.13}$$

Where:

E, O, C, W, EO: ethylene, oxygen carbon dioxide, water, ethylene oxide respectively

k_r : Reaction rate constant

P_E : partial pressure of ethylene

K_E : adsorption coefficient of ethylene

For ethylene oxidation reaction i=1 and for total combustion i=2. According to the Arrhenius law, the reaction and adsorption rate constants are assumed to be dependent on the temperature:

Reaction rate constant:

$$k_r^i = k_{r,\infty}^i \exp\left(-\frac{T_{act}}{T}\right) \tag{7.14}$$

Adsorption rate constants:

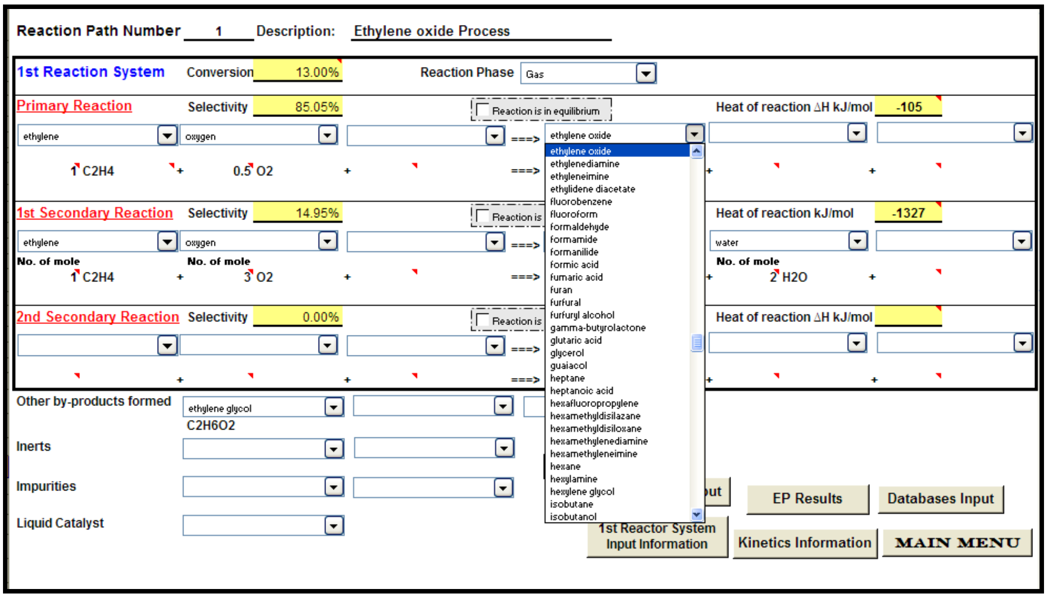
$$K_j^i = k_{j,\infty}^i \exp\left(-\frac{T_{ads}}{T}\right) \tag{7.15}$$

Other kinetic studies were conducted by Al-Saleh et al. (1988); Mezaki and Inoue (1991); Ravindran et al. (2006); Lou et al (2006).

The rate constant for the noncatalytic hydration of ethylene oxide to ethylene glycol was reported by Schwaar (1997):

$$k = 7.123 \times 10^8 \exp\left(-21{,}193 / RT\right) \tag{7.16}$$

Figure 7.9, is a screenshot of the user interface showing input process chemistry information for ethylene oxidation and side reactions.


Reaction Path Number 1 Description: Ethylene oxide Process

1st Reaction System Conversion 13.00% Reaction Phase Gas

Primary Reaction Selectivity 85.05% Heat of reaction ΔH kJ/mol -105

ethylene oxygen ===> ethylene oxide

1 C2H4 + 0.5 O2 + ===>

1st Secondary Reaction Selectivity 14.95% Heat of reaction kJ/mol -1327

ethylene oxygen ===> water

No. of mole 1 C2H4 + No. of mole 3 O2 + ===> No. of mole 2 H2O +

2nd Secondary Reaction Selectivity 0.00% Heat of reaction ΔH kJ/mol

Other by-products formed ethylene glycol C2H6O2

Inerts

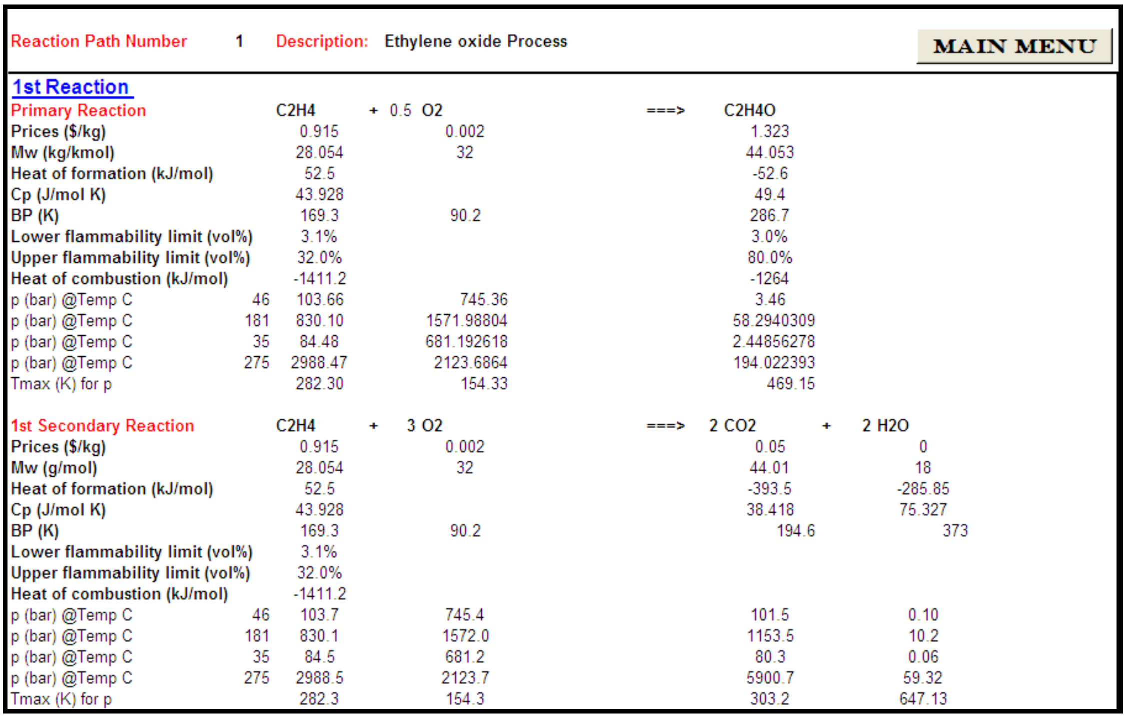
Impurities

Liquid Catalyst

Figure 7.9: Process chemistry input screen.

Analysis by the software of alternative synthesis routes for ethylene glycol production shows that the route via ethylene oxidation and ethylene oxide hydration is economically viable as long as the other production costs are sufficiently lower than the gross profit. Once the chemistry information is provided, the IKBS import the required information for the synthesis of the process form the internal database as illustrated in figure 7.10. Input information from the database includes for example, chemical prices, molecular weight, heat of formation, heat capacities, boiling points, lower and upper flammability limits, heat of combustion and vapour pressure at different temperatures.

Economic potential analysis accounts for the recycle of unreacted materials and the recovery of product. In other words, the IKBS preliminary economic evaluation accounts for the reaction conversion and selectivity as well as the separation of reactor effluent and recycle of unreacted materials based on a heuristic design rule suggested by Douglas (1988). Douglas, 1988, suggests the recovery of more than 99% of all valuable materials. However, any changes in prices might affect this preliminary economical evaluation. Results from the economic evaluation are illustrated in Figure 7.11.



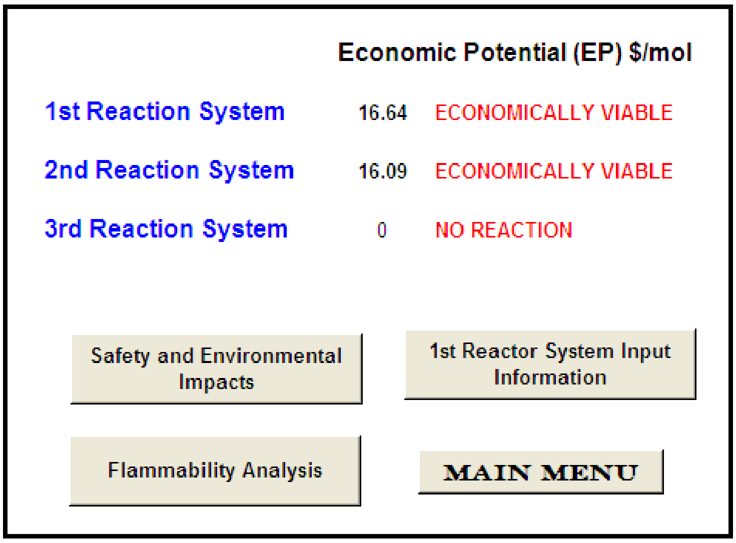
Reaction Path Number 1 Description: Ethylene oxide Process

1st Reaction

Primary Reaction		C2H4	+	0.5 O2	===>	C2H4O
Prices ($/kg)		0.915		0.002		1.323
Mw (kg/kmol)		28.054		32		44.053
Heat of formation (kJ/mol)		52.5				-52.6
Cp (J/mol K)		43.928				49.4
BP (K)		169.3		90.2		286.7
Lower flammability limit (vol%)		3.1%				3.0%
Upper flammability limit (vol%)		32.0%				80.0%
Heat of combustion (kJ/mol)		-1411.2				-1264
p (bar) @Temp C	46	103.66		745.36		3.46
p (bar) @Temp C	181	830.10		1571.98804		58.2940309
p (bar) @Temp C	35	84.48		681.192618		2.44856278
p (bar) @Temp C	275	2988.47		2123.6864		194.022393
Tmax (K) for p		282.30		154.33		469.15

1st Secondary Reaction		C2H4	+	3 O2	===>	2 CO2	+	2 H2O
Prices ($/kg)		0.915		0.002		0.05		0
Mw (g/mol)		28.054		32		44.01		18
Heat of formation (kJ/mol)		52.5				-393.5		-285.85
Cp (J/mol K)		43.928				38.418		75.327
BP (K)		169.3		90.2		194.6		373
Lower flammability limit (vol%)		3.1%						
Upper flammability limit (vol%)		32.0%						
Heat of combustion (kJ/mol)		-1411.2						
p (bar) @Temp C	46	103.7		745.4		101.5		0.10
p (bar) @Temp C	181	830.1		1572.0		1153.5		10.2
p (bar) @Temp C	35	84.5		681.2		80.3		0.06
p (bar) @Temp C	275	2988.5		2123.7		5900.7		59.32
Tmax (K) for p		282.3		154.3		303.2		647.13

Figure 7.10: Example of reactor system synthesis input information from the databases.



	Economic Potential (EP) $/mol	
1st Reaction System	16.64	ECONOMICALLY VIABLE
2nd Reaction System	16.09	ECONOMICALLY VIABLE
3rd Reaction System	0	NO REACTION

Figure 7.11: Preliminary economic evaluation results.

The octanol/water partition coefficient can be used to predict the environmental behaviour of organic pollutants. It is therefore important to have the partition coefficient values for chemicals that are carcinogenic, toxic, or otherwise potentially dangerous. The octanol/water partition coefficient for ethylene oxide is -1.36 which indicates that the solubility of ethylene oxide in octanol is less than in water. Therefore, it has low bio-concentration and soil sedimentation tendencies. The ethylene glycol partition coefficient is -0.3 which means it has higher bio-concentration and soil sedimentation tendencies than ethylene oxide.

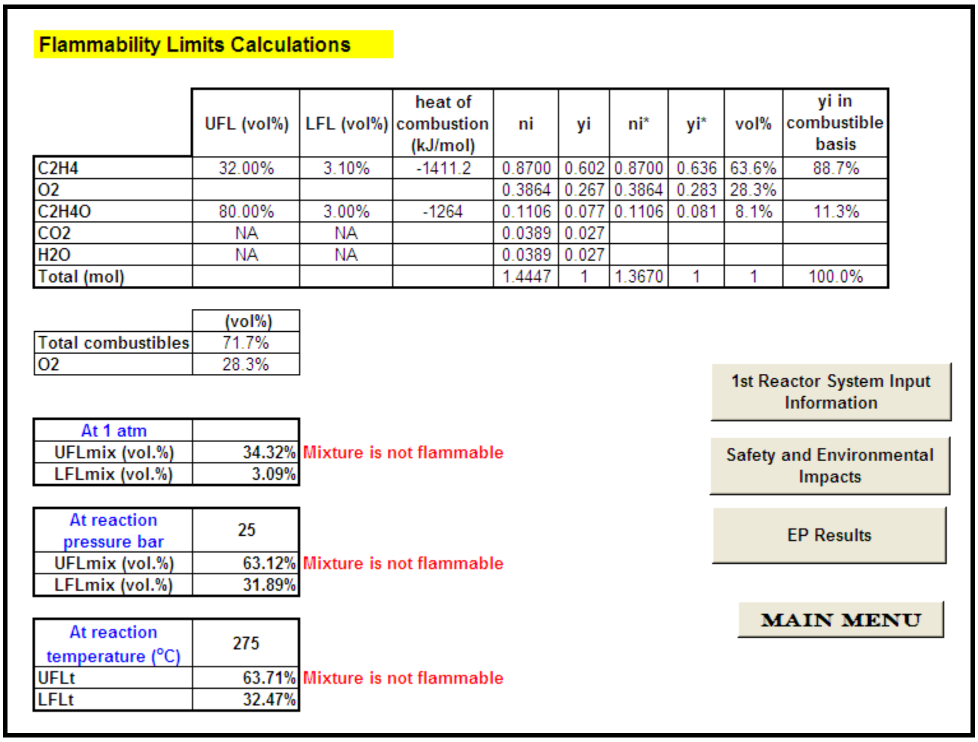
Ethylene oxide is rated “4” in the severity of the flammability hazard on a scale of 0 to 4 with 4 being the most severe. It is also dangerous to health as it is rated based on the health rating of “2”. On the other hand Ethylene glycol is rate 1 in the flammability and health hazards. Based on the LD50 values, ethylene oxide is more toxic than the ethylene glycol. Table 7.5, summarise some of the IKBS information from the database which was used in the safety and environmental evaluations. The IKBS safety and environmental databases also include information on species route of entry, target organs, corrosivity, autoignition temperature, flash point, upper and lower explosive limits, and threshold limits**.**

This safety and environmental impact analysis can also be used to understand the potential dangers to the environment, or it can be used to evaluate other alternative solvents, reactants, or intermediates.

Table 7.5: Summary of the IKBS database information on the safety and environmental impacts of ethylene oxide and ethylene glycol.

Species	**Carcinogenicity**	**Flammability**	**Health**	**Reactivity**	**LD_{50}** Oral (mg/kg)	**Partition coefficient**
Ethylene oxide	Yes	4	2	3	72	-1.36
Ethylene glycol	No	1	1	0	4700	-0.3

To account for the potential flammability of the reaction mixture, the upper and lower flammability limits at the reaction condition have been calculated using information from the database. Flammability analyses show that the reaction mixture at reaction temperature and pressure is not within the flammability limit as illustrated in Figure 7.12. Any changes in the reactants molar ratio during the optimization process should maintain the mixture within the allowable limits.



Flammability Limits Calculations

	UFL (vol%)	LFL (vol%)	heat of combustion (kJ/mol)	ni	yi	ni*	yi*	vol%	yi in combustible basis
C2H4	32.00%	3.10%	-1411.2	0.8700	0.602	0.8700	0.636	63.6%	88.7%
O2				0.3864	0.267	0.3864	0.283	28.3%	
C2H4O	80.00%	3.00%	-1264	0.1106	0.077	0.1106	0.081	8.1%	11.3%
CO2	NA	NA		0.0389	0.027				
H2O	NA	NA		0.0389	0.027				
Total (mol)				1.4447	1	1.3670	1	1	100.0%

	(vol%)
Total combustibles	71.7%
O2	28.3%

At 1 atm		
UFLmix (vol.%)	34.32%	Mixture is not flammable
LFLmix (vol.%)	3.09%	

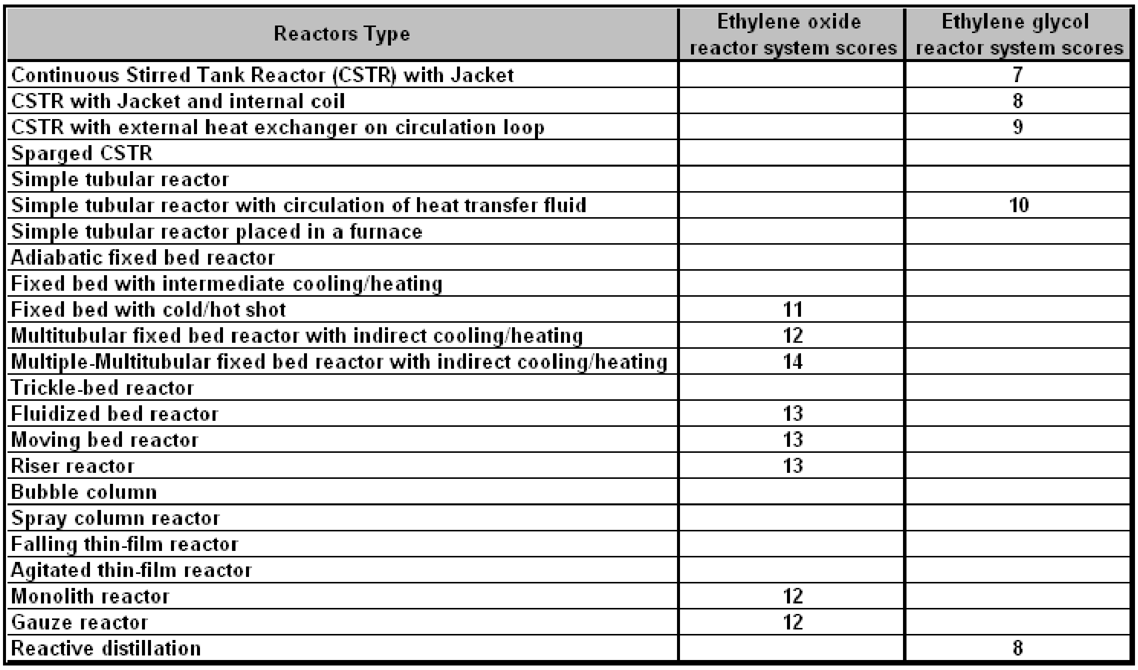
At reaction pressure bar	25	
UFLmix (vol.%)	63.12%	Mixture is not flammable
LFLmix (vol.%)	31.89%	

At reaction temperature (°C)	275	
UFLt	63.71%	Mixture is not flammable
LFLt	32.47%	

Figure 7.12: Flammability limits analysis.

Selection results are shown in Table 7.6, illustrating that two reactor systems are required. It should be noted that the user will not be required to specify the number of reaction systems involved. The IKBS will make this decision based on the information provided, such as reaction conditions and phases, the use of catalyst, lifetime of the catalyst, the speed of the reaction, reaction exotherm, the sensitivity to heat etc. the table shows the total score for each reactor. The scores are the sum of each selection criteria score. Each selection criteria can be in the range from 0 to 3. If any selection criteria indicate that the reactor is not suitable, the reactor is eliminated and no score will be given to the reactor. The value of the score is only used at this level as an indication and further analysis of the alternatives will take place at the subsequent synthesis steps.

Table 7.6: List of proposed reactors for ethylene oxide and ethylene glycol processes.



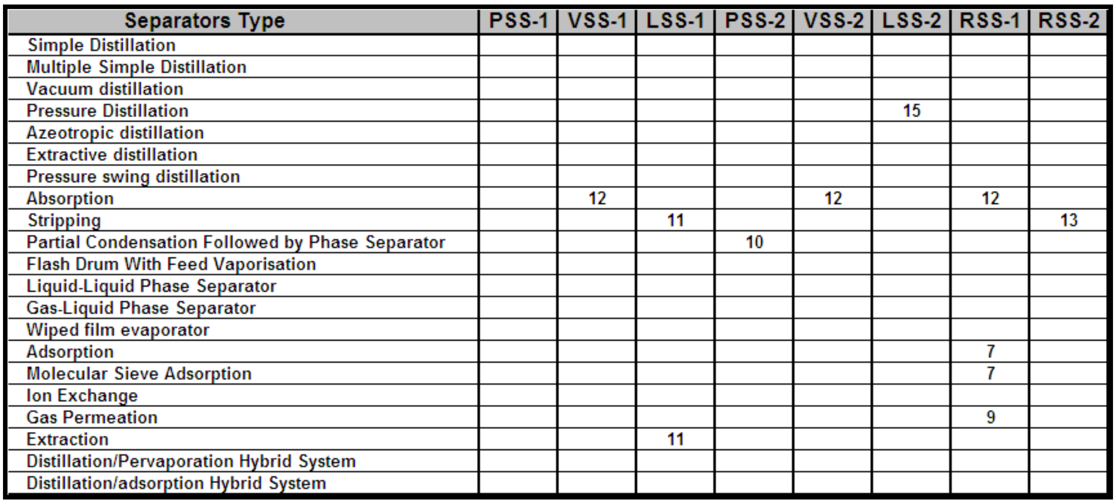
Reactors Type	Ethylene oxide reactor system scores	Ethylene glycol reactor system scores
Continuous Stirred Tank Reactor (CSTR) with Jacket		7
CSTR with Jacket and internal coil		8
CSTR with external heat exchanger on circulation loop		9
Sparged CSTR		
Simple tubular reactor		
Simple tubular reactor with circulation of heat transfer fluid		10
Simple tubular reactor placed in a furnace		
Adiabatic fixed bed reactor		
Fixed bed with intermediate cooling/heating		
Fixed bed with cold/hot shot	11	
Multitubular fixed bed reactor with indirect cooling/heating	12	
Multiple-Multitubular fixed bed reactor with indirect cooling/heating	14	
Trickle-bed reactor		
Fluidized bed reactor	13	
Moving bed reactor	13	
Riser reactor	13	
Bubble column		
Spray column reactor		
Falling thin-film reactor		
Agitated thin-film reactor		
Monolith reactor	12	
Gauze reactor	12	
Reactive distillation		8

For the ethylene oxide reactor system, the multiple multi-tubular fixed bed reactor has the highest scores among the reactor alternatives. This reactor is currently used in commercial processes because of the special requirements on temperature control throughout the catalyst bed.

The next highest scores were given to a fluidized bed, riser and moving bed reactors. The use of these reactors can improve the heat removal from such a highly exothermic reaction. These three reactors may have two drawbacks, possible catalyst attrition and the back mixing of ethylene oxide may result in a long residence time; hence more oxidation of ethylene oxide. Fixed bed reactors with intermediate cooling or cold shot are alternatives currently under consideration in industrial research (Schwaar, 1997). Monolith and gauze reactors are low pressure drop alternatives that can be recommended for this highly exothermic and fast catalytic gas phase reaction. The software carries out a heat balance, which suggests that the reactors should be operated isothermally. A heat carrier such as methane can be used to increase the rate of heat transfer. This temperature control will reduce the loss of selectivity and catalyst performance.

Table 7.7, summaries the alternative separators for the ethylene oxide process with reference to the proposed generic superstructure illustrated in Figure 7.13. The scores are the sum of each selection criteria score as explained above in the reactor systems selection.

Table 7.7: List of alternative separators for ethylene oxide process.



Separators Type	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Simple Distillation								
Multiple Simple Distillation								
Vacuum distillation								
Pressure Distillation						15		
Azeotropic distillation								
Extractive distillation								
Pressure swing distillation								
Absorption		12			12		12	
Stripping			11					13
Partial Condensation Followed by Phase Separator				10				
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption							7	
Molecular Sieve Adsorption							7	
Ion Exchange								
Gas Permeation							9	
Extraction			11					
Distillation/Pervaporation Hybrid System								
Distillation/adsorption Hybrid System								

The analysis of the process shows that for reactor effluent, phase splitting at 35^{o}C cooling water should be used. The gas contains CO2, O2 and Ethylene and the liquid phase contains ethylene oxide and water. However the analysis shows that complete separation can not be achieved and about 10% of the ethylene oxide will be recycled with gas stream to the reactor. Therefore, the first phase separator (PSS1) is not required. Results from the separation system synthesis show that an absorber followed by a supercritical extraction using carbon dioxide can be used to extract ethylene oxide from the absorber liquid output stream. The liquid from the extraction is sent to a flash separator.

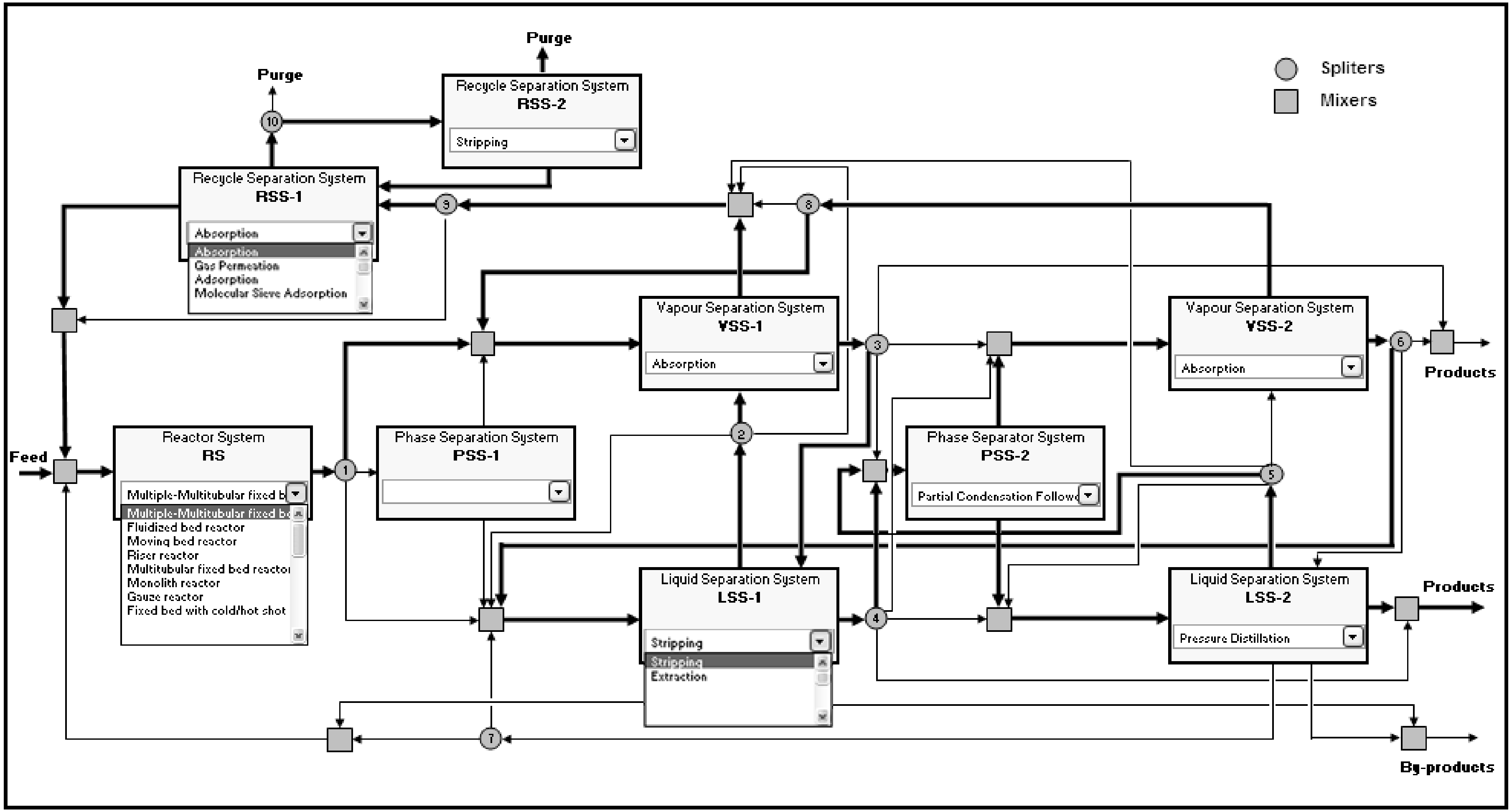


Figure 7.13: Ethylene oxide synthesis results illustrated in the generic superstructure.

Alternatively, absorption (VSS-1) of ethylene oxide followed by steam stripping (LSS-1) can be used. The ethylene oxide/water mixture is sent to a phase separator (PSS-2). The liquid from the phase separator can be sent to a pressure distillation column (LSS-2) as ethylene oxide is vapour at ambient condition. The vapour can be sent to a secondary absorber (VSS-2) for further recovery of ethylene oxide. The recycled gas contains mostly combustion gases and unreacted oxygen and ethylene. This steam can be sent to an absorber (RSS-1) to separate the carbon dioxide and then to steam stripping (RSS-2) as water is one of the species used in the process. Alternatively, membrane separation and adsorption (RSS-1) can be used to separate the carbon dioxide from the recycle gas. If the user selects membrane separation or adsorption in (RSS-1), the stripping separation in (RSS-2) disappears as it is not required.

Results for the ethylene glycol reactor system show CSTRs and tubular reactors can be used. As the reactions are of a mixed parallel and series type, excess of one reactant can be used to improve the selectivity and plug flow reactors are preferred to back mixed reactors (CSTR) to minimize the formation of higher glycols. Based on the heat balance carried out by the software, the reaction can take place adiabatically. Therefore, an adiabatic tubular reactors may be the best choice for such liquid phase reactions. This type of reactor is currently implemented in industry. Another alternative is the use of reactive distillation columns where reaction and separation take place simultaneously (Alqahtani *et al.* 2005, Teo *et al.* 2005). This can be an attractive option as it combines the reaction and separation step in a single unit (Alqahtani, 2004), which reduces the capital cost and utilises the heat required for the reaction to separate the desired product from unreacted material.

Suggested separation systems are illustrated in Table 7.8 and Figure 7.14. Pressure distillation column (LSS-1) is suggested to make steam as the reactor effluent contains a significant amount of excess water reactant. This can be followed by separation of glycols using a train of vacuum distillation columns (LSS-2) to account for the mono-ethylene glycol and other higher glycols degradation temperature which can be below the normal boiling point. A hybrid system of distillation and pervaporation may also be used as an alternative to the conventional approach.

Table 7.8: List of alternative separators for ethylene glycol process.

Separators Type	PSS-1	VSS-1	LSS-1	PSS-2	VSS-2	LSS-2	RSS-1	RSS-2
Simple Distillation								
Multiple Simple Distillation								
Vacuum distillation						15		
Pressure Distillation			16					
Azeotropic distillation								
Extractive distillation								
Pressure swing distillation								
Absorption								
Stripping								
Partial Condensation Followed by Phase Separator								
Flash Drum With Feed Vaporisation								
Liquid-Liquid Phase Separator								
Gas-Liquid Phase Separator								
Wiped film evaporator								
Adsorption								
Molecular Sieve Adsorption								
Ion Exchange								
Gas Permeation								
Extraction								
Distillation/Pervaporation Hybrid System						13		
Distillation/adsorption Hybrid System								

The synthesis results depend to some extent, on the user's basic knowledge about the process and the availability of the other required input information in the database, if the user is not able to provide most of the required information, fewer alternatives are proposed and parts of the software are not going to be utilised such as the optimization.

The developed flowsheet is simulated using Aspen HYSYS. Figure 7.15, is a screen shot from the IKBS. It shows the results from the simulation of selected streams. The user can change the process variables in Excel. New input information is exported to Aspen HYSYS and then the new simulation results are imported to the Excel interface in the IKBS This what-if scenario can be useful during the optimization and the analysis of different process configurations.

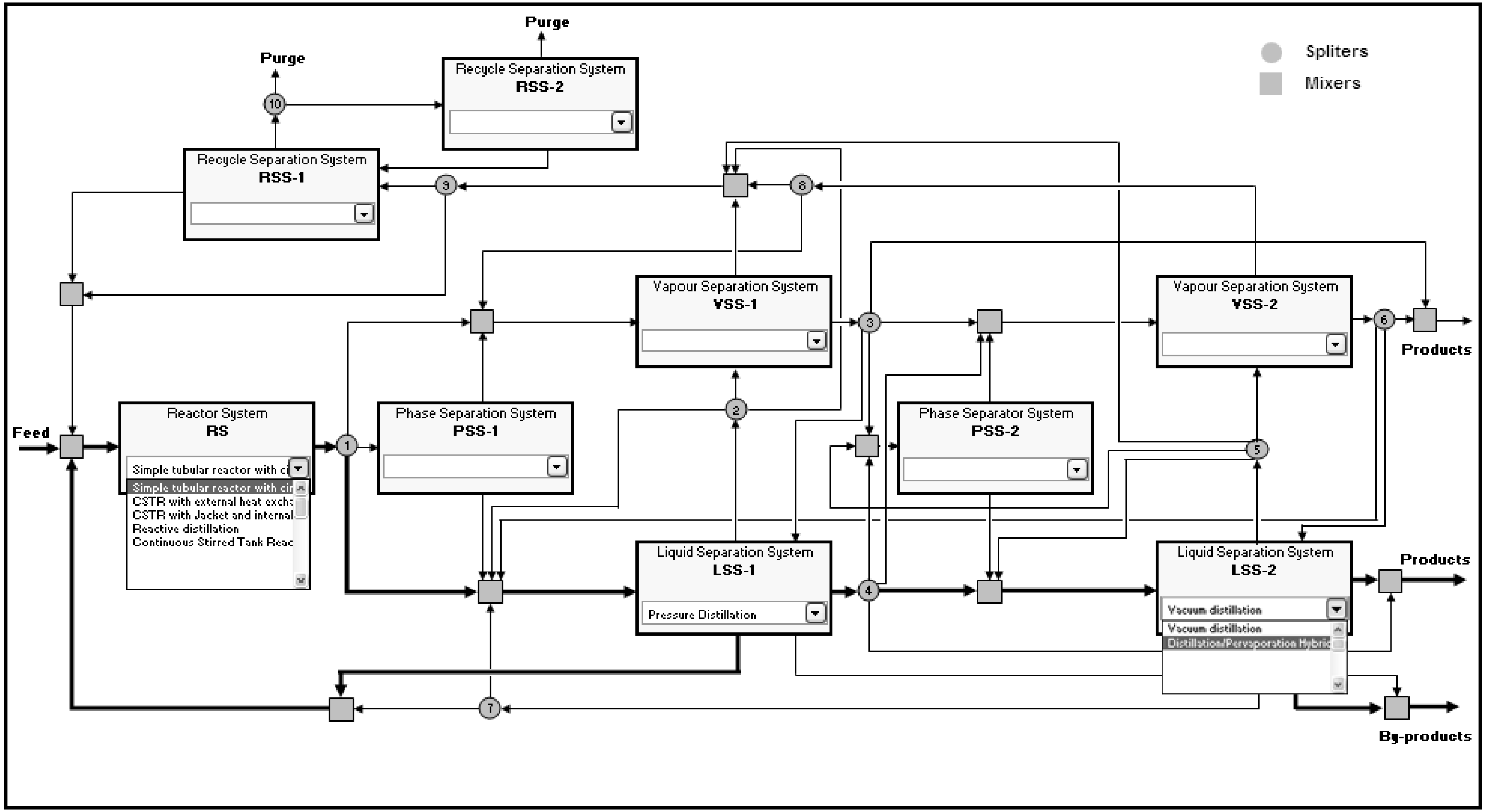
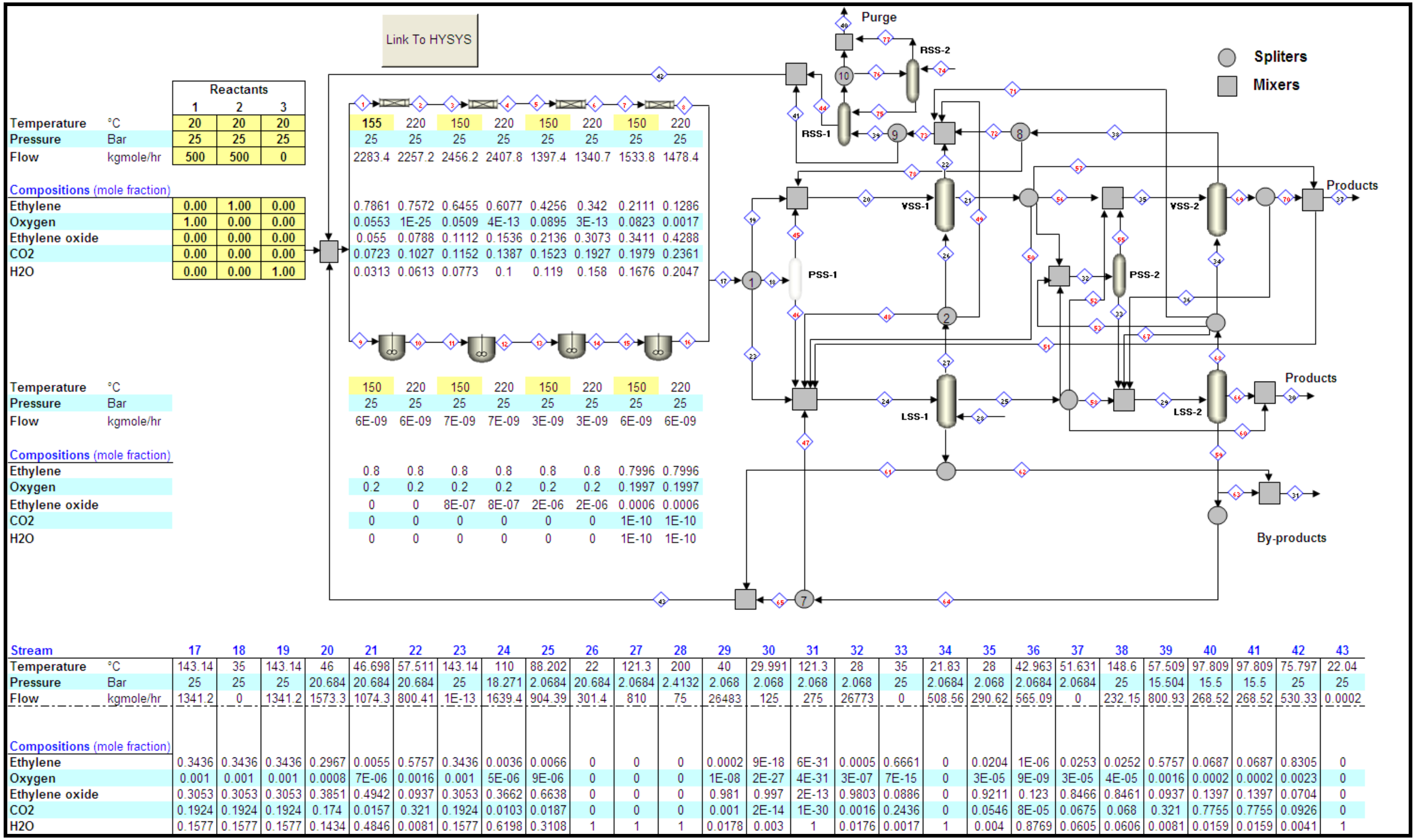


Figure 7.14: Ethylene glycol synthesis results illustrated in the generic superstructure.



		Reactants 1	Reactants 2	Reactants 3								
Temperature	°C	20	20	20	155	220	150	220	150	220	150	220
Pressure	Bar	25	25	25	25	25	25	25	25	25	25	25
Flow	kgmole/hr	500	500	0	2283.4	2257.2	2456.2	2407.8	1397.4	1340.7	1533.8	1478.4
Compositions (mole fraction)												
Ethylene		0.00	1.00	0.00	0.7861	0.7572	0.6455	0.6077	0.4256	0.342	0.2111	0.1286
Oxygen		1.00	0.00	0.00	0.0553	1E-25	0.0509	4E-13	0.0895	3E-13	0.0823	0.0017
Ethylene oxide		0.00	0.00	0.00	0.055	0.0788	0.1112	0.1536	0.2136	0.3073	0.3411	0.4288
CO2		0.00	0.00	0.00	0.0723	0.1027	0.1152	0.1387	0.1523	0.1927	0.1979	0.2361
H2O		0.00	0.00	1.00	0.0313	0.0613	0.0773	0.1	0.119	0.158	0.1676	0.2047

Temperature	°C	150	220	150	220	150	220	150	220
Pressure	Bar	25	25	25	25	25	25	25	25
Flow	kgmole/hr	6E-09	6E-09	7E-09	7E-09	3E-09	3E-09	6E-09	6E-09
Compositions (mole fraction)									
Ethylene		0.8	0.8	0.8	0.8	0.8	0.8	0.7996	0.7996
Oxygen		0.2	0.2	0.2	0.2	0.2	0.2	0.1997	0.1997
Ethylene oxide		0	0	8E-07	8E-07	2E-06	2E-06	0.0006	0.0006
CO2		0	0	0	0	0	0	1E-10	1E-10
H2O		0	0	0	0	0	0	1E-10	1E-10

Stream		17	18	19	20	21	22	23	24	25	26	27	28	29
Temperature	°C	143.14	35	143.14	46	46.698	57.511	143.14	110	88.202	22	121.3	200	40
Pressure	Bar	25	25	25	20.684	20.684	20.684	25	18.271	2.0684	20.684	2.0684	2.4132	2.068
Flow	kgmole/hr	1341.2	0	1341.2	1573.3	1074.3	800.41	1E-13	1639.4	904.39	301.4	810	75	26483
Compositions (mole fraction)														
Ethylene		0.3436	0.3436	0.3436	0.2967	0.0055	0.5757	0.3436	0.0036	0.0066	0	0	0	0.0002
Oxygen		0.001	0.001	0.001	0.0008	7E-06	0.0016	0.001	5E-06	9E-06	0	0	0	1E-08
Ethylene oxide		0.3053	0.3053	0.3053	0.3851	0.4942	0.0937	0.3053	0.3662	0.6638	0	0	0	0.981
CO2		0.1924	0.1924	0.1924	0.174	0.0157	0.321	0.1924	0.0103	0.0187	0	0	0	0.001
H2O		0.1577	0.1577	0.1577	0.1434	0.4846	0.0081	0.1577	0.6198	0.3108	1	1	1	0.0178

Stream		30	31	32	33	34	35	36	37	38	39	40	41	42	43
Temperature	°C	29.991	121.3	28	35	21.83	28	42.963	51.631	148.6	57.509	97.809	97.809	75.797	22.04
Pressure	Bar	2.068	2.068	2.068	25	2.0684	2.068	2.0684	2.0684	25	15.504	15.5	15.5	25	25
Flow	kgmole/hr	125	275	26773	0	508.56	290.62	565.09	0	232.15	800.93	268.52	268.52	530.33	0.0002
Compositions (mole fraction)															
Ethylene		9E-18	6E-31	0.0005	0.6661	0	0.0204	1E-06	0.0253	0.0252	0.5757	0.0687	0.0687	0.8305	0
Oxygen		2E-27	4E-31	3E-07	7E-15	0	3E-05	9E-09	3E-05	4E-05	0.0016	0.0002	0.0002	0.0023	0
Ethylene oxide		0.997	2E-13	0.9803	0.0886	0	0.9211	0.123	0.8466	0.8461	0.0937	0.1397	0.1397	0.0704	0
CO2		2E-14	1E-30	0.0016	0.2436	0	0.0546	8E-05	0.0675	0.068	0.321	0.7755	0.7755	0.0926	0
H2O		0.003	1	0.0176	0.0017	1	0.004	0.8769	0.0605	0.0606	0.0081	0.0159	0.0159	0.0041	1

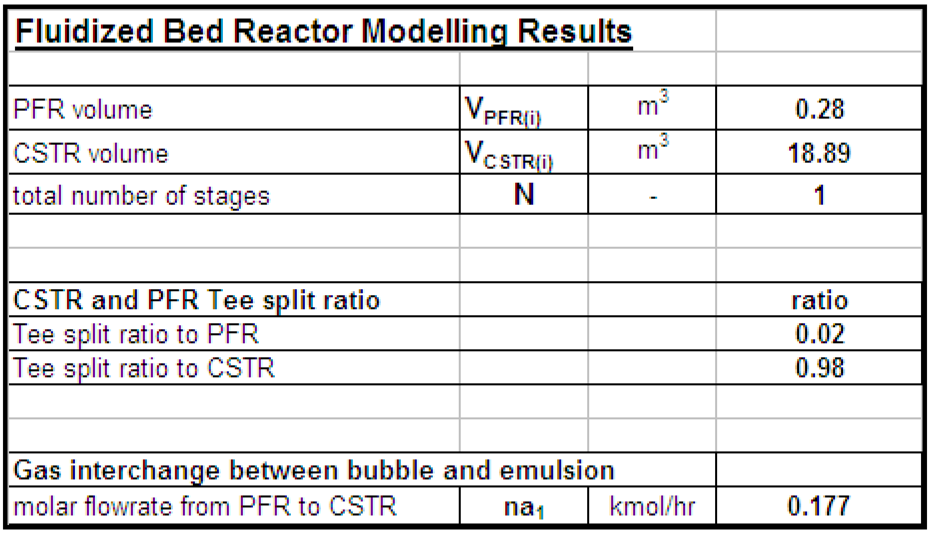
Figure 7.15: Simulated process in IKBS interface.

The specification of the computer used by the IKBS is: Acer® TravelMate 4002LCi, Intel® Pentium® M 725 processor, 1.6 GHz, 400 MHz FSB, 2 MB L2 cache and 512GB DDR. The IKBS does not run in pre-Windows 95 or UNIX systems. The cost of the computer used is only 500 GBP.

To examine the time required to run the generic flowsheet simulation, the molar flowrate of the reactants and the reactors feed temperature have been adjusted. The change of molar ratio of the makeup feed of a reactant by 10 kmol/hr takes 55 seconds for the simulation to converge. Changing the four reactors feed temperature by 2 ^oC takes 4.5 min. However, increasing the reactors feed temperature by 5 ^oC takes around 30 minutes. This can be reduced to 10 mints by ignoring the last distillation column in the flowsheet. Once the simulation in converged the column can be reactivated and then the whole flowsheet is converged in additional 3 seconds. It is recommended to select the fastest CPU and to use at lease 1 GB or higher physical memory for the proposed generic flowsheet. A computer with better specifications may cost about 1,000 GBP.

Fluidized bed reactors have been modelled based on the use of a series of CSTRs and PFRs in parallel. In this work, the fluidized bed reactor is divided into several segments in series. In each stage, the flow of gas is considered to be in plug flow for the bubbles and perfectly mixed for the emulsion phase.

The Kunii-Levenspiel model is used in the modular simulation in the fluidized bed. The exchange coefficients between bubble and cloud phase, and between the cloud and emulsion phase are calculated. Results from the modelling of a fluidized bed reactor are illustrated in Figure 7.16. Results show that only one stage of CSTR and PFR is required as the reaction is very fast. The calculated feed stream ‘Tee’ split ratio to PFR is 0.02 and to the CSTR is 0.98.



Fluidized Bed Reactor Modelling Results			
PFR volume	$V_{PFR(i)}$	m^3	0.28
CSTR volume	$V_{CSTR(i)}$	m^3	18.89
total number of stages	**N**	-	1
CSTR and PFR Tee split ratio			**ratio**
Tee split ratio to PFR			0.02
Tee split ratio to CSTR			0.98
Gas interchange between bubble and emulsion			
molar flowrate from PFR to CSTR	na_1	kmol/hr	0.177

Figure 7.16: Fluidized bed reactor modular simulation results input information to Aspen HYSYS.

The split ratio to PFR is smaller than to the CSTR because only a small volume of PFR is required compared with the volume of CSTR. The gas interchange between bubble and emulsion i.e. from the PFR to CSTR is 0.177 kmol/hr. These results are the input information to Aspen HYSYS generic flowsheet simulation to perform the modular simulation of a fluidized bed reactor using the HYSYS ideal CSTR and PFR.

7.5 Conclusion

To validate and demonstrate the proposed systematic approach and its implementation in the integrated knowledge based system for the synthesis of chemical process flowsheets, four case studies were illustrated. Comprehensive study of the ethylene oxide and ethylene glycol process was presented to account for most of the IKBS features. The acetic acid and cumene process were studied to examine the selection process decisions used in the first two case studies. Results show that suggested alternative reactor separation recycle systems can be divided into three types: IKBS suggest reactor separation recycle system that currently used in commercial processes, other suggested alternatives are recommended by industrial research, and novel reactor separation recycle systems which are first suggested for these processes.

Chapter 8

Conclusions and Future Work

8.1 Conclusions

A design problem is always open ended and there is never a single solution. The solution depends on design decisions taken at different stages of process development to fulfil technical, economical, safety, or environmental constraints. The systematic generation of alternatives is the most important feature of the conceptual chemical process design. The best solution is identified in the context of design constraints by using consistent evaluation and ranking of alternatives. This research deals with the design of innovative chemical processes by means of systematic methods and an integrated knowledge based system.

In this work, a new proposed integrated approach to the systematic synthesis of chemical process flowsheet has been presented. The systematic procedure was implemented using an integrated knowledge based system. The Integrated knowledge based system is able to use previously defined design rules to solve new design problems. The proposed structure of the integrated knowledge based system (IKBS) uses Excel and Visual Basic for Application (VBA) as a backbone of the expert system. Excel and Excel VBA are integrated with third party software such as Aspen HYSYS. Aspen Icarus Process Evaluator (IPE) can also be integrated to the developed IKBS in the future development of the software to obtain a rigorous design and sizing of flowsheet units, and to estimate the cost of alternative flowsheets.

Internal databases were successfully incorporated to provide key information on the species involved in the process as: physical properties, azeotropes, dissociation constants, solvents, adsorbing agents, prices, and safety and environmental impacts. Some of the properties are calculated by the IKBS using the mathematical correlations at the design operating conditions, such as vapour pressure calculations using Antoine equation.

Interfacing the IKBS with Aspen HYSYS process simulation was accomplished by developing a VBA programming code. The integration between Excel and Aspen HYSYS is being used to run ‘what-if scenarios’ and examine the process performance at different design parameters such as reactor feed composition, flowrate, pressure and temperature. The developed VBA programming codes export the new variables to Aspen HSYSY and run the simulation, and then import the new simulation results back to the IKBS Excel interface.

The proposed systematic approach accounts for collecting input information on the process at multi levels of complexity with the aid of internal databases to select alternative reactor-separator-recycle systems using third party software. Chemistry evaluation considers all reaction routes that user provides for analysis. Once primary and secondary reactions are provided, all available information on the species is imported from the internal databases. A preliminary economic evaluation is considered at the early stage of the synthesis by selecting the economically viable reaction routes and accounting the recycle of unreacted materials and the recovery of products. Detailed economic evaluation is suggested using the Aspen Icarus Process Evaluator (IPE) in the second phase of the IKBS for future development.

The safety and environmental analysis of the process is considered by highlighting the impacts of different species on the process and environment. Flammability limits calculation is one of the safety analyses by the IKBS that uses information from the reaction and databases to indicate if the reaction mixture is within the allowable limits.

The proposed systematic approach also accounts for the interaction between the reaction and separation systems instead of synthesising the reaction and separation systems in isolation. Considering the interaction between the reactor-separator-recycle systems, yields good design decisions and optimization. This is due to the fact that reactor performance is affected by the recycle, and the separation design and operation depend on the reactor effluents.

A wide range of 23 reactors and 21 separator processes are evaluated by the IKBS based on a set of criteria. Each criterion is given a score depending on the level of suitability with each evaluated reactor, or separator. The scoring system can be easily amended to improve the design decisions when necessary. A wide range of reactors and separators are proposed by the IKBS. The proposed lists of suitable reactors and separators by the IKBS depend on the input information provided by the user and the databases. The design problem can be under-defined, due to the lack of data. If some key information is not provided, the list will not include some of the advanced technology. The IKBS can be extended to account for additional criteria and also to evaluate more reactors and separator processes. The currently evaluated reactors and separators include conventional units in addition to advanced techniques, and hybrid and reactive separation systems.

As Aspen HYSYS can only simulate ideal CSTRs and PFRs, non ideal and technical reactors suggested by the IKBS can not be directly simulated. HYSYS has been successfully customised to simulate non-conventional process operation, such as the simulation of gas permeation using HYSYS extensibility methods for creating new unit operations. The same methods can be extended to simulate more reactors and separators other than those unit operations available in HYSYS.

To account for the non-ideal behaviour of chemical reactors, a modular simulation of fluidized bed reactors for ethylene oxide gas phase catalytic reaction has been successfully conducted based on the K-L model. The results from the modelling determined the number of parallel CSTR and PFR stages required in an Aspen HYSYS generic flowsheet simulation, and exchange between the reactors based on the interchange coefficient between the bubbles (PFR) and emulsions (CSTR). The modelling also determines the feed split ratio to each reactor.

A generic flowsheet in Aspen HYSYS and superstructure for reactor-separator-recycle systems simulation and optimization were proposed. The generic superstructure contains four reactor systems of CSTR and PFR in parallel, in addition to two separation systems for phase splitting, two liquid separation systems, two vapour separation systems, and two recycled gas separation systems. The superstructure includes internal recycle between the reaction zones and feed distribution to different reactor inlet. It also provides the interconnectivity among vapour and liquid separation systems. Reaction and separation systems are also connected by gas recycle separation systems and liquid recycles. This superstructure is useful for exploring different design configurations performance and optimization of reactor-separator-recycle systems.

The generic flowsheet in Aspen HYSYS, benefits from the flexibility to use different combination of reactors and separators. Therefore, it is capable of simulating different types of petrochemical processes flowsheets. This has been applied to simulate the ethylene oxide process flowsheet. The proposed generic flowsheet and superstructure were found to be widely applicable when compared with several industrial petrochemical processes.

The prototype software has been successfully applied in the synthesis of reactor-separator-recycle systems for four petrochemical processes: ethylene oxide, ethylene glycol, acetic acid and cumene manufacturing processes. The synthesis results for the four process superstructures show that the developed software is capable of suggesting appropriate novel reactor and separator systems for petrochemical processes, in addition to suggesting reactor and separator systems which are currently employed in the commercial processes. The identified superstructures and process flowsheets have been successfully validated using existing commercial processes and industrial research practice.

The proposed systematic procedure and its implementation in the knowledge based systems were demonstrated to potential users in the petrochemical industry. It was found that it can be used as one of the tools in developing a new process technology and in possibly in the retrofit design of existing processes. Furthermore is has been indicated that it can be further developed to match specific requirements and applications. The total chemical flowsheet synthesis systematic procedure and software is expected to yield significant improvements in the petrochemical industries by providing a cost effective chemical process flowsheeting strategy.

8.2 Future Work

As process synthesis is an open ended problem, there still can be an opportunity for extending the accomplished work on the synthesis of reactor-separator-recycle systems. This can be by accounting for new areas of improvement and full implementation of the systematic procedure in the integrated knowledge based system. Suggested tasks for future work include the following:

1. Further implementations of the systematic procedure in the integrated knowledge based system by including flowsheet optimization using Aspen HYSYS, and detailed flowsheet sizing and economic evaluation using Aspen Icarus.

2. To make further improvements in the design decisions, weighting the selection criteria of process units by allocating different values to each criterion is an important future task to account for the fact that some criteria may have a bigger effect on the selection of the reactor-separator-recycle system than others.

3. Extending the current use of the IKBS with Aspen HYSYS, to all process streams and unit operations in the generic flowsheet. This should allow for exploring the entire generic flowsheet design performance and optimization.

4. Extending the proposed generic flowsheet by adding extra phase separation systems, vapour separation systems, and liquid separation systems. The extended generic flowsheet would be able to simulate and optimize more complex process flowsheet.

5. Process controllability may be included to the integrated systematic approach. This is due to the close relation between chemical process design and controllability where the high performance design of each individual process unit operation might be counter productivity for the controllability of the whole process flowsheet.

6. Separation operating conditions can be extended to aid the design decisions for the separation processes synthesis. This can be achieved, for example, by implementing a set of heuristic rules in the IKBS to suggest an initial operating condition for each unit operation.

7. Heat integration can be introduced to the proposed systematic procedure to analyse the process and suggest an optimum management of energy as well as the design of the corresponding heat exchanger network in the generic flowsheet in Aspen HYSYS.

8. The current internal databases can be easily be updated and extra sets of databases can also be added. Linking the IKBS to external databases such as DETHERM® database, is recommended to provide the software with a wider range of information which should lead to better design decisions.

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Appendix A: VBA code for linking Excel to Aspen HYSYS as a part of integrating the KBS with third party software.

```
Option Explicit

Public Sub LinkToHysys()
    Dim hyApp As HYSYS.Application
    Dim hyCase As HYSYS.SimulationCase
    Dim hyStream As HYSYS.ProcessStream
    Dim varComposition As Variant
    Dim intCount As Integer
   Dim hyFluidPkg As HYSYS.FluidPackage
   Dim hyPRFluidPkg As HYSYS.UNIQUACPropPkg

    'Setup Error Handler
    On Error GoTo ErrorHandler

    'Link to HYSYS
    Set  hyApp  =  GetObject(,  "HYSYS.Application")      'Only  works  if
HYSYS is open
    'Get the currently open case
    Set hyCase = hyApp.ActiveDocument
    If hyCase Is Nothing Or LCase(hyCase.Title.Value) <> LCase("GF-EO-
21-04-08-1.hsc") Then
        MsgBox "Make sure Hysys is open with ""GF-EO-21-04-08-1.hsc""
as the current case", , "Error"
        Exit Sub
    End If

    'Establish a link to the stream Reactant-1
  Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("Reactant-1")

    'Turn off the solver - stops HYSYS from resolving on each change
made
    hyCase.Solver.CanSolve = False

    'Set Reactant-1 Properties
    With hyStream
        .Temperature.SetValue Range("Reactant1T").Value, "C"
        .Pressure.SetValue Range("Reactant1P").Value, "bar"
        .MolarFlow.SetValue Range("Reactant1F").Value, "kgmole/h"

        'Initialise the variable to hold compositions
        varComposition = .ComponentMolarFractionValue
        'Since   mole   fractions   don't   have   any   units   use   the
.ComponentMolarFractionValue property
        'Could also have used
        'varComposition = .ComponentMolarFraction.GetValues("")
```

```
        'Get compositions from the spreadsheet
        For intCount = 0 To UBound(varComposition)
            varComposition(intCount)                                   =
Range("Reactant1C").Offset(intCount, 0).Value
        Next 'intCount

        'HYSYS automatically normalises the data if it isn't
        .ComponentMolarFractionValue = varComposition

        'Get it back in case HYSYS normalised it
        varComposition = .ComponentMolarFractionValue
        For intCount = 0 To UBound(varComposition)
           Range("Reactant1C").Offset(intCount,       0).Value        =
varComposition(intCount)
        Next 'intCount

    End With

  'Establish a link to the stream Reactant-2
  Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("Reactant-2")

  'Turn  off  the  solver  -  stops  HYSYS  from  resolving  on  each  change
made
    hyCase.Solver.CanSolve = False

'Set Reactant-2 Properties
    With hyStream
        .Temperature.SetValue Range("Reactant2T").Value, "C"
        .Pressure.SetValue Range("Reactant2P").Value, "bar"
        .MolarFlow.SetValue Range("Reactant2F").Value, "kgmole/h"

        'Initialise the variable to hold compositions
        varComposition = .ComponentMolarFractionValue
        'Since   mole   fractions   don't   have   any   units   use   the
.ComponentMolarFractionValue property
        'Could also have used
        'varComposition = .ComponentMolarFraction.GetValues("")

        'Get compositions from the spreadsheet
        For intCount = 0 To UBound(varComposition)
            varComposition(intCount)                                   =
Range("Reactant2C").Offset(intCount, 0).Value
        Next 'intCount

        'HYSYS automatically normalises the data if it isn't
        .ComponentMolarFractionValue = varComposition

        'Get it back in case HYSYS normalised it
        varComposition = .ComponentMolarFractionValue
        For intCount = 0 To UBound(varComposition)
           Range("Reactant2C").Offset(intCount,       0).Value        =
varComposition(intCount)
        Next 'intCount

    End With
```

```
    'Establish a link to the stream Reactant-3
  Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("Reactant-3")

    'Turn off the solver - stops HYSYS from resolving on each change
made
    hyCase.Solver.CanSolve = False

    'Set Reactant Properties
    With hyStream
        .Temperature.SetValue Range("Reactant3T").Value, "C"
        .Pressure.SetValue Range("Reactant3P").Value, "bar"
        .MolarFlow.SetValue Range("Reactant3F").Value, "kgmole/h"

        'Initialise the variable to hold compositions
        varComposition = .ComponentMolarFractionValue
        'Since   mole   fractions   don't   have   any   units   use   the
.ComponentMolarFractionValue property
        'Could also have used
        'varComposition = .ComponentMolarFraction.GetValues("")

        'Get compositions from the spreadsheet
        For intCount = 0 To UBound(varComposition)
            varComposition(intCount)                                 =
Range("Reactant3C").Offset(intCount, 0).Value
        Next 'intCount

        'HYSYS automatically normalises the data if it isn't
        .ComponentMolarFractionValue = varComposition

        'Get it back in case HYSYS normalised it
        varComposition = .ComponentMolarFractionValue
        For intCount = 0 To UBound(varComposition)
    Range("Reactant3C").Offset(intCount,           0).Value           =
varComposition(intCount)
        Next 'intCount

    End With

    'Make HYSYS solve
    hyCase.Solver.CanSolve = True

    'Now get the data from the stream#1
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("1")

        With hyStream
        .Temperature.SetValue Range("S1T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S1F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S1F").Value = "<empty>"
        End If
```

```
        If .Pressure.IsKnown = True Then
            Range("S1P").Value = .Pressure.GetValue("bar")
        Else
            Range("S1P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
      If varComposition(0) <> -32767 Then               '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S1C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S1C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

     'Now get the data from the stream#2
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("2")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S2F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S2F").Value = "<empty>"
        End If

        If .Temperature.IsKnown = True Then
            Range("S2T").Value = .Temperature.GetValue("C")
        Else
            Range("S2T").Value = "<empty>"
        End If

        If .Pressure.IsKnown = True Then
            Range("S2P").Value = .Pressure.GetValue("bar")
        Else
            Range("S2P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S2C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S2C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If
```

```
    End With

    'Now get the data from the stream#3
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("3")

           With hyStream
        .Temperature.SetValue Range("S3T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S3F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S3F").Value = "<empty>"
        End If

        If .Pressure.IsKnown = True Then
            Range("S3P").Value = .Pressure.GetValue("bar")
        Else
            Range("S3P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S3C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S3C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

    'Now get the data from the stream#4
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("4")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S4F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S4F").Value = "<empty>"
        End If

         If .Temperature.IsKnown = True Then
            Range("S4T").Value = .Temperature.GetValue("C")
        Else
            Range("S4T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
```

```
            Range("S4P").Value = .Pressure.GetValue("bar")
        Else
            Range("S4P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S4C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S4C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

End With

     'Now get the data from the stream#5
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("5")

        With hyStream
        .Temperature.SetValue Range("S5T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S5F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S5F").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S5P").Value = .Pressure.GetValue("bar")
        Else
            Range("S5P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S5C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S5C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

         'Now get the data from the stream#6
```

```
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("6")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S6F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S6F").Value = "<empty>"
        End If

        If .Temperature.IsKnown = True Then
            Range("S6T").Value = .Temperature.GetValue("C")
        Else
            Range("S6T").Value = "<empty>"
        End If

        If .Pressure.IsKnown = True Then
            Range("S6P").Value = .Pressure.GetValue("bar")
        Else
            Range("S6P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S6C").Offset(intCount,         0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S6C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

     'Now get the data from the stream#7
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("7")

        With hyStream
        .Temperature.SetValue Range("S7T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S7F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S7F").Value = "<empty>"
        End If

        If .Pressure.IsKnown = True Then
            Range("S7P").Value = .Pressure.GetValue("bar")
        Else
            Range("S7P").Value = "<empty>"
        End If
```

```
        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S7C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S7C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

     'Now get the data from the stream#8
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("8")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S8F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S8F").Value = "<empty>"
        End If

        If .Temperature.IsKnown = True Then
            Range("S8T").Value = .Temperature.GetValue("C")
        Else
            Range("S8T").Value = "<empty>"
        End If

        If .Pressure.IsKnown = True Then
            Range("S8P").Value = .Pressure.GetValue("bar")
        Else
            Range("S8P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
   Range("S8C").Offset(intCount, 0).Value = varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
        Range("S8C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


      'Now get the data from the stream#9
      Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("9")
```

```
    With hyStream
        .Temperature.SetValue Range("S9T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S9F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S9F").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S9P").Value = .Pressure.GetValue("bar")
        Else
            Range("S9P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S9C").Offset(intCount,         0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S9C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

    'Now get the data from the stream#10
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("10")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S10F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S10F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S10T").Value = .Temperature.GetValue("C")
        Else
            Range("S10T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S10P").Value = .Pressure.GetValue("bar")
        Else
            Range("S10P").Value = "<empty>"
```

```
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S10C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S10C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

    'Now get the data from the stream#11
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("11")

           With hyStream
        .Temperature.SetValue Range("S11T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S11F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S11F").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S11P").Value = .Pressure.GetValue("bar")
        Else
            Range("S11P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S11C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S11C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

    'Now get the data from the stream#12
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("12")
```

```
    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S12F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S12F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S12T").Value = .Temperature.GetValue("C")
        Else
            Range("S12T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S12P").Value = .Pressure.GetValue("bar")
        Else
            Range("S12P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S12C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S12C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

        'Now get the data from the stream#13
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("13")

           With hyStream
        .Temperature.SetValue Range("S13T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S13F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S13F").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S13P").Value = .Pressure.GetValue("bar")
        Else
```

```
            Range("S13P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S13C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S13C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


    'Now get the data from the stream#14
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("14")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S14F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S14F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S14T").Value = .Temperature.GetValue("C")
        Else
            Range("S14T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S14P").Value = .Pressure.GetValue("bar")
        Else
            Range("S14P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S14C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S14C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If
```

```
    End With


    'Now get the data from the stream#15
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("15")

           With hyStream
        .Temperature.SetValue Range("S15T").Value, "C"
        End With

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S15F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S15F").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S15P").Value = .Pressure.GetValue("bar")
        Else
            Range("S15P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S15C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S15C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


    'Now get the data from the stream#16
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("16")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S16F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S16F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S16T").Value = .Temperature.GetValue("C")
        Else
```

```
            Range("S16T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S16P").Value = .Pressure.GetValue("bar")
        Else
            Range("S16P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S16C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S16C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

     'Now get the data from the stream#17
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("17")


    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S17F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S17F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S17T").Value = .Temperature.GetValue("C")
        Else
            Range("S17T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S17P").Value = .Pressure.GetValue("bar")
        Else
            Range("S17P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
```

```
               Range("S17C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S17C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


        'Now get the data from the stream#18
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("18")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S18F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S18F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S18T").Value = .Temperature.GetValue("C")
        Else
            Range("S18T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S18P").Value = .Pressure.GetValue("bar")
        Else
            Range("S18P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S18C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S18C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


    'Now get the data from the stream#19
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("19")
```

```
    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S19F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S19F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S19T").Value = .Temperature.GetValue("C")
        Else
            Range("S19T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S19P").Value = .Pressure.GetValue("bar")
        Else
            Range("S19P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S19C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S19C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


  'Now get the data from the stream#20
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("20")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S20F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S20F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S20T").Value = .Temperature.GetValue("C")
        Else
            Range("S20T").Value = "<empty>"
        End If
```

```
        If .Pressure.IsKnown = True Then
            Range("S20P").Value = .Pressure.GetValue("bar")
        Else
            Range("S20P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S20C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S20C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#21
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("21")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S21F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S21F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S21T").Value = .Temperature.GetValue("C")
        Else
            Range("S21T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S21P").Value = .Pressure.GetValue("bar")
        Else
            Range("S21P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S21C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
```

```
               Range("S21C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#22
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("22")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S22F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S22F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S22T").Value = .Temperature.GetValue("C")
        Else
            Range("S22T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S22P").Value = .Pressure.GetValue("bar")
        Else
            Range("S22P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S22C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S22C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


   'Now get the data from the stream#23
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("23")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S23F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S23F").Value = "<empty>"
```

```
        End If


        If .Temperature.IsKnown = True Then
            Range("S23T").Value = .Temperature.GetValue("C")
        Else
            Range("S23T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S23P").Value = .Pressure.GetValue("bar")
        Else
            Range("S23P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S23C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S23C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#24
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("24")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S24F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S24F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S24T").Value = .Temperature.GetValue("C")
        Else
            Range("S24T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S24P").Value = .Pressure.GetValue("bar")
        Else
            Range("S24P").Value = "<empty>"
        End If
```

```
        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S24C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S24C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#25
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("25")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S25F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S25F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S25T").Value = .Temperature.GetValue("C")
        Else
            Range("S25T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S25P").Value = .Pressure.GetValue("bar")
        Else
            Range("S25P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S25C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S25C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With
```

```
     'Now get the data from the stream#26
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("26")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S26F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S26F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S26T").Value = .Temperature.GetValue("C")
        Else
            Range("S26T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S26P").Value = .Pressure.GetValue("bar")
        Else
            Range("S26P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S26C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S26C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#27
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("27")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S27F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S27F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S27T").Value = .Temperature.GetValue("C")
        Else
```

```
            Range("S27T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S27P").Value = .Pressure.GetValue("bar")
        Else
            Range("S27P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S27C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S27C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#28
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("28")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S28F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S28F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S28T").Value = .Temperature.GetValue("C")
        Else
            Range("S28T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S28P").Value = .Pressure.GetValue("bar")
        Else
            Range("S28P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
```

```
               Range("S28C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S28C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

      'Now get the data from the stream#29
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("29")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S29F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S29F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S29T").Value = .Temperature.GetValue("C")
        Else
            Range("S29T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S29P").Value = .Pressure.GetValue("bar")
        Else
            Range("S29P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S29C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S29C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


     'Now get the data from the stream#30
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("30")

    With hyStream
```

```
        If .MolarFlow.IsKnown = True Then
            Range("S30F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S30F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S30T").Value = .Temperature.GetValue("C")
        Else
            Range("S30T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S30P").Value = .Pressure.GetValue("bar")
        Else
            Range("S30P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S30C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S30C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


      'Now get the data from the stream#31
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("31")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S31F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S31F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S31T").Value = .Temperature.GetValue("C")
        Else
            Range("S31T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
```

```
            Range("S31P").Value = .Pressure.GetValue("bar")
        Else
            Range("S31P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S31C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S31C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#32
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("32")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S32F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S32F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S32T").Value = .Temperature.GetValue("C")
        Else
            Range("S32T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S32P").Value = .Pressure.GetValue("bar")
        Else
            Range("S32P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S32C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S32C").Offset(intCount, 0).Value = "<empty>"
```

```
            Next 'intCount
        End If

    End With


          'Now get the data from the stream#34
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("34")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S34F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S34F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S34T").Value = .Temperature.GetValue("C")
        Else
            Range("S34T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S34P").Value = .Pressure.GetValue("bar")
        Else
            Range("S34P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#34
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("34")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S34F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S34F").Value = "<empty>"
        End If
```

```
        If .Temperature.IsKnown = True Then
            Range("S34T").Value = .Temperature.GetValue("C")
        Else
            Range("S34T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S34P").Value = .Pressure.GetValue("bar")
        Else
            Range("S34P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

          'Now get the data from the stream#34
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("34")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S34F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S34F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S34T").Value = .Temperature.GetValue("C")
        Else
            Range("S34T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S34P").Value = .Pressure.GetValue("bar")
        Else
            Range("S34P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
```

```
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#34
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("34")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S34F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S34F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S34T").Value = .Temperature.GetValue("C")
        Else
            Range("S34T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S34P").Value = .Pressure.GetValue("bar")
        Else
            Range("S34P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S34C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With
```

```
    'Now get the data from the stream#35
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("35")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S35F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S35F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S35T").Value = .Temperature.GetValue("C")
        Else
            Range("S35T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S35P").Value = .Pressure.GetValue("bar")
        Else
            Range("S35P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S35C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S35C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#36
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("36")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S36F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S36F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S36T").Value = .Temperature.GetValue("C")
        Else
            Range("S36T").Value = "<empty>"
```

```
        End If


        If .Pressure.IsKnown = True Then
            Range("S36P").Value = .Pressure.GetValue("bar")
        Else
            Range("S36P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S36C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S36C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

          'Now get the data from the stream#37
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("37")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S37F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S37F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S37T").Value = .Temperature.GetValue("C")
        Else
            Range("S37T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S37P").Value = .Pressure.GetValue("bar")
        Else
            Range("S37P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S37C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
```

```
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S37C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

         'Now get the data from the stream#38
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("38")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S38F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S38F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S38T").Value = .Temperature.GetValue("C")
        Else
            Range("S38T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S38P").Value = .Pressure.GetValue("bar")
        Else
            Range("S38P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S38C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S38C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#39
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("39")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S39F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
```

```
            Range("S39F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S39T").Value = .Temperature.GetValue("C")
        Else
            Range("S39T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S39P").Value = .Pressure.GetValue("bar")
        Else
            Range("S39P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then              '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S39C").Offset(intCount,        0).Value         =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S39C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

         'Now get the data from the stream#40
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("40")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S40F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S40F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S40T").Value = .Temperature.GetValue("C")
        Else
            Range("S40T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S40P").Value = .Pressure.GetValue("bar")
        Else
            Range("S40P").Value = "<empty>"
        End If
```

```
        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S40C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S40C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With

          'Now get the data from the stream#41
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("40")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S41F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S41F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S41T").Value = .Temperature.GetValue("C")
        Else
            Range("S41T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S41P").Value = .Pressure.GetValue("bar")
        Else
            Range("S41P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S41C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S41C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With
```

```
         'Now get the data from the stream#42
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("42")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S42F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S42F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S42T").Value = .Temperature.GetValue("C")
        Else
            Range("S42T").Value = "<empty>"
        End If


        If .Pressure.IsKnown = True Then
            Range("S42P").Value = .Pressure.GetValue("bar")
        Else
            Range("S42P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S42C").Offset(intCount,        0).Value        =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S42C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


         'Now get the data from the stream#43
    Set hyStream = hyCase.Flowsheet.MaterialStreams.Item("43")

    With hyStream
        If .MolarFlow.IsKnown = True Then
            Range("S43F").Value = .MolarFlow.GetValue("kgmole/h")
        Else
            Range("S43F").Value = "<empty>"
        End If


        If .Temperature.IsKnown = True Then
            Range("S43T").Value = .Temperature.GetValue("C")
        Else
            Range("S43T").Value = "<empty>"
```

```
        End If


        If .Pressure.IsKnown = True Then
            Range("S43P").Value = .Pressure.GetValue("bar")
        Else
            Range("S43P").Value = "<empty>"
        End If

        varComposition = .ComponentMolarFractionValue
        If varComposition(0) <> -32767 Then             '-32767 is how
HYSYS represents <empty> internally
            For intCount = 0 To UBound(varComposition)
               Range("S43C").Offset(intCount, 0).Value =
varComposition(intCount)
            Next 'intCount
        Else
            For intCount = 0 To UBound(varComposition)
               Range("S43C").Offset(intCount, 0).Value = "<empty>"
            Next 'intCount
        End If

    End With


    'Get rid of all our object vars - good practice
    Set hyApp = Nothing
    Set hyCase = Nothing
    Set hyStream = Nothing

    'End of normal procedure
    Exit Sub

'Error handling routine
ErrorHandler:

    If Err.Number = 429 Or Err.Number = 483 Then
        MsgBox "Make sure Hysys is open with ""GF-EO-21-04-08-1.hsc""
as the current case", , "Error"
    ElseIf Err.Number = -2147467259 Then
        MsgBox "Required Stream not found" and vbCrLf and "Make sure
Hysys is open with ""GF-EO-21-04-08-1.hsc"" as the current case", ,
"Error"
    Else
        MsgBox "The following error (" and Err.Number and ") occurred:
" and Err.Description, , "Error"
    End If

End Sub
```

Appendix B: Potential user's questionnaire

To ensure that the software is going to be used effectively by the users, a short questionnaire illustrated in Figure B.1 was completed by 12 Process Engineers at the Saudi Basic Industries Corporation Industrial Complex for Research and Technology (SABIC R&T) in Saudi Arabia. The main objective of the questionnaire was to identify the potential user's requirements and the level of knowledge that they might have about the process. The questionnaire is divided into three parts. The first part asks the users if they can provide, or find, particular information about the process to be synthesised. The information is divided into reaction information, separation information and other general information. The second part asks for any further information that can be provided. The final part asks the users for general comments and advice.

Results from the questionnaires are illustrated in Table B.1. The result shows that the potential users can be classified into three categories. The first group of users are those who can use the software to synthesise a total chemical process flowsheet. The second group of users are those who can either provide information on reactor, or separation systems synthesis. The third group of users are those who can not utilize the software because of not providing the minimum required information on the process. This third group of users is notified at an early stage of the synthesis steps, that certain items of information are required before they can start using the software.

It can also be noticed from the results that some key information are not widely known by most of the users such as: reaction activation energy, overall order of reactions, order with respect to species, difference in partitioning behaviour between two liquids, difference in affinity for adsorption on a solid surface, permeability, dissociation constant and the number of phases. These limitations on the user's input/output information requirements were considered during the development of the software. Some of this information will be obtained form the databases, assumed, or calculated.

Integrated knowledge based system for chemical process synthesis:

Potential user's questionnaire

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An integrated knowledge based system for the development of a complete chemical process flowsheet is under development. The developed software will use heuristics, mathematical simulation, process equipment sizing and economic evaluation to develop alternative flowsheets for petrochemical applications.

The objective of this questionnaire is to identify potential user's requirements and the level of knowledge that he or she might has about the process to be synthesised.

Access to the research will be provided to those who complete this questionnaire.

1. Please tick only the information that you think you would be able to provide or find. This information will be used as input to the process synthesis software.

Reaction Information	Separation Information	Other Information
☐ reaction rate equation	☐ relative volatility	☐ chemical prices
☐ desired conversion	☐ azeotrope formation	☐ plant capacity
☐ reaction selectivity	☐ mass separating agent	☐ number of phases exist
☐ reaction temperature range	☐ difference in partitioning behaviour between two liquids	☐ reactants and product composition and flowrate
☐ reaction pressure	☐ difference in affinity for adsorption on solid surface	☐
☐ activation energy	☐ solubility	☐
☐ reactor production rate	☐ permeability	☐
☐ overall order of reactions	☐ selectivity in absorbent	☐
☐ order with respect to species	☐ separation efficiency	☐
☐ need for catalyst	☐ dissociation constant	☐
☐ catalyst life time	☐	☐
☐ adsorption coefficient	☐	☐

2. What is the other information that you would be able to provide or find?

1- -- 2- --
3- -- 4- --

3. Please write below your general comments and advices.

Answered by: **Position:**

Figure B.1: Potential user's questionnaire.

Table B.1: Potential user's questionnaires result

	Users													
Input Information	First Group						Second Group			Third Group				
Reaction Information	1	2	3	4	5	6	7	8	9	10	11	12	total	%
reaction rate equation	√	√	√	√	√		√	√					7	58%
desired conversion	√	√	√	√	√	√	√	√			√		9	75%
reaction selectivity	√	√	√	√	√	√	√	√		√	√		10	83%
reaction temperature range	√	√	√	√	√	√	√	√		√			9	75%
reaction pressure	√	√	√	√	√	√	√	√		√			9	75%
activation energy				√			√	√		√			4	33%
reactor production rate	√	√	√	√	√	√		√					7	58%
overall order of reactions	√	√		√								√	4	33%
order with respect to species	√	√	√	√									4	33%
need for catalyst	√	√	√	√	√	√	√	√			√	√	10	83%
catalyst life time	√	√	√	√			√				√	√	7	58%
adsorption coefficient				√		√							2	17%
Separation Information														
relative volatility	√	√	√	√	√	√			√	√	√		9	75%
azeotrope formation	√	√	√	√	√				√		√		7	58%
mass separating agent	√	√		√					√		√		5	42%
difference in partitioning behaviour between two liquids			√	√		√			√				4	33%
difference in affinity for adsorption on solid surface				√									1	8%
solubility	√	√	√	√	√	√			√				7	58%
permeability		√							√				2	17%
selectivity in absorbent	√	√	√						√				4	33%
separation efficiency	√	√	√		√				√	√			6	50%
dissociation constant														0%
Other Information														
chemical prices	√	√	√	√	√	√	√	√	√	√			10	83%
plant capacity	√	√	√	√	√	√	√	√	√	√			10	83%
number of phases exist	√		√			√			√	√			5	42%
reactants and product composition and flowrate	√	√	√	√	√	√		√	√	√			9	75%
Total	20	20	19	21	14	14	10	11	12	10	7	3		
%	77	77	73	81	54	54	38	42	46	38	27	12		

Appendix C: VBA programming code for sorting and listing the alternative Reactor-separator-recycle systems in the IKBS generic superstructure.

```
Sub Macro15()
'
' Macro15 Macro
' Macro recorded 25/01/2008 by Abdullah
'
  Sheets("1st & 2nd RS& SS Results").Select

    ActiveWindow.SmallScroll Down:=-27
    Range("C7:D50").Select
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=18
    Range("C53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-39
    Range("C7:C50").Select
    ActiveWindow.SmallScroll Down:=-54
    Range("C7:C50,E7:E50").Select
    Range("E7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=63
    Range("C103").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-87
    ActiveWindow.SmallScroll ToRight:=5
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-33
    Range("J7:J50,R7:R50").Select
```

```
    Range("R7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=18
    Range("J53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-33
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-36
    Range("J7:J50,S7:S50").Select
    Range("S7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=15
    Range("L53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-39
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-21
    Range("J7:J50,T7:T50").Select
    Range("T7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=0
    Range("N53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-30
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-33
    Range("J7:J50,U7:U50").Select
    Range("U7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=18
```

```
    Range("P53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-42
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-33
    Range("J7:J50,V7:V50").Select
    Range("V7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    Range("R53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-27
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-27
    Range("J7:J50,W7:W50").Select
    Range("W7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=12
    Range("T53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-36
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-15
    ActiveWindow.SmallScroll ToRight:=3
    ActiveWindow.SmallScroll Down:=-15
    Range("J7:J50,X7:X50").Select
    Range("X7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    Range("V53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
```

```
    ActiveWindow.SmallScroll Down:=-48
    Range("J7:J50").Select
    Application.CutCopyMode = False
    Selection.Copy
    ActiveWindow.SmallScroll Down:=-27
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-30
    Range("J7:J50,Y7:Y50").Select
    Range("Y7").Activate
    ActiveWindow.SmallScroll Down:=18
    Range("X53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.ScrollColumn = 8
    ActiveWindow.ScrollColumn = 6
    ActiveWindow.ScrollColumn = 4
    ActiveWindow.ScrollColumn = 3
    ActiveWindow.ScrollColumn = 2
    ActiveWindow.ScrollColumn = 1
    ActiveWindow.SmallScroll Down:=12
    Range("C53:D96").Select
    Application.CutCopyMode = False
    Selection.Sort Key1:=Range("D53"), Order1:=xlDescending,
Header:=xlNo, _
        OrderCustom:=1, MatchCase:=False, Orientation:=xlTopToBottom,
_
        DataOption1:=xlSortTextAsNumbers
    ActiveWindow.SmallScroll Down:=48
    Range("C103:D146").Select
    Selection.Sort Key1:=Range("D103"), Order1:=xlDescending,
Header:=xlNo, _
        OrderCustom:=1, MatchCase:=False, Orientation:=xlTopToBottom,
_
        DataOption1:=xlSortTextAsNumbers
    ActiveWindow.SmallScroll ToRight:=5
    ActiveWindow.SmallScroll Down:=-36
    Range("J53:K96").Select
    Selection.Sort Key1:=Range("K53"), Order1:=xlDescending,
Header:=xlGuess _
```

```
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    Range("L53:M96").Select
    Selection.Sort Key1:=Range("M53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    Range("N53:O96").Select
    Selection.Sort Key1:=Range("O53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    Range("P53:Q96").Select
    Selection.Sort Key1:=Range("Q53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    Range("R53:S96").Select
    Selection.Sort Key1:=Range("S53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    ActiveWindow.SmallScroll ToRight:=2
    ActiveWindow.SmallScroll Down:=14
    Range("T53:U96").Select
    Selection.Sort Key1:=Range("U53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    ActiveWindow.SmallScroll ToRight:=3
    Range("V53:W96").Select
    Selection.Sort Key1:=Range("W53"), Order1:=xlDescending,
Header:=xlGuess _
```

```
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    Range("X53:Y96").Select
    Selection.Sort Key1:=Range("Y53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortNormal
    ActiveWindow.SmallScroll Down:=-18
    Range("Y53").Select
    ActiveWindow.SmallScroll Down:=-27
    ActiveWindow.SmallScroll ToRight:=-2
    Range("J7:J27,Y7:Y27").Select
    Range("Y7").Activate
    Selection.Copy
    ActiveWindow.SmallScroll Down:=27
    Range("X53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=-27
    Range("J7:J50").Select
    ActiveWindow.SmallScroll Down:=-27
    Range("J7:J50,Y7:Y50").Select
    Range("Y7").Activate
    Application.CutCopyMode = False
    Selection.Copy
    Range("X53").Select
    Selection.PasteSpecial Paste:=xlPasteValues, Operation:=xlNone,
SkipBlanks _
        :=False, Transpose:=False
    ActiveWindow.SmallScroll Down:=15
    Application.CutCopyMode = False
    Selection.Sort Key1:=Range("Y53"), Order1:=xlDescending,
Header:=xlGuess _
        , OrderCustom:=1, MatchCase:=False,
Orientation:=xlTopToBottom, _
        DataOption1:=xlSortTextAsNumbers
    ActiveWindow.SmallScroll Down:=3
```

```
    Sheets("1st & 2nd RS& SS Results").Select
    Range("E33").Select
    Sheets("1st System Results").Select
    Range("P62").Select
End Sub
```

Appendix D: VBA programming code for integrating and disintegrating unit operations in the IKBS generic flowsheet.

```
Sub Macro16()
' Macro16 Macro
'integrating and Disintegrating unit operation in the IKBS generic
flowsheet

    Sheets("1st and 2nd RSand SS Results").Select

        If Range("K51").Value = 0 Then
        Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 12").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.87
    Selection.ShapeRange.PictureFormat.Contrast = 0.1
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

    Sheets("1st and 2nd RSand SS Results").Select

        If Range("K51").Value = 1 Then
        Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 12").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.5
    Selection.ShapeRange.PictureFormat.Contrast = 0.5
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

    Sheets("1st and 2nd RSand SS Results").Select

        If Range("M51").Value = 0 Then
        Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 737").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.87
    Selection.ShapeRange.PictureFormat.Contrast = 0.1
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

        Sheets("1st and 2nd RSand SS Results").Select

        If Range("M51").Value = 1 Then
        Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 737").Select
```

```
Selection.ShapeRange.PictureFormat.Brightness = 0.5
Selection.ShapeRange.PictureFormat.Contrast = 0.5
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

    Sheets("1st and 2nd RSand SS Results").Select

    If Range("O51").Value = 0 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 61").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.87
Selection.ShapeRange.PictureFormat.Contrast = 0.1
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

    Sheets("1st and 2nd RSand SS Results").Select

    If Range("O51").Value = 1 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 61").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.5
Selection.ShapeRange.PictureFormat.Contrast = 0.5
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

        Sheets("1st and 2nd RSand SS Results").Select

    If Range("Q51").Value = 0 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 747").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.87
Selection.ShapeRange.PictureFormat.Contrast = 0.1
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

    Sheets("1st and 2nd RSand SS Results").Select

    If Range("Q51").Value = 1 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 747").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.5
Selection.ShapeRange.PictureFormat.Contrast = 0.5
Selection.ShapeRange.PictureFormat.CropLeft = 0#
```

```
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

            Sheets("1st and 2nd RSand SS Results").Select

    If Range("S51").Value = 0 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 758").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.87
Selection.ShapeRange.PictureFormat.Contrast = 0.1
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

    Sheets("1st and 2nd RSand SS Results").Select

    If Range("S51").Value = 1 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 758").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.5
Selection.ShapeRange.PictureFormat.Contrast = 0.5
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

     Sheets("1st and 2nd RSand SS Results").Select

    If Range("U51").Value = 0 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 752").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.87
Selection.ShapeRange.PictureFormat.Contrast = 0.1
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
Range("R14").Select
   End If

    Sheets("1st and 2nd RSand SS Results").Select

    If Range("U51").Value = 1 Then
    Sheets("Link to HYSYS-2").Select
ActiveSheet.Shapes("Picture 752").Select
Selection.ShapeRange.PictureFormat.Brightness = 0.5
Selection.ShapeRange.PictureFormat.Contrast = 0.5
Selection.ShapeRange.PictureFormat.CropLeft = 0#
Selection.ShapeRange.PictureFormat.CropRight = 0#
Selection.ShapeRange.PictureFormat.CropTop = 0#
Selection.ShapeRange.PictureFormat.CropBottom = 0#
```

```
    Range("R14").Select
       End If

        Sheets("1st and 2nd RSand SS Results").Select

       If Range("W51").Value = 0 Then
       Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 731").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.87
    Selection.ShapeRange.PictureFormat.Contrast = 0.1
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

        Sheets("1st and 2nd RSand SS Results").Select

        If Range("W51").Value = 1 Then
        Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 731").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.5
    Selection.ShapeRange.PictureFormat.Contrast = 0.5
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

        Sheets("1st and 2nd RSand SS Results").Select

       If Range("Y51").Value = 0 Then
       Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 732").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.87
    Selection.ShapeRange.PictureFormat.Contrast = 0.1
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
       End If

        Sheets("1st and 2nd RSand SS Results").Select

       If Range("Y51").Value = 1 Then
       Sheets("Link to HYSYS-2").Select
    ActiveSheet.Shapes("Picture 732").Select
    Selection.ShapeRange.PictureFormat.Brightness = 0.5
    Selection.ShapeRange.PictureFormat.Contrast = 0.5
    Selection.ShapeRange.PictureFormat.CropLeft = 0#
    Selection.ShapeRange.PictureFormat.CropRight = 0#
    Selection.ShapeRange.PictureFormat.CropTop = 0#
    Selection.ShapeRange.PictureFormat.CropBottom = 0#
    Range("R14").Select
      End If
  End Sub
```

Appendix E: Publications

Journal paper submitted to the Computers and Chemical Engineering Journal on 12 February 2008:

Integrated Approach to Chemical Process Flowsheet Synthesis

Abdullah Alqahtani [1],Klaus Hellgardt [2],Richard Holdich [1], Iain Cumming [1]

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Abstract

Over the past four decades, very few systematic procedures have been proposed for the synthesis of chemical process flowsheets. Most approaches for new designs use heuristics based on studying reaction and separation systems in isolation. This paper discusses the development of process synthesis systematic procedure and software that integrates a knowledge based system (KBS) with HYSYS process simulator, HYSYS optimizer and Aspen Icarus economic evaluator, utilising knowledge from existing industrial processes to obtain heuristic rules. A proposed generic superstructure for the synthesis and optimization of reaction-separation-recycle systems has been validated. The prototype IKBS has been applied for the selection of reactor and separator systems for the ethylene oxide and ethylene glycol manufacturing processes. A wide range of chemical reactors and separators are considered during the selection process and then elimination of alternative reactor and separator types to select the best process alternatives for simulation, optimization and economic evaluation.

Keywords: Chemical process synthesis, reactor-separator-recycle systems, knowledge based system, modular process simulation.

Conference paper in the Saudi Innovation Conference, Newcastle (2007):

Saudi Innovation conference
Newcastle upon Tyne

AN INTEGRATED KNOWLEDGE BASED SYSTEM FOR CHEMICAL PROCESS FLOWSHEET SYNTHESIS

Abdullah Alqahtani [a],Klaus Hellgardt [b],Richard Holdich [c], Iain Cumming [d]

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Abstract

Very few systematic procedures have been proposed for the synthesis of a complete chemical process flowsheet. Mathematical design and heuristics are the two main methods usually employed in process synthesis. Most approaches use heuristics based on studying reaction and separation systems in isolation. Heuristic methods alone do not provide optimal design. Mathematical programming methods are powerful but require a substantial investment of time and only a limited size of problem can be handled. The combined use of heuristics such as expert systems, databases, mathematical process simulators, equipment sizing, cost estimation and process optimizers is a potential way of exploring improved chemical process synthesis. We report on the development of process synthesis software that integrates knowledge based system with Aspen HYSYS process simulator, Aspen Icarus economic evaluator and HYSYS optimizer utilising knowledge from existing processes to obtain heuristic rules. The structure and the systematic procedure of the proposed Integrated Knowledge Based System (IKBS) are discussed. The prototype IKBS has been applied for the selection of reactor systems for the ethylene oxide and ethylene glycol manufacturing processes. A wide range of chemical reactors are considered during the selection process, and then elimination of reactors takes place at different steps until better alternatives are selected and justified. Analysis by the software suggests the use of two reactor systems and a list of suitable reactors. The list contained new and currently used reactor types in addition to the recommended reactors by industrial research. The proposed integrated knowledge based approach to chemical process flowsheet synthesis is expected to yield a cost effective design methodology for petrochemical industry.

Keywords: Chemical process synthesis, chemical reactor system selection, knowledge based system, modular process simulation.

Conference paper in the 17th European Symposium on Computer Aided Process Engineering, Romania (2007):

17th European Symposium on Computer Aided Process Engineering – ESCAPE17
V. Plesu and P.S. Agachi (Editors)

Integrated Knowledge Based System for Process Synthesis

Abdullah Alqahtani,[a] Klaus Hellgardt,[b] Richard Holdich[a], Iain Cumming[a]

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[b]*Department of Chemical Engineering and Chemical Technology, Imperial College London, London, SW7 2AZ, UK.*

Abstract

The combined use of heuristics such as expert systems, databases, mathematical process simulators, equipment sizing and cost estimation is a potential way of exploring improved chemical process synthesis. We report on the development of a software that integrates knowledge based system with HYSYS process simulator and Icarus economic evaluator utilising knowledge from existing processes to obtain heuristic rules. The structure and the systematic procedure of the proposed Integrated Knowledge Based System (IKBS) have been discussed. The prototype IKBS has been applied for the selection of reactor systems for the ethylene oxide and ethylene glycol manufacturing processes. Analysis by the software suggests the use of two reactor systems and a list of suitable reactors. The list contained new and currently used reactors in addition to the recommended reactors by industrial research.

Keywords: Chemical process synthesis, chemical reactor system selection, knowledge based system.

Conference paper in the 7th Saudi Engineering Conference, Saudi Arabia (2007):

ON THE DEVELOPMENT OF AN INTEGRATED KNOWLEDGE BASED SYSTEM FOR CHEMICAL PROCESS FLOWSHEET SYNTHESIS

Abdullah Alqahtani [1],Klaus Hellgardt [2],Richard Holdich [1], Iain Cumming [1]
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2: Department of Chemical Engineering and Chemical Technology, Imperial College London, London, SW7 2AZ, UK. K.Hellgardt@ic.ac.uk

ABSTRACT

Since the last four decade, very few systematic procedures have been proposed for the synthesis of a complete chemical process flowsheet. Mathematical design and heuristics are the two main methods usually used in process synthesis. Most approaches use heuristics based on studying reaction and separation systems in isolation. The combined use of heuristics such as expert systems, databases, mathematical process simulators, equipment sizing, cost estimation and process optimizers is a potential way of exploring improved chemical process synthesis. This paper discusses the development of process synthesis software that integrates knowledge based system with Aspen HYSYS process simulator, HYSYS optimizer and Aspen Icarus economic evaluator utilising knowledge from existing industrial processes to obtain heuristic rules. The prototype IKBS has been applied for the selection of reactor systems for the ethylene oxide and ethylene glycol manufacturing processes. A wide range of chemical reactors are considered during the selection process, and then elimination of reactors takes place at different steps until better alternatives are selected and justified. Analysis by the software suggests the use of two reactor systems and a list of suitable reactors. The list contained new and currently used reactor types in addition to the recommended reactors by industrial research. Modular simulation of reactors has been conducted to account for the non-ideal behaviour.

Keywords: Chemical process synthesis, chemical reactor system selection, knowledge based system, modular process simulation.