Inventory Estimation for Inherently Safer Design

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Abstract

Traditional approaches to safety in process plants tend to rely on 'added-on' safety measures as a means of minimising risk. During the design process the first stage at which safety is considered in detail is the HAZOP study. Inherent safety, where safety is designed into a plant has been found to have great benefits with regards to both safety performance and operating costs. In order to implement inherent safety fully it must be considered as early as possible in the design process, before decisions have been made which are fixed and costly to change. The major barrier to this is the lack of data available in the early design stage, which prevents different options being assessed for safety. The most important variable is that of inventory, as the quantity of material present is a major factor in determining the hazard posed by that material. The use of short-cut design methods together with simplifying assumptions was investigated to determine if they could be used in an inventory estimation study. It was found that such methods could be used. Although there are uncertainties in the available data it would be possible to use the methods to estimate the inventory of a process at the route selection stage of the design study. This would enable the comparison of different process routes in order to select the route that is the safest in relation to hazardous inventories and also to pinpoint which areas of a process have the greatest effect on safety. This would aid the design engineer to focus on the most hazardous items in a process plant and minimise that hazard.

Key words: Inherent Safety, design, inventory, route selection, estimation.

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1.0   Inherent Safety

Inherent safety can be described as the philosophy of eliminating hazards, rather than attempting to reduce the risks of that hazard arising. Traditionally chemical engineers have tended to accept that hazards can be controlled [26], for example through a Hazard and Operability Study (HAZOP). The plant is designed, the hazards identified and systems deployed to lower the frequency of occurrence of the hazard as much as is possible. This can be done by a range of equipment e.g. relief valves, sensors, interlocks, control systems, active safety features (such as water sprays) and passive safety features (such as insulation jackets).

Inherent Safety (IS) differs in that instead of safety being a rear end design function (i.e. after detailed design, at the HAZOP stage), it becomes a front-end design function – before any detailed design work is done. By this technique hazards can be eliminated, rather than controlled, and the plant is designed with safety foremost in mind rather than as an 'add-on'. IS is a concept that is becoming increasingly important in the process industry. It has been advocated since the Flixborough disaster in 1974 [27]. One of the main proponents of IS was Trevor Kletz who wrote the first paper devoted solely to IS design [23] and who was the first to outline the principles of inherent safety [24] [1.2].

Although knowledge of IS principles is increasing in industry – spurred on by events such as the Bhopal disaster – there is still much work to be done, and many companies are still unsure as to how to implement IS designs [16]. It is worth remembering however that inherent safety has existed since the late 19th Century, when in the Solvay process for manufacture of Sodium Carbonate every time the distillation column was charged the manhole cover at the top had to be opened and soda lime (calcium hydroxide) tipped in. This operation could lead to the escape of ammonia vapour and as such was hazardous. Ludwig Mond suggested that instead of tipping in soda lime, milk of lime (aqueous calcium hydroxide) could be pumped in instead. This design is inherently safer as it removes the hazard of ammonia escape during batch charging [27]. Nevertheless for the most part inherently safer design has been ignored by the process industry, especially with the advent of computer-controlled systems and the ability of these systems to have more precise control over the process. However, after the Flixborough and Bhopal disasters (and later incidents like Seveso and Piper Alpha) there was a

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realisation that safety systems could fail, and procedures could be overlooked. To prevent a recurrence of these disasters it was necessary to remove the hazard rather that merely make sure that the risk was minimised. Another disaster that could have been avoided if IS design had been chosen was the reactor explosion at the Chernobyl nuclear power station. The reactor design was such that it was inherently unsafe because it could be prone to an uncontrollable temperature excursion if the power output dropped to a certain level [35]. If the plant had been designed with inherent safety in mind, the Chernobyl disaster could have been avoided.

It is worth remembering at this point that there can never be any such thing as an inherently *safe* plant. Due to the very nature of chemicals hazards will always be present to some degree. The aim of IS is to eliminate the hazards as much as possible before taking steps to minimise the remaining hazards, or to compare two processes so the safer process can be selected for construction. Throughout this document there will be reference to hazards and risk. These will be defined as:

Hazard –   The danger posed by a certain deviation from normal operating conditions.

Risk   –   A combination of the consequences of a particular hazard and the probability of that hazard occurring.

When considering changes to a process plant all possible knock-on effects must be considered. For example, in an attempt to improve the safety of process plant traditional refrigerants such as ammonia and hydrocarbons were replaced with Chlorofluorocarbons, or CFCs [17]. The danger of refrigerants in the past was that they were flammable, or toxic, or both. CFCs are non-toxic and non-flammable. However today the damaging effects of CFCs on the ozone layer are well known. So whereas CFCs were inherently safer with respect to toxicity and flammability they where inherently less safe with regard to the environment. By concentrating only on safety the adverse effect on the environment was not understood until it was too late. It is for this reason that many companies such as ICI now consider Inherent SHE (Safety, Health and Environment) and not just safety, so that all possible outcomes are considered [43]. Today CFCs are being phased out, and hydrocarbons and ammonia are finding reuse in the process industry. The popular media reports on their environmental benefits, but does not mention their flammability and toxicity [29]. In this instance although returning to hydrocarbons results in inherently less safe plants, the benefit to the environment is seen to offset

this adverse effect on safety. It is therefore necessary to think of Inherent SHE to ensure that hazards are being eliminated and not merely being transformed to a different hazard that lies outside the scope of study. This is one of the major problems with inherent safety in that there will frequently be a choice between two or more options, all of which are hazardous. For example after the Bhopal disaster where thousands died following a Methyl Isocyanate leak (MIC) it was pointed out that there was a different process for manufacturing carbaryl (under the trade name Sevin) which did not require MIC (Fig 1). In the Bhopal process phosgene and methylamine were reacted together to form MIC. This was then reacted with α-napthol to form carbaryl. Another process used the same feed stocks, but instead the process reacted α-napthol with phosgene to form a chloroformate ester, and this was then reacted with methylamine to form carbaryl [25]. The second of these processes is an inherently safer option as it eliminates MIC, but it must be remembered that it not inherently safe due to the extremely toxic properties of phosgene. *Only if phosgene risk is less than MIC risk. Hazard is surely similar?*
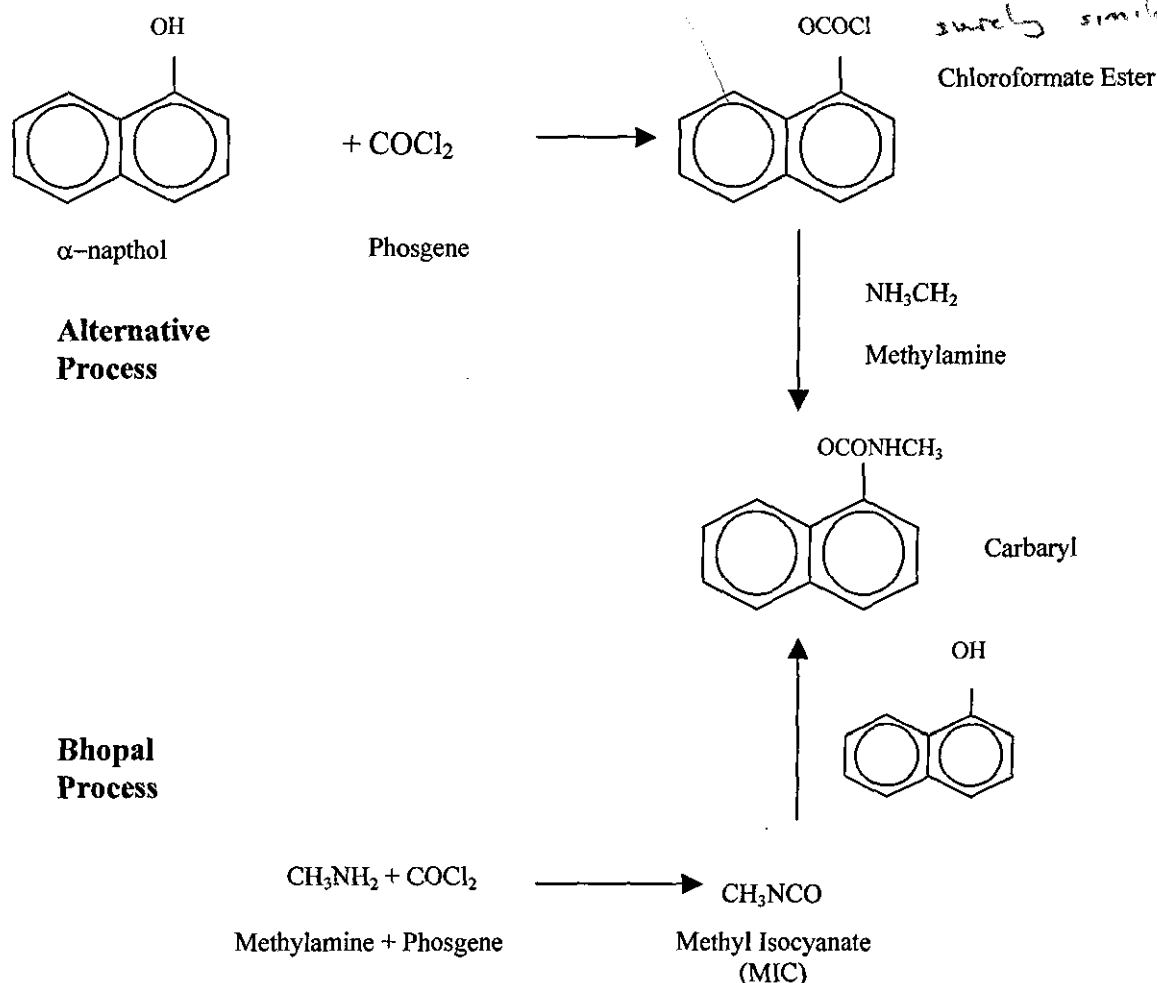
Fig. 1 - Synthesis routes to Carbaryl [25]

When inherent safety is referred to it is not enough merely to design individual items of equipment to inherently safe standards. Inherent SHE must be considered at all steps in the design process, not just the equipment design stage. Only then can we move towards the goal of maximum total inherent safety. However, this leads to the need for some way of choosing a route based on safety before design activities begin. A route will be defined in this report as the steps that must be taken to convert raw materials into the desired end product. It refers to the basic chemical and physical steps that must be taken – such as reaction and separation. A process differs from the route insofar that the process is more detailed and concerns itself with the type of reactor, heat transfer equipment, the method of separation etc. Traditionally route selection has been based on economics or logistics. The choice of raw materials can fix the route and so what is an extremely important choice is sometimes not given the due consideration it deserves. Economic route appraisals do not account for the benefits of inherent safety. For example there is less need for costly added-on safety measures, and this will lead to a lower maintenance requirement and therefore a savings in running costs [34]. Other benefits could possibly be found in reduced insurance premiums due to decreased risk of major accidents.

Therefore, there is the need to integrate inherent safety into the design process. In order to eliminate hazards alterations must be made as soon as possible in the design process. Attempting to change the design later in the process will have negative consequences in the form of higher costs and longer development times [30]. The problem can be thought of by considering the design process as being a downward slope, and the hazard as being a ball rolling down this slope. If the ball rolls off course at the top of the slope it only takes a small impulse to correct the trajectory of the ball. However, later in the process, at the bottom of the slope the momentum is so great that a very much larger impulse is required to correct the trajectory – it is much more difficult to alter the path.

1.1   Status of Inherent Safety Research

A wide range of material has been published on inherent safety. This material can be broadly categorised as inherent safety theory, qualitative methodology, and quantitative methodology. Of these the most important are the quantitative methodologies, as these would be used in the comparison of different routes. A number of methods have been developed which vary in both the variables considered in the analysis and the purpose of the analysis itself. Some methods are to be used as part of a design study whilst others concentrate on modifications to existing plant.

The design stage methods have not found use in industry because they are still at the prototype stage. There is still debate on which variables should be included, and also on the data to be used with each variable. The most important of the problems yet to be overcome is that of inventory. An expert panel showed concerns in the method of calculating inventory in several methods citing it as being oversimplified [34]. Therefore it was decided that the most appropriate way in which to advance inherent safety research was to focus on improving the use of this variable.

The need for integrating Inherent SHE analysis into the design stage has been well documented by many authors. Kletz states that it is important to consider Inherent SHE at the conceptual design stage to decide on the chemical route for production of the desired material [24]. At a later design stage to make alterations to improve the inherent safety of the plant would be very costly in terms of time and money [30]. Englund states that major constraints have been imposed on process design by the time the process has been developed and in the design stage [12]. However, there are major factors to be overcome in developing a method to assess safety at the route selection stage. Koller et al. point out that the amount and quality of data is low at this stage [31]. Therefore, assumptions will have to be made and because of the lack of data it is important to realise that any method will not give completely accurate quantitative results. This is not a major problem however as a study of the current views on inherent safety in industry carried out by Gupta and Edwards [16] found that 'the number of potential options for chemical routes...is usually low, so a qualitative approach is sufficient'. In order to assess the Inherent SHE of different process alternatives some method of quantifying their Inherent SHE is required. Khan and Abbasi gave reasons for favouring an index system for this purpose [22]:

a) An index system can be calculated very quickly providing a swift means of hazard identification

b) An index provides net scores which enable easy interpretation of results; net scores (the sum of individual scores for each variable under consideration) can be compared to get an idea of the hazards posed by the chemical/unit under study

c) Scores enable a comparison of hazards by alternatives, helping decision making

d) Index systems do not require a high level of expertise from the user.

The last point, that of index scores not requiring a high level of user expertise is very important in today's industry. Turney et al. show that only 15% of developmental or design departments have any significant awareness of the principles of Inherent SHE, and only 10% of organisations include inherent SHE in their training programmes [51]. This lack of awareness means that any method developed must be easy to use, so as not to assume that the user will have great skills or experience in the field.

This is a bit patronising — most design engineers enjoy at least average intelligence. They can't be expected to blindly apply anything.

1.1.1 Inherent Safety Index

Edwards and Lawrence developed the Inherent Safety Index (ISI) [11]. This index used parameters relating to the chemicals used in a process (inventory, toxicity, flammability and explosiveness) and to the process itself (temperature, pressure, yield) to calculate an index value indicating the inherent safety of the process. They calculated the scores for six routes available for the production of Methyl Methacrylate (MMA) to determine which was the inherently safest route. They then compared these scores to the costs of these plants to see if there was a link between inherent safety and plant costs. They found that there that there might be a relationship between inherent safety and reduced overall plant costs.

1.1.2 Inherent Safety Index 2

Heikkila developed another Inherent Safety Index (ISI2) that expanded on the ISI by including variables such as chemical interaction, equipment safety, safe process structure, corrosiveness and heat of reaction [18]. However some of these variables – those pertaining to the type of equipment involved in a process – would be unknown at the chemical route selection stage, which is the stage at which inherently safer design would have the most effect. Nevertheless the identification of variables such as heat of reaction and chemical interaction are very important steps, as these must be taken into account when considering excursions for normal plant operation.

1.1.3 Environmental Hazard Index

Cave and Edwards developed an Environmental Hazard Index (EHI), the aim of which was to determine the most environmentally friendly route to produce MMA [3]. The results from the EHI

complemented those from the ISI insofar as there was good correlation between the ranking of plants in terms of inherent safety and of inherent environmental hazard. This was to be expected as both indices are based on the inventory of the process and the hazards of the chemicals involved in the process.

1.1.4   Environment, Health and Safety Index

Koller et al. developed the Environment, Health and Safety Index (EHS), which takes into account many factors not only relating to the safety of the route but to the possible environmental damage and occupational health risks of any accident [31]. The EHS differs from indices such as ISI and the Dow Fire and Explosive Index insofar that it uses a continuous function to evaluate index scores, rather than a step function. In the ISI, ISI2 and EHI an index score will be an integer that corresponds to a range of the variable under consideration. The index is easier to use as a result, however it means that there can be a large degree of discontinuity in the score – for example in the ISI 0.1kg of a substance is indicated to be as hazardous as 250kg, but 251kg is indicated to be twice as hazardous as 250kg in terms of the inventory score alone. A small change in the variable can lead to a large change in the index score, but a large change in the variable may result in no change in index score. A continuous index, where the index score is proportional to some function of the variable in question would remove this discontinuity. It may be argued however that for a small amount of dangerous material a continuous index will give a negligible score whilst a step index will give a certain score as soon as that material exists, which could be justified because as soon as a hazardous material exists in a plant certain measures must be taken to ensure there can be no release of that material [30]. It may be that some compromise would give the best result – a continuous score that also includes a fixed penalty for a hazardous material existing in the process.

surely there is some measure of relative hazard ?

1.1.5   INSET Toolkit

The INSET Toolkit (Inherent SHE Evaluation Tool), which was developed by Turner, Mansfield et al. [52]. It was the output of a European Union co-funded research project to improve awareness of inherently safer design, encourage application of inherently safer principles and to develop a toolkit to aid inherently safer design. It was developed by a collaboration of industrial firms across Europe – AEA Technology, VTT Manufacturing Technology, INBUREX, Kemira Agro, Eutech Engineering Solution and TNO. The toolkit encompassed four stages of plant design – Chemistry

route selection, Chemistry route detailed evaluation, Process design optimisation and Process Plant design. The toolkit was designed in such a way that the user could select those tools that they felt were most necessary, as few or as many as required. In order to aid in the selection of the chemistry route they developed an index method that combined indices for fire and explosions, acute toxic hazard, health hazards, acute environmental incidents, transport hazards, gaseous emissions, aqueous emission, solid wastes, energy consumption, reaction hazards and process complexity. In order to compare different available routes they developed another tool to enable the comparative evaluation of all of these separate indices (the indices cannot simply be added as they are of varying magnitudes). The disadvantage of this is that comparing the index scores can become a difficult task, with a recommendation of a team consisting of a chemist, a process engineer, an environmental health specialist and a safety expert required to carry out the study. The toolkit does not provide weighting factors to allow the index values to be combined as such weightings may vary from one process type to another. This may lead to a widespread discrepancy in the usefulness of this toolkit, depending on the familiarisation of the users in inherent safety. It may prove that to use the toolkit effectively (certainly the index values) a degree of knowledge of inherent safety is required which is at odds with the posit that an index should not require any great degree of user expertise.

1.1.6 Dow and Mond Indices

The Dow Fire and Explosion Index (Dow F&EI) was one of the first indices developed for calculating hazard potential [11]. The Mond division of ICI expanded upon this by including variables such as toxicity and equipment type in developing the Mond Fire Explosion and Toxicity Index (Mond FET) [19]. The Dow and Mond indices were developed for the estimation of loss due to fire or explosion in a process. They require a detailed plant layout, and therefore are unsuitable for route selection.

1.1.7 Hazard Identification and Ranking Index

Khan and Abbasi developed the Hazard Identification and Ranking index (HIRA) to rank industrial sites on the basis of hazard magnitude but this too requires detailed information about site layout [21]. The use of this index is limited to modifications to existing plant, and not the design of new plant.

1.1.8   Accident Hazard Index

The Accident Hazard Index (AHI) developed by Khan and Abbasi expanded upon the HIRA by adding factors such as population density, environment and economic factors of the surrounding area [22]. As with the HIRA it is limited to use in existing plants.

Abbreviation	Name	Author(s)	Reference
ISI	Inherent Safety Index	Edwards, D.W. and Lawrence, D.	11
ISI2	Inherent Safety Index	Heikkila, A.M.	18
EHS	Environment, Health and Safety Index	Koller, G., et al.	30
EHI	Environmental Hazard Index	Edwards, D.W. and Cave, S.R.	3
Dow F&EI	Dow Fire and Explosion Index	Dow Chemicals	10
Mond FET	Mond Fire, Explosion and Toxicity Index	ICI Mond division	19
HIRA	Hazard Identification and Ranking Index	Khan, F.I. and Abbasi, S.A.	22 .
AHI	Accident Hazard Index	Khan, F.I., and Abbasi, S.A.	21
INSET	Inherent SHE Evaluation Tool	Turner, Mansfield et al.	51

Table 1 – Summary of Inherent Safety Methodologies

Table 1 summarises the quantitative methods available for assessing the inherent safety of a process. The Safety Index methods proposed by Lawrence and Edwards, Heikkila and Koller et al. would appear to be the best methods available at this point. They are quick, relatively easy to carry out, and enable the user to make determinations about the relative safety of different routes. However, they are not without their disadvantages, and detractors. As Hendershot points out they include judgement factors [17]. This can give rise to inaccuracies. For example, exactly how do you judge how flammable a material should be before the hazard is equivalent to a toxic material? Also, different users may modify the index, and adjust the weightings, meaning that it can become extremely difficult to make analysis on two different processes. Heikkila points out however that the Dow and Mond indices – two of the most widely accepted methods – also contain judgement factors [18]. It appears to be a necessary uncertainty because of the very nature of safety means that it can be hard to quantify. Also, it must be stressed that the indices are at the prototype stage. Edwards and Lawrence asked a group of experts in industry, chosen because of their experience and stature to comment on their index

and to determine what further work needed to be done on the balancing of each component [11]. There is still much work that needs to be done – weighting of the hazard, deciding on variables to be included in the index, and most importantly ensuring that industry can agree on the methods in the index – before the index can be accepted as a design tool. The indices at present are the first step in the journey, not the destination.

1.1.9   Barriers to Inherent Safety

The research has also shown that there are numerous barriers to be overcome to achieve inherently safer plant. As previously stated the field of inherent safety was pioneered in the 1970's after the Flixborough disaster. Yet today the subject still has not reached its full potential. Plants are still designed using the same old methodology. Inherent safety – for all its advantages – still has not been fully adopted by the chemical industry. There are many different reasons for this:

Lack of knowledge and enthusiasm from recent graduates.

From recent experience I can say that the majority of engineering students do not have a great deal of interest in safety. This is extremely worrying, but talking to many of my class-mates and co-workers most did not want to pursue safety to any great extent, instead preferring to concentrate on what they felt as 'real' engineering – solving process problems. Safety is not an issue that can easily be broken down into numbers, and calculated in the same way one would calculate e.g. the flow regime in a pipe. This was a position noted by Kletz who stated "many engineers are happier carrying out calculations than handling ideas"[28]. Many of my classmates with whom I graduated had no interest in safety, and instead see Health and Safety matters as being of concern only to the safety engineer – with their only area of concern in safety being HAZOP. It can only be hoped that their attitude will change with industrial experience, but it is still a very big barrier. Also, many universities do not teach inherent safety and so those graduates taking up employment in the process industry have no knowledge of inherent safety. This problem is exacerbated by the lack of training in inherent safety offered by companies. Turney et al. found that only 10% of organisations included inherent SHE in their training programs, and it therefore becomes very difficult to get recent graduates interested in the ideas and goals of inherent SHE [51]. These people will become the plant managers of tomorrow. As Kletz pointed out, inherent safety must be accepted in the modern syllabus [28]. But until there is a

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widespread realisation that engineering cannot always be broken down into a series of equations this will be very slow in happening.

Business Structure

Each chemical company usually breaks down its accounts into individual plants – each plant has its profit/loss account [28]. This means that each plant can be seen as a competitor within the company – each plant manager wants their plant to be the most profitable. This has unfortunate consequences. Individual plants are unwilling to try new methods or new technologies for fear that if these fail, the losses would be great – reflecting badly on them. Therefore it becomes a leap of faith to implement new techniques and technologies. The only way around this is if the company as a whole meets the cost of doing something new, rather than the individual plant [28]. This however would involve a complete restructure of company business – with instead of costs being met on a plant basis, costs being allocated on a function basis i.e. centralised design sections.

Resistance of the industry to change

One of the main trends of the industry is the relatively small number of chemical engineers who have done post graduate research compared to, for example, chemists [28]. The effect of this is that the industry is wary of new ideas and is resistant to change. This is demonstrated by Kletz who states that out of 17 projects put forward to management all but 2 had as a major benefit that they required no innovation – a worrying state of affairs because it shows exactly how management is unwilling to accept innovative ideas [28]. Gupta and Edwards found that companies were too conservative and less likely to take risks in a tighter financial climate, even though many companies have found that inherently safer design does not result in any major increase in cost [16]. If the inherently safer design is performed early in the design process the cost is minimal and many people have found costs savings in inherently safer design. Many companies however do not seem to realise that inherently safer designs may reap financial benefits.

Lack of Tools and Methodologies

There are no tried and tested tools for estimating inherent SHE in plants. Those methodologies so far developed are still at the prototype stage and more tests must be done to ensure

consistency across a wide range of plants such as Petrochemicals, bulk chemicals, speciality chemicals, pharmaceuticals etc. before any methodology can be accepted by the industry.

Before inherent safety can fulfil its potential these problems must be overcome. The most important one is to make young engineers aware of inherent safety. By getting graduate engineers interested in the subject the impetus and enthusiasm would make the other factors less important - teaching the plant managers of tomorrow about the topic this would overcome the resistance of the industry as a whole. This is a catch-22 situation however. To a certain extent universities prefer teaching methods rather than ideas. Until there is a methodology for determining and comparing inherent safety progress will be slow. Only by making advances will the majority of universities and students become interested in inherent safety. The EPSRC (Engineering and Physical Sciences Research Council) safety network can accelerate this process. Other projects like the recent INSIDE project will also help to improve the awareness of inherent SHE.

In order to overcome these barriers steps are being taken. More researchers are devoting their efforts to inherent safety. Gupta and Edwards [16] found from their questionnaire that many of the respondents were very interested in inherent safety and will be including inherently safer design (ISD) in lectures at their institutions. However it must be noted that most of the respondents were already aware of inherently safer design and so may therefore not be part of the majority – if only 10% of companies have training in inherently safer design it can be inferred that many engineers have little or no knowledge of it. So whereas the results of the survey are promising they may not be indicative of the industry as a whole. Professional bodies (such as IChemE) should make ISD part of their approved degree syllabus to improve knowledge in graduates and increasing awareness of ISD principles to everyone involved in the design process, from chemists to managers and accountants [16].

Legislation could act as another spur to making inherent safety more accepted in industry. Fitzgerald et al. reported on how the Worst Case Scenario of the Risk Management Programs (a requirement of the Clean Air Act in the United States of America) allows companies to only consider the mitigating effects of passive measures – forcing companies to consider inherently safer design which does not require a great number of active control systems such as interlocks to improve process

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safety [13]. In the UK the COMAH (Control of Major Accident Hazards) legislation requires

demonstration of ISHE in the design process. By forcing companies to consider inherent safety the

increase in understanding of the technique can be accelerated. However, companies should not look at

ISHE as something they must do to comply with law, but rather as something that they should do to

improve performance because it is only with the requisite enthusiasm that the full benefits can be

obtained.

1.2   Inherent SHE Principles

The principles of inherent safety are the ways in which inherently safer designs can be

achieved. They are not equal in effect, so different ways of improving inherent safety will be more or

less efficient. Kletz [24] stated that there are principles of inherent safety. These are:

1)   Elimination

2)   Intensification

3)   Substitution

4)   Attenuation

5)   Simplification

6)   Limitation of Effects

1.2.1   Elimination

Elimination is the best possible method of removing hazards. It is always better to remove,

rather than attempt to control, a hazard. This is the same principle as applies to the use of Personal

Protective Equipment (PPE). PPE is always the last resort, after all other methods of eliminating the

hazard have failed. In the same way control systems should be considered as being the last resort, and

elimination as being the key goal.

Edwards and Lawrence [11] state that 'elimination has the greatest benefit when the chemical

reaction path is being chosen…. changes can be made to the choice of reactants and reactions before

the design becomes too advanced'. The most compelling example that might have been avoided by

elimination is the Bhopal disaster. A quantity of Methyl Isocyanate (MIC) that was being kept in

intermediate storage, from which a large volume was released killing approximately 4000 people [35].

Many more people were injured – the number varies between sources, and may never be known due to conditions in the area. The affected people lived in conditions where we cannot know how many people were in the vicinity of the plant. Kletz [25] gives examples of how the reaction path could have been altered to avoid having any MIC in the plant (and thus, none to leak). The process he described is an economically viable process – the process is used in Israel. It is worth recognising however that the Israeli plant also contains phosgene so it is not by any means an inherently safe plant – but it is inherently *safer*. We must also remember that it was not necessary to store the MIC at Bhopal. It was done for convenience rather than for process requirements.

1.2.2   Intensification

If elimination is impossible then reducing the quantity of hazardous material should be a major consideration. This can be done by a variety of methods – changes in reactor design, improving mixing, improving heat transfer, or through catalysts (it must be noted however than some catalysts are toxic – an analysis would have to be performed to ensure that there is a benefit to reducing inventory at the cost of bringing in another toxic material). More efficient separation techniques can alleviate the need for large columns (and hence large inventories).

The most widely quoted example of intensification is the manufacture of nitro-glycerine [26]. In the 1950's the process was carried out in a 1000kg batch reactor. By replacing the batch reactor with a continuous reactor similar to a gas ejector the residence time was reduced from 2 hours to 2 minutes. This reduced the inventory from 1000kg to 1 kg.

Considering intensification early in the design process at the route stage is most beneficial as inventories can be reduced without requiring the re-design of process equipment [34].

1.2.3   Substitution

If it proves impossible to minimise the amount of hazardous material, it is necessary to consider using a less hazardous material instead. Instead of using flammable oils as heating fluids in heat exchangers steam could be used instead. As stated earlier however we must be extremely cautious

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about using 'less-hazardous' materials – using CFC's instead of traditional refrigerants such as ammonia is an example of substitution that failed due to the unknown hazards of CFC's.

1.2.4   Attenuation

If hazards cannot be removed through the preceding methods then we must look at ways to alter the processing so that it is more difficult to achieve an unsafe state, so reducing the risk. For example, if a flammable material must be used altering the process so that it operates away from flammable limits will reduce the risk.

An example of attenuation is the storage of chlorine. Instead of storing it under pressure it should be stored at atmospheric pressure with cooling to ensure that the material remains as a liquid. This ensures that if there is a failure of a vessel then the loss is minimised because there is no driving force for evaporation. If there is a leak, the evaporation of Chlorine will cool it further and minimise the escape. Under pressure there will be a pressure gradient, which will force the chlorine out. Refrigeration also reduces the vapour pressure, reducing the driving force for a leak [12]. Again, it must be noted that this is not inherently safe as a hazard can arise if the refrigeration system fails.

1.2.5   Simplification

Chemical plants are by nature complicated. In order to improve safety and facilitate easy operation the traditional method has been to add control loops, interlocks, trips, alarms and protective equipment. This gives rise to a bigger requirement for regular maintenance and therefore increases the risk of human error. As previously stated, these measures should be a last resort and not first choice for tackling hazards in the process plant. By making design changes – sometimes very simple ones, sometimes more ingenious ones – we can remove the need for unnecessary equipment. Kletz [26] gives a chain of events, which leads to unnecessary complications:

1) A manhole cover that can leak flammable material.

2) A 4m vent was added, to protect passers-by.

3) The material was flammable, so a flame arrestor was necessary.

4) The flame arrestor needed to be cleaned and maintained, so an access platform became necessary.

5) Health and Safety requirements lead to a handrails being added to the platform.

A more effective solution would be to prevent the leak by use of better seals.   *would it ?*
Is the visible flame
arrestor less reliable
than a hidden
seal ?

1.2.6   Limitation of Effects

If a hazard is still present, even after all the above strategies have been employed there are still

methods available to reduce the size of the potential hazard.

Consider the reaction:

A   +   B   ⟶   D

C   +   D   ⟶   E
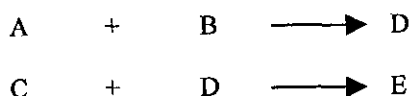
Where E is the desired product, and A, B and C are raw materials, and D is an intermediate.

However, suppose that :

A   +   C   ⟶   F
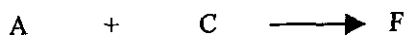
Where F is a very toxic material. The process must be defined such that A and C can never

react. If there is only one reactor there is a possibility that C could be added instead of B to react with

A. This can be solved by having two reactor vessels – in the first only A and B can react (it is

impossible to add C). In the second vessel only C and the product from the first reactor can react. The

chemicals cannot be added in the wrong order, so the risk is reduced.
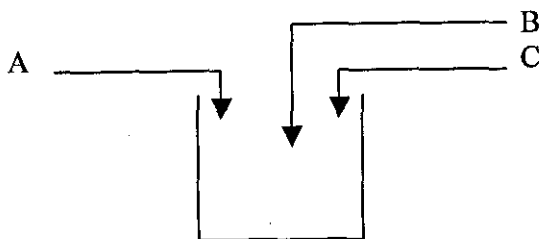
Inherently unsafe – C could be added instead of B if the wrong valve is opened.
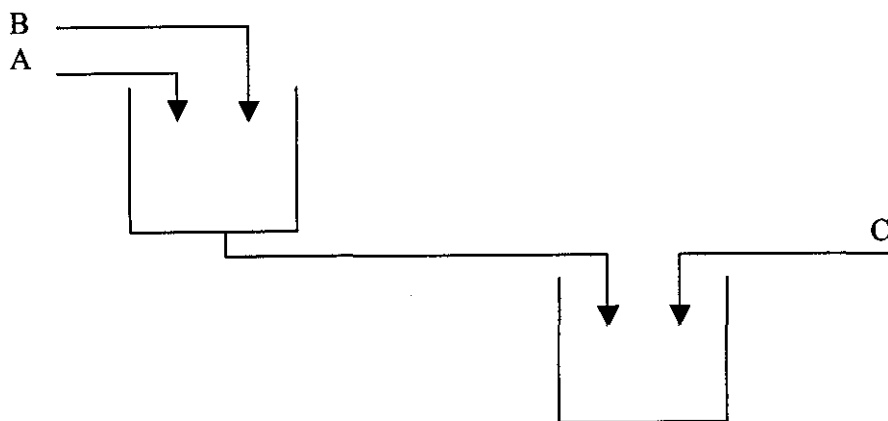
This is inherently safer, as it minimises (but does not eliminate) the risk of C being added to directly to A.

1.3 Parameters Considered in Index Methods

Index methods require the use of different variables to determine inherent safety. Heikkila and Lawrence disagree on some points, but are in agreement on the inclusion of:

1) Pressure

2) Temperature

3) Flammability

4) Explosiveness

5) Toxicity

6) Inventory

Also, Heat of reaction – included by Dr. Heikkila in her index [18] – would appear to be a very important variable, a position shared by Kreysa [32].

The data on some of these variables – Toxicity, Flammability, Explosiveness and Heat of Reaction – are usually relatively easy to obtain or calculate (although it should be recognised that this is not always the case). Indeed, many books and other literature have been written containing this data. Pressure and Temperature data should also be easy to obtain – this information should be available at the conceptual design level, before the flowchart stage.

Inventory, however, is different. At the flowchart stage we do not know how much chemical material will be in the plant. A mass balance only gives the throughput, not the equipment size. This is

inventory is normally calculated → loading calculated

a problem with current design packages – they do not calculate inventory, because there has never been

Almost always want RT = $\frac{V}{F}$

any need for them to calculate inventory [46]. Traditionally chemical engineers have accepted that a

plant will hold whatever it holds, and that the inventory can be controlled. There is still a belief that

large inventories are not dangerous, even after disasters such as Flixborough and Bhopal [28]. The

method used by both Lawrence and Heikkila for inventory estimation is very simplistic – the

throughput is calculated, and a hold-up time of 1 hour is assumed. From this the inventory in each

vessel is calculated. It can be immediately seen that although the method is very quick and very

simple, it is also very inaccurate. For example, consider reactor vessels where there is a choice of

CSTR and plug flow reactor. Using this method the same inventory would be calculated for both –

which is illogical and demonstrates the drawback of the method. In Lawrence [34] a panel of experts

were asked to commentate on ISI. All 7 experts who responded had some problem accepting the

method used for calculating the inventory– either with the actual calculation, or with the scoring. One

expert made the observation that for the highest inventory in the scoring table (which would only be

found in a very large oil storage facility) a throughput of 300 million tonnes per year would be required

– again demonstrating the inaccuracies of the method. Without any method for calculating inventory

there can never be any method for determining safety before the detailed design stage. We cannot hope

to minimise the inventory of hazardous materials if we don't know what the inventory is [28].

The importance of an improved method for calculating inventory was also noted in the

development of an Inherent Environmental Hazard Index [3]. Therefore, it has been decided that the

main focus of this research should be the development of a method for calculating inventory in process

plant at the route selection stage of process design.

1.4 Foreseen Problems

Time is a critical factor in design. Due to marketing pressures the time taken from identifying

the need for a process plant to start-up should be an absolute minimum. If the design takes too long the

company could miss its marketing window [28] with serious financial consequences.

Therefore time is a key factor in developing a method. The inventory is not calculated for one

route only, but for as many different routes that are feasible for synthesising the desired product. A

complicated method would never find use because the time taken to perform the analysis would be too great. One of the advantages of I.S. is cost reduction [14]. By developing a time consuming method this advantage us nullified. Therefore, the method must avoid unnecessary complexities.

However the method must be accurate enough that the results obtained are useful for the purpose for which they are to be employed, although it be must recognised that due to the information available at a very early stage in design there is a limit to the accuracy. It will be impossible to differentiate between e.g. 30 tonnes and 32 tonnes. The method will only enable a determination of a 'ballpark' figure. One of the main issues in this project will therefore be determining how accurate is accurate enough. An inaccurate method is useless, as the results will bear little or no relation to the actual quantities in the plant. Accuracy though is inextricably linked to time. An accurate method will be a time consuming method. A trade-off between speed and accuracy will have to be made.

It may prove that a beneficial side effect to the calculating of inventory will be the improvement of the accuracy of early cost forecasts. By estimating the inventory we can make a better estimate of equipment size, and henceforth the cost of the equipment.

no you are estimating size → inventory

1.5   Methods to Predict Inventory

There are two ways to progress with inventory estimation:

1)   First Principles

2)   Rule of Thumb

First Principles

Design equations for each item of equipment will be available – they are well documented in literature, with many standard texts available, for example the Coulson and Richardson Chemical Engineering series. From calculating vessel sizes it would not be too difficult to calculate inventories – there are different design calculations available for calculating liquid hold up on e.g. different types of plate in a distillation column.

However, these calculations are developed using the data that would only be available at the detailed design stage. This information is not available in the early stages. Also, these methods could be too time consuming considering that the design would have to be done for every item of equipment in each possible route. Any method must only use the data available to the engineer at the early design stage together with assumptions that compensate for the lacking information.

The question has to be asked – could we compensate for the unavailable data? Would the assumptions be good enough? It may prove that by attempting to derive equations the method is too inaccurate because of incorrect assumptions or that the equations are inconsistent – they work in some instances, but when the assumptions break down the results become too inaccurate.

Rules of Thumb

This operates on the principle that empirical data could be used to develop methods for predicting the required information. Companies have data on inventory quantities in different process equipment. Using this information it may be possible to develop a method to determine inventory by scaling up or down. The hope is that by using a method like this accuracy would be improved because we would be working with known inventory sizes – there would already be a starting point. The disadvantage to this is the amount of data required. A large quantity of data from many plants would be required to develop a method, as well as from a wide variety of different types of process to ensure that any method is not restricted to only one type of plant. For example a large number of data sets would be required from refineries, bulk chemicals, fine chemicals and pharmaceutical plants in order to develop a universal method.

1.6   Inherent Safety Summary

The experience of disasters such as Bhopal and Flixborough has demonstrated the importance of inherent safety in the process industry. The technique of attempting to control and minimise risk has been shown to be insufficient in preventing major disasters. Although inherent safety will not prevent accidents because chemical plants will always involve the processing of hazardous material it will reduce the total hazard, further reduce risks and give an overall cost benefit.

Although the importance of inherent safety is accepted by the majority of engineers in the process industry the use of inherently safer techniques is limited. There are many reasons for this, the most important being a general lack of knowledge of how to implement inherently safer techniques. A working methodology is important, as it would give engineers a well-defined set of tools to use that would compensate for the lack of detailed knowledge on inherent safety.

The most appropriate stage to conduct an inherent safety assessment is at the route selection phase of the design process. An index method is the best method for use at this stage due to its ease of use, speed and the ability to compare different routes. Different researchers have developed a variety of methods however none have found use in industry due to uncertainties in data. A key variable in assessing the safety of a process is the amount of hazardous material present, yet currently this is calculated on the basis of an assumed hold-up time. This can be seen to be insufficient as it gives rise to large inaccuracies and does not take into account routes that may have more intensive technologies, for example certain reactor vessels.

There are two ways to develop a method for estimating inventory. One is to work from first principles and using short-cut design methods to estimate the major dimensions of equipment items and calculate the inventory from this. The other approach is to obtain inventory data from existing plants and attempt to correlate this inventory with throughput, equipment type and chemical properties. Although each has advantages and disadvantages a method based on short-cut design methods would use techniques already familiar to engineers. This would aid in the use and uptake of any method. Also it may be difficult to obtain sufficient data on inventory from existing plants with the effect that there is not enough data on which to base statistical conclusions.

2.0   Inventory Estimation in Process Plant

The first step in calculating inventory is to decide what equipment will be required in the process, as the choice of equipment will have a large effect on total inventory. For example the choice between a stirred tank reactor and plug flow reactor, or plate distillation versus packed column will influence greatly the final result. Therefore a set of rules must be developed to help select process equipment.

There are many different types of equipment in process plant and many different technologies that can be used. The requirement is for a simple set of rules that can be used at a preliminary stage, because one of the most important criteria is that the method is quick, easy to use and does not require specialised knowledge. Therefore, we should focus only upon a small range of technologies in each category that are the most likely to be found in the process industries. It must also therefore be recognised that the particular equipment type that is assumed here will not necessarily be the same that we decide upon in the detailed design step.

It must be noted that this section is intended as a guideline. Some routes may require specialised technology not considered in this section. In such instances the engineer must decide if it is feasible to carry out a simplified design on this equipment. If it is not then the equipment must be excluded from the study. It may be appropriate in such circumstances to consider another similar equipment type that can be easily designed, or else there will be an underprediction in the total inventory estimated. If this occurs then the method would fail as the results would not be consistent – excluding a significant equipment item from a study would unfairly bias the results towards one particular route.

2.1   Reactor Vessels

Reactor vessels are probably the most difficult to make assumptions for. This is because the design of the reactor and the operating conditions depend greatly on the result of laboratory scale experiments.

The type of reactor used firstly depends on the type of process – batch or continuous. For batch systems stirred tank reactors are by far the most commonly used, for two main reasons [55]:

1) They are already plentiful in industry – therefore to keep development time for new processes to a minimum companies develop their new processes to use this existing technology.

2) Chemists almost invariably use stirred beakers in laboratory scale experiments to determine reaction parameters. It is faster to scale this up to stirred tanks, again minimising development times.

It is worth recognising at this point that there are a variety of technologies that can be used for batch reactor systems that may have an advantage over stirred tanks in both efficiency and lower inventory for certain applications' Such technologies are being researched as part of the BRITEST project (Batch Route Innovative Technology Evaluation and Selection Techniques) [55]. However there are no heuristics for selecting these reactors and all design must start at the laboratory stage. It is important to realise that these technologies could be invaluable for inventory minimisation (replacing a stirred tank reactor with a static mixer can result in a $1*10^6$ reduction in reactor volume [55]). The BRITEST project could prove invaluable in the field of inventory reduction, and much attention should be paid to its progress.

2.2 Gas-Gas Separation

According to Douglas [9] the most common choices for vapour recovery systems are:

1) Condensation – high pressure, low temperature or both

2) Absorption

3) Adsorption

4) Membrane separation

5) Reaction systems

For gas-vapour separation the two most widely used technologies are adsorption and absorption [48]. Therefore, for our preliminary design it will be assumed that the technologies used will be condensation, absorption and adsorption since these are the technologies most widely found in the process industry. Also, there is a great deal of information available for the short cut design of such

vessels whereas such information is harder to come upon for membrane processes [9]. Again, it must be stressed that technologies such as membrane separation are finding widespread use in industry and the use of such technologies must be carefully considered at the detailed design stage.

The choice of which technology to use from condensation, absorption and adsorption is left to the individual engineer bearing in mind stream composition and properties – the engineer should use their best judgement.

2.3   Liquid-Liquid Separation

There is a large selection of technologies available for liquid-liquid separations. The technology used depends on the properties of the liquids to be separated. Firstly, it can be said that there are two types of liquid-liquid solutions, miscible and immiscible. For immiscible solutions (for example, oil-water) a decanter could be used to separate the light and heavy liquids.

For miscible solutions other technologies must be considered. Distillation is one of the most common separation technologies used in the chemical industry, and should therefore be one of the first things considered. The use of distillation depends on the relative volatilities of the solution to be separated. The use of distillation is assumed if the relative volatility is greater than 1.1[9].

There are two main types of distillation schemes – simple distillation, and complex distillation. Simple distillation is where there is only a top product and bottoms product, in complex distillation there is side-stream removal [9]. The design of complex columns is more intensive than that of simple columns. Many short-cut design equations available are for use only in simple distillation columns – the addition of separate side streams means that these equations cannot be used. This introduces a complication into any method. To keep the method as uncomplicated as possible the use of simple distillation will be assumed. This will give a higher number of columns, and hence a higher inventory. It is better to overestimate inventory than underestimate as it gives an added safety factor.

The sequencing of columns must also be considered. There are a number of different criteria that must be taken into consideration when deciding the order in which materials should be recovered, for example corrosiveness, removal of light fractions, ease of separations, degree of recovery required, cost of separations. Due to the number of different factors column sequencing can be a complicated topic and one which would require a great deal of research. The purpose of this project is inventory estimation and research into column sequencing is beyond the scope of this project. The design engineer should be familiar with different techniques that can be used for the sequencing of columns, either published in literature or using in-house tools. Therefore because of the complexity of the subject matter the sequencing of columns should be left to the individual engineer. For further reading Tedder and Rudd [50] have published a list of heuristics for distillation column sequencing.

Azeotropic systems require a different separation technology. The design of azeotropic distillation columns, or reactive distillation columns is more complex than simple distillation columns (For ternary azeotropes there are 113 types of residue curve maps [9]. The number of different possibilities grows very rapidly as the number of components present in the mixture increases).   To avoid unnecessary complication some other technology must be used, such as liquid-liquid extraction.

For relative volatilities below 1.1 distillation cannot normally be used. This is because the distillation becomes very expensive – a large reflux ratio is required, resulting in larger columns and larger condensers and reboilers. The increase in capital and running costs means that an alternative procedure must be found. Douglas [9] states that the following technologies are available when distillation cannot be used:

Extraction

Extractive distillation

Azeotropic distillation

Reactive distillation

Crystallisation

As discussed above, azeotropic distillation will not be considered at this stage due to the complexity of the design problem. Likewise, reactive distillation would require much laboratory experimentation and would be a very complicated design. As this stage we would not be able to afford the laboratory time

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necessary and therefore would not be able to confirm this as a suitable technology. Crystallisation depends on the difference in freezing points, rather than volatilities. Freezing the solution and centrifuging to separate the liquid and crystals, often using a recycle, can achieve the desired separation.

Extractive distillation requires the addition of a component that will alter the vapour-liquid equilibrium, followed by distillation. For example, HNO_3 and H_2O can be distilled by addition of H_2SO_4. By distillation pure HNO_3 can be removed overhead from the first column, pure H_2O from the second column, and the H_2SO_4 recycled from the bottom of the second column back to the first column [9]. Extractive distillation has the same drawback of reactive distillation – the laboratory time required to determine if there is a substance that can alter the vapour-liquid equilibrium to the extent that we require.

Extraction requires the addition of a solvent to a liquid stream to separate the components. For example, by adding solvent S to a stream containing B+C, in an extraction vessel two product streams B+S and C+S (+B) are obtained. Distillation is used to separate the components in these streams – so we obtain pure B and pure S from the first stream, and from the second stream we obtain pure S and a stream containing C (+B). If we require pure C, or if the amount of B in the stream is such that it must be recovered, then we must carry out B-C distillation. However, the amount of B has been greatly reduced and therefore the required degree of separation has been greatly reduced. This can mean that this B+C separation becomes feasible [9].

Therefore, it seems that the most appropriate methods available at this stage for relative volatilities below 1.1 are crystallisation and extraction. The exact option chosen will depend on the physical properties of the materials in solution.

For liquid-liquid extraction however, there are a number of different technologies that can be used. For example there are staged contactors, and differential contactors. Staged contactors require the contacting of the liquids, allowing equilibrium to be reached, and then mechanical separation of the liquids. This corresponds to mixing the liquids, and then settling the dispersion that is obtained, so that

staged contactors are called mixer-settlers. In batch operation, the mixing and settling can be done in the same item of equipment. In continuous processes however the mixing and settling is usually done in separate vessels (it must be noted however that this is not always the case, and that sometimes one vessel may be used in continuous processes).

Differential contactors are those in which multistage countercurrent contact between two insoluble liquids occurs. This contact occurs without complete separation of the liquids from each other between stages. The liquids remain in continuous contact with each other throughout the equipment, and are separated at the end of the equipment. Differential contactors therefore do not require separate equipment for the separation of the vessels, and only one item of equipment is required. It is therefore assumed that differential contactors will be used.

There are different types of differential contactors that can be used. Perry [42] gives several different types of equipment – non-agitated equipment, agitated equipment that uses rotating elements (discs or impellers) or agitated equipment that uses reciprocating plates, or pulsing of the liquids.

Whilst these have advantages and disadvantages as to their use we are limited insofar as we desire those equipment for which we can determine a relatively simple method for determining inventory. Some of these technologies show great potential for inventory reduction – for example, pulsed columns. However, pulsed columns have found use almost exclusively in the atomic energy industry for the separation of metals from solution [42]. Therefore their use cannot be assumed, as we must only use those items of equipment that are most likely to be found in process plant. However, we must keep such technologies in mind for ways in which to reduce inventory. Therefore, by selecting those items of equipment that have found widespread use in the process industry and also prevent unnecessary complications we arrive at a choice between two types of equipment – packed columns, or plate columns. The main advantages and disadvantages of each type are [48]:

1. Plate columns can handle a wider range of gas and liquid flow rates than packed columns.

2. Packed columns are not suitable for very low liquid rates.

3. Plate efficiency can be more accurately determined than the equivalent for packing.

4. Plate columns can be designed with greater assurance than packed columns. There is always doubt that good liquid distribution can be maintained throughout a packed column under all operating conditions, especially in large columns.

5. It is easier to make provision for cooling in plate columns.

6. If the liquid causes fouling plate columns can be more easily cleaned by installing manways on the plates. However, with small diameter columns it may be more economical to use packing and replace the packing when it becomes fouled.

7. For corrosive liquids, packed columns will usually be cheaper than plate columns.

8. Liquid hold-up is appreciably lower in packed columns. This means packed columns are preferable when dealing with hazardous materials.

9. Packed columns are more suitable for foaming systems.

10. Pressure drop per equilibrium stage can be lower for packing or plates; packing should always be considered for vacuum columns.

11. Packing should be considered for small diameter columns (<0.6m), where plates are expensive and difficult to install.

Ultimately, the choice should be left to the design engineer bearing in mind the properties of the system involved.

Summary

For immiscible systems, use a decanter

For miscible, non-azeotropic systems with a relative volatility of greater than 1.1, use simple distillation

For miscible systems with a relative volatility less than 1.1, or an azeotropic mixture, use crystallisation or liquid-liquid extraction – either packed columns or plate columns.

2.4   Gas-Solid and Liquid-Solid Separation

The major problem with selecting equipment for these tasks at a preliminary stage is that one of the major criteria for selection of equipment to remove solid particles is particle size. At a preliminary stage we may not know what the size distribution of the particles will be, so there is insufficient data on which to make an assumption. Therefore it will be very hard to calculate solids

hold-up. It may prove that for gas-solids separation equipment the inventory is negligible, as the solids hold-up will be negligible compared to the inventory of the solids storage tank. Due to the low density of gases the mass inventory of the fluids will also be low.

2.5   Heat Transfer Vessels

The need for heating or cooling process streams should be known from a flowchart showing the process route [9]. From this we should be able to predict the number of heat exchangers necessary. There are many types of heat exchangers found in the chemical industry, each having different uses. Shell and Tube heat exchangers are most widely found in the chemical industry, and can be used for most applications [48]. Therefore the use of Shell and Tube heat exchangers will be assumed, as these are the heat exchangers we could most reasonably expect to find in process plant. The largest obstacle is the design of cooler-condensers, by nature a complicated, time-consuming procedure. Also, vaporisers and condensers will require careful consideration in inventory estimation, due to the large difference in vapour and liquid densities. The assumption as to liquid-vapour ratio in these vessels will have a very large effect on the total mass inventory.

3.0   Calculation of Inventory in Equipment Items

It has been decided to use short-cut design methods to size equipment items and calculate inventory. Rule-of-thumb methods, derived through statistical analysis of inventory data from existing chemical plants would require too many data sets to enable meaningful conclusions to be made. Companies would be resistant to sharing such data due to security concerns and commercial sensitivity. This section presents the methodologies used to calculate the inventory of major equipment items.

3.1   Reactor Inventory

The reactor is an item of fundamental importance in any process scheme. The choice of reactor and reaction conditions will determine the flowrate and stream composition through downstream vessels. The reactor is often an inherently unsafe item of equipment, due to a variety of factors relating to the reaction itself such as the heat of reaction, temperature, pressure, runaway temperature (and how close the reactor operates to runaway temperature), side reactions and unintended reactions that might occur upon deviation from standard operating procedures.

The choice of reaction route may have a large effect on the type and size of the reactor. Whether or not the reaction is homogenous or heterogeneous will result in not only different technologies but also very different design methodologies. With homogenous reactions the choice of reactor is usually limited to batch reactors, Plug Flow reactors or Continuously Stirred Tank Reactors (CSTR). Normally the choice as to which reactor to use will depend on the choice of laboratory test by the chemist initially examining the reaction, whether or not the test was carried out in a length of tube (plug flow) or a stirred beaker (CSTR).

In heterogeneous reactions the kinetic rate is only one factor in the overall rate of reaction, and may not be the rate controlling step. The movement of reactants from one phase to another must also be considered in the overall rate equation – so there will be a combination of kinetic rate and mass transfer rate. This adds a level of complexity to any inventory estimation procedure for heterogeneous systems. Also, the choice of reactor vessel will be very different, depending on the phases present in the reaction. Due to the large differences in the mechanisms involved and the operation of the different technologies it must be understood that there can be no one simple method for estimating the inventory

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in heterogeneous reactor systems. The difference in the methods of design of vessels for different types of contacting – for example liquid-liquid, or gas-solid – precludes any one estimation procedure adequately encompassing all technologies. Ways to proceed around this difficulty will be discussed later in this section.

3.1.1   Design of a Reactor

The first step in a design of a chemical reactor is to collate all available information from the literature. Encyclopaedias of chemical technology may prove invaluable for giving details about reaction pathways and reactor conditions. The type of reactor, rate equation and economic conversion may be found in these texts. If not, then the required variables may be found in research journals or patents. Another source of data may be records from existing plants owned by the company concerned that involve the same reaction. The first step should be therefore to determine what data is available and what data is required to estimate the inventory.

3.1.2   Reactor Conversion

The reactor conversion is one of the most important variables, as it will determine the size of the recycle. A large conversion will result in a low recycle, and vice-versa. The danger of a low conversion can be seen in the Flixborough disaster, where with a conversion of approximately 6% per pass there was a very large recycle. When there was a rupture in the reactor chain the magnitude of the flowrate led to a large escape with catastrophic consequences. A large recycle will also lead to large flowrates – and hence inventories – in downstream equipment.

If there is no data pertaining to conversion in the literature then the conversion can be calculated from a thermodynamic analysis of the reactions taking place. The equilibrium constant, k_e can be calculated using the Gibbs Free Energies at the reaction conditions, and from this it is possible to calculate equilibrium conversion, or in the case of non-equimolar gas phase reactions calculate the dependence of equilibrium conversion on pressure. It must be recognised that this may be different from the reactor conversion in the detailed design. The actual conversion will depend on the equilibrium conversion, side reactions, reversible reaction and economics [9].

Calculation of Equilibrium Conversion

It can be shown that the equilibrium constant, K can be found from the equation [42]:

$$\prod_i \hat{a}_i^{\nu_{i,j}} = K_j$$

Where $\hat{a}_i$ = Activity of species i in solution, dimensionless.

$\nu_{i,j}$ = Stoichiometric number of species i in reaction j.

$$K_j = e\left(\frac{-\Delta G_j^0}{RT}\right)$$

ΔG_j^0 = Gibbs-energy change of reaction, J/mol

R = Universal Gas Constant = 8.313 J/mol^{o}K

T = Reaction temperature, K

For gas-phase reactions, $\hat{a}_i = y_i \hat{\phi}_i P / f_i^0$

It can be shown that if it is assumed that the phase is an ideal gas, the equilibrium equation simplifies

to:

$$\prod_i (y_i)^{\nu_{i,j}} \left(\frac{P}{P^0}\right)^{\nu_j} = K_j$$

Where P = Reaction pressure

P^0 = Standard state pressure (100kPa), expressed in the same units as P.

y_i = Vapour phase mole fraction of species i, dimensionless.

$\hat{\phi}_i$ = Fugacity coefficient of species i in solution, dimensionless.

f_i^0 = Fugacity of species i at standard state, kPa

For liquid-phase reactions, $\hat{a}_i = \gamma_i x_i f_i / f_i^0$

Where γi = Activity coefficient of species i, dimensionless

x_i = Liquid phase mole fraction of species i, dimensionless

f_i = Fugacity of pure species I, kPa

If the pressure is not in the critical region, and the assumption is made that we are dealing with an ideal

liquid then the equilibrium equation simplifies to:

$$\prod_i (x_i)^{v_{i,j}} = K_j$$

Subscript i refers to each individual species, and j refers to the reaction.

The method for calculation of equilibrium conversion can be found in detail with worked examples in

Denbigh [7], or Perry [42]

Perry [42] gives an example on the use of these equations for calculating equilibrium conversion for a

single reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2$$
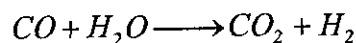
With the reaction taking place at 1000K and atmospheric pressure.

The feed stream contains 4 mols CO and 2 mols H_2O.

$n_{CO} = 4 - x$

$n_{H_2O} = 2 - x$

$n_{CO_2} = x$

$n_{H_2} = x$

$\Sigma n_i = 6$

Therefore $y_i = n_i/6$

At 1000K, $\Delta G^0 = -2680$J/mol

$$K = e\left(\frac{2680}{8.314 * 1000}\right) = 1.38$$

$$\prod_i y_i^{v_i} = \frac{\left(\dfrac{x}{6}\right)\left(\dfrac{x}{6}\right)}{\left(\dfrac{4-x}{6}\right)\left(\dfrac{2-x}{6}\right)} = K = 1.38$$

$\varepsilon = 1.42$

For the equilibrium mixture:

$n_{CO} = 2.58$

$n_{H_2O} = 0.58$

$n_{CO_2} = 1.42$

$n_{H_2} = 1.42$

So the equilibrium conversion with respect to Carbon Monoxide

$x_e = (4-2.58)/4 = 0.36$

As a first estimate for conversion in the reactor one can say that the conversion is equal to

0.98*equilibrium conversion [9].   Therefore $x = 0.98x_e = 0.35$.

3.1.3   Reaction rate

The next step is to determine the reaction rate. There will be several different variables

involved in this, dependant on the type of system. The best case scenario is that either the full rate

equation will be known – this is essential for heterogeneous systems, where the mass transfer and

kinetic rates must be known to determine the rate of reaction, or the space-time, τ of the reactor. The

space-time of a reactor is defined as the time required to process one reactor volume of feed at

specified conditions. It is the ratio of the reactor volume to volumetric flowrate. Since the volumetric

flowrate would be known from a mass balance it enables a quick estimation of reactor volume.

If this data is not available, then some assumptions must be made to attempt to work around this.

Firstly assumptions must be made as to the operation of the reactor. The design of a reactor increases

in complexity if the operating conditions vary. Therefore it will be assumed that the reactor is

isothermal and under constant pressure. This will simplify the design and result in a more rapid

method. Also the reaction will be assumed to be irreversible and that no competing reactions occur i.e.

only the main reaction is considered. This will also simplify the kinetics. The overall order of the

reaction is one of the most important variables as the design equation can change considerably as the

order changes. First and second order reactions are most common, with zero and third order reactions

being comparatively rare. Therefore first and second order reactions will be examined to identify the

effect of changing reaction order on total volume for plug flow and CSTR reactions.   The magnitude

of variation will depend on the conversion in the reactor, the coefficient of expansion, ε (the ratio of the

amount of moles of reaction products to reaction feedstocks) and the inlet composition into the reactor.

Tables 2 and 3 show the effect of changing the order of reaction and coefficient of expansion on reactor

volume for Plug Flow and CSTR reactors:

Comparison of Sizes, $V_{Plug-Flow}$(2nd order)/$V_{Plug-Flow}$(1st order)				
X_A	$\varepsilon=0$	$\varepsilon=0.5$	$\varepsilon=1$	$\varepsilon=2$
0.1	1.055	1.08	1.11	1.169
0.2	1.120	1.18	1.25	1.382
0.3	1.202	1.31	1.42	1.653
0.4	1.305	1.47	1.65	2.007
0.5	1.443	1.69	1.95	2.485
0.6	1.637	2.00	2.38	3.167
0.7	1.938	2.49	3.05	4.228
0.8	2.485	3.37	4.28	6.160
0.9	3.909	5.67	7.47	11.153

Comparison of Sizes, V_{CSTR} (2nd order)/V_{CSTR} (1st order)				
X_A	$\varepsilon=0$	$\varepsilon=0.5$	$\varepsilon=1$	$\varepsilon=2$
0.1	1.11	1.67	2.22	3.33
0.2	1.25	1.88	2.5	3.75
0.3	1.43	2.14	2.86	4.28
0.4	1.67	2.50	3.33	5.00
0.5	2.00	3.00	4.00	6.00
0.6	2.50	3.75	5.00	7.50
0.7	3.33	5.00	6.67	10
0.8	5	7.50	10	15
0.9	10	15.00	20	30

Table 2 – Comparison of reactor volumes with changing conversion and expansion

(For second order systems $C_{A0} = 1$ kmol/m^3)

Comparison of Sizes, $V_{Plug-Flow}(2^{nd}$ order$)/V_{Plug-Flow}(1^{st}$ order$)$

X_A	$\varepsilon=0$	$\varepsilon=0.5$	$\varepsilon=1$	$\varepsilon=2$
0.1	2.11	2.17	2.22	2.34
0.2	2.24	2.37	2.50	2.76
0.3	2.40	2.62	2.84	3.31
0.4	2.61	2.94	3.29	4.01
0.5	2.89	3.38	3.90	4.97
0.6	3.27	4.00	4.76	6.33
0.7	3.88	4.97	6.11	8.46
0.8	4.97	6.74	8.57	12.32
0.9	7.82	11.33	14.95	22.31

Comparison of Sizes, $V_{CSTR}(2^{nd}$ order$)/V_{CSTR}(1^{st}$ order$)$

X_A	$\varepsilon=0$	$\varepsilon=0.5$	$\varepsilon=1$	$\varepsilon=2$
0.1	2.22	3.33	4.44	6.67
0.2	2.50	3.75	5.00	7.50
0.3	2.86	4.29	5.71	8.57
0.4	3.33	5.00	6.67	10.00
0.5	4.00	6.00	8.00	12.00
0.6	5.00	7.50	10.00	15.00
0.7	6.67	10.00	13.33	20.00
0.8	10.00	15.00	20.00	30.00
0.9	20.00	30.00	40.00	60.00

Table 3 – Comparison of reactor volumes with changing conversion and expansion

(For second order systems $C_{A0} = 0.5$ kmol/m^3)

It can be seen that second order kinetics will always give a larger inventory than first order kinetics. Therefore assuming second order kinetics will tend to give a higher inventory and therefore an added safety margin. Unless it is apparent that the reaction is first order a second order reaction should be assumed.

The reaction rate constant must be known in order to size the reactor. This data must be obtained otherwise no sizing can be done. Therefore laboratory scale reactions must be commissioned to calculate this data. This must be recognised to increase cost and time especially if a number of routes are under consideration. If it is not practical to calculate the rate constant for every route the engineer must either screen options to qualitatively determine the most suitable routes for laboratory study, or it must be realised that at this stage it is impossible to estimate inventory. Screening of routes can be done by analysing the known data pertaining to each reaction route. The engineer should ask questions such as, but not limited to:

- What are the operating conditions in the reactor? If a reaction requires a temperature or pressure far in excess of other alternatives then the hazard posed by a process rises with these variables.

- What phase does the reaction take place in? Gas phase reactions have a lower inventory than liquid phase reactions and may therefore have inherent safety benefits.

- How difficult are the products to separate? Difficult separations may give rise to larger separation vessels and larger inventories and as such should be avoided if possible.

- What is the reactor conversion? The conversion in the reactor will be a major factor in determining the recycle and reactor volume. A low conversion will lead to a large reactor, and more importantly for our purposes a large recycle. This will mean a large flowrate through downstream separation vessels and hence large inventories in the process.

- Does any route have a material that should be avoided 'at all costs'? If one route has an extremely hazardous material (for example, Phosgene) then it should be avoided if possible in favour of reactions with less hazardous materials. Although the quantity of the material is the major factor in determining the hazard posed by that material, once an extremely toxic material is present even if just in small quantities it requires specialised care and design to

prevent escape. On this basis it can be said that extremely hazardous materials should be

avoided, even if they would only be present in small quantities.

If it is decided not to carry out laboratory experiments then there is no possible way to estimate process

inventory. If this is the case, then the reactor will not be included in the study.

From Tables 2 and 3 it can be seen that for low conversions (<0.4) the volume of a plug flow

reactor does not vary greatly with order of reaction. Therefore it may be possible to assume first order

kinetics for plug flow reactors if this results in an appreciable lowering of the time taken to carry out

the method. Since gas phase reactions tend to be carried in plug flow reactors it may be said that gas

phase reactions can assumed to be first order.

The same can be said of CSTR reactors. CSTR reactions will tend to be liquid phase

systems where there will be a constant volume i.e. $\varepsilon = 0$. Examining only the first column in tables 3

and 4 shows that for low conversions (<0.4) the system may be approximated to first order.

3.1.4   Calculating Reactor Size

Once the required variables – rate constant and the rate equation – have been obtained from

laboratory experiments the reactor can be sized, through a variety of equations for different reactor

types. The derivation and use of these equations can be found in different texts, such as [37]. The type

of reactor sized will depend greatly on the laboratory experiments – for example in homogenous

systems the choice of plug flow, batch or CSTR will depend on the type of vessel the chemist used for

his analysis.

For homogenous reactions the sizing equations are:

CSTR $$V = F_{A0} \cdot \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$

Assuming constant volume i.e. gas phase reactions are carried out in plug flow reactors:

For first-order systems, this can be re-written: $kr = k\dfrac{C_{A0}V}{F_{A0}} = \dfrac{X_A}{1 - X_A}$

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For second order systems : $k\tau = k\dfrac{C_{A0}V}{F_{A0}} = \dfrac{X_A}{C_{A0}(1-X_A)^2}$

Plug Flow $\qquad V = F_{A0}\displaystyle\int_{X_{Ai}}^{X_{Af}} \dfrac{dX_A}{-r_A}$

For first-order systems: $k\tau = k\dfrac{C_{A0}V}{F_{A0}} = -(1+\varepsilon_A)In(1-X_A)-\varepsilon_A X_A$

For second-order systems $k\tau = k\dfrac{C_{A0}V}{F_{A0}} = 2\varepsilon(1+\varepsilon)\ln(1-X_A)+\varepsilon^2 X_A +\dfrac{(1+\varepsilon)^2 X}{1-X}$

Where: V = Reactor volume, m^3

F_{A0} = Feed rate of A at reactor inlet, $= \dfrac{F_{FA}}{x}$, kmol/s

F_{FA} = Fresh feed rate of A, kmol/s

x = Reactor Conversion, Dimensionless

X_{Af} = Conversion at reactor outlet, Dimensionless

X_{Ai} = Conversion at reactor inlet, Dimensionless

r_A = Reaction rate, kmol/m^{3}s

$(r_A)_f$ = Reaction rate at reactor outlet, kmol/m^{3}s

τ = Space time = $\dfrac{VC_{A0}}{F_{A0}}$, s

C_{A0} = Concentration of A at reactor inlet, kmol/m^3

For heterogeneous systems due to many different types of reactors the methods of design will not be written here as this extends outside the bounds of this project. The engineer should instead reference any text on reactor design for heterogeneous systems.

The calculation of the inventory of each species in a reactor vessel depends on the nature of the vessel. For example in a CSTR reactor the composition is assumed to be equal to the composition of the outlet flow.

A Plug Flow reactor is different as the composition of the flow in the reactor changes along its length. The inventory will be calculated in the same way as other equipment items with variable composition – to divide the plug flow reactor into two sections, with one section having a composition

equal to the inlet flow composition and the other having a composition equal to the outlet flow composition.

3.1.5   Design Methodology

1) If a full suite of data – reactor type, reaction rate, rate constant and reactor conversion are available calculate vessel size.

2) If this data is unavailable for heterogenous systems the inventory can not be calculated.

For homogenous systems:

3) If the reaction vessel is unknown assume the use of a plug flow reactor for a gas system. For liquid systems texts such as [9] may aid in selecting a reactor type.

4) If conversion data is unavailable calculate equilibrium conversion from Gibbs free energies. Let conversion equal 0.98 times equilibrium conversion.

5) If the rate equation is unknown assume second order kinetics unless the conversion is less than 0.4 when first order kinetics may be used if advantageous in terms of time required to calculate the rate constant.

6) If the rate constant is unknown commission laboratory experiments to enable calculation of this variable. If the number of routes under study is too large for this to be viable screen routes to eliminate less favourable routes. If the experiments cannot be commissioned through time or financial pressures the inventory cannot be estimated.

Once the data has been obtained size the reactor using the design equations above.

Nomenclature:

$\hat{a}_i$ = Activity of species i in solution, Dimensionless

C_{A0} = Concentration of A at reactor inlet, kmol/m^3

f_i^0 = Fugacity of species i and standard state, kPa

f_i = Fugacity of species I, kPa

F_{FA} = Fresh feed rate of A, kmol/s

ΔG_j^0 = Gibbs-energy change of reaction, J/mol

k = Reaction rate constant, Variable

K = Equilibrium Constant, Dimensionless

r_A = Reaction rate, kmol/m^{3}s

$(r_A)_f$ = Reaction rate at reactor outlet, kmol/m^{3}s

P = Reaction pressure, Pa

P^0 = Standard state pressure = 100kPa

R = Universal Gas Constant = 8.313 J/mol^{o}K

T = Reaction temperature, K

$t_{1/2}$ = Reaction half-life, s

V = Reactor Volume, m^3

x = Reactor Conversion, Dimensionless

x_i = Liquid phase mole fraction of species i, Dimensionless

X_{Af} = Conversion of A at reactor outlet, Dimensionless

X_{Ai} = Conversion of A at reactor inlet, Dimensionless

y_i = Vapour phase mole fraction of species i, Dimensionless

γi = Activity coefficient of species i, Dimensionless

ε = Coefficient of expansion, (number of moles in – number of moles out/number of moles in)

$\hat{\phi}_i$ = Fugacity coefficient of species i in solution

$$\tau = \frac{VC_{A0}}{F_{A0}} = \text{Space-Time, s}$$

3.2   Distillation Columns

There are many different methods available for sizing distillation columns, depending on the level of accuracy required. Since a large accuracy is not possible at this stage, a short-cut method will be sufficient for the purposes of inventory estimation. This will enable a rapid estimate of column height and diameter. The varying liquid and vapour compositions throughout the column will lead to complications in deriving an inventory. Some degree of simplification is required to maintain a quick, efficient method. This will be achieved by dividing the column into two sections – above the feed plate having a composition equal to the top product composition, below the feed plate having a composition equal to the bottoms product composition.

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Design Equations for Distillation Columns

Zomosa [56] has developed a short-cut method for the design of plate distillation columns. The use of this method is recommended due to its speed and ease of use. However, this method has two drawbacks. It cannot be used for packed columns, or for systems where the vapour-liquid equilibrium curve cannot be approximated by a straight line (one of the assumptions in the Zomosa method). For these systems it would be more appropriate to draw a McCabe-Thiele diagram to determine the number of stages required for the separation. This would be slightly more time consuming, but will give more accurate results.

3.2.1   Zomosa's Method

Zomosa has developed a short cut method for the design of distillation columns using Nomographs.   This method uses imperial units.

1.   Step One

Determine R_m, the minimum reflux ratio from:

$$R_m = \frac{x_D\left[1 + (\alpha - 1)x_F\right] - \alpha x_F}{x_F(\alpha - 1)(1 - x_F)}$$

Assuming $x_D = 1$, then this simplifies to

$$R_m = \frac{1}{(\alpha - 1)x_F}$$

Where:

α = Relative volatility

x_D = Mole fraction of most volatile component in distillate

x_F = Mole fraction of most volatile component in feed

(This is one of the approximations of the Underwood equation, and is applicable for $0.2 < x_F < 0.8$, and when x_D is approximately 1).

2.   Determine the Reflux Ratio

The optimum reflux ratios are usually in the range 1.1-$1.5 * R_m$. An average of this range is taken so that $R = 1.3R_m$.

3.   Number of Trays at Total Reflux

This is determined from a diagram developed by Smoker (Fig. 2). A line is drawn between x_D and x_W to establish a point on the tie line. Another line is drawn from this to α to find S_m (Min number of plates at total reflux). This is a graphical interpretation of the Fenske equation.
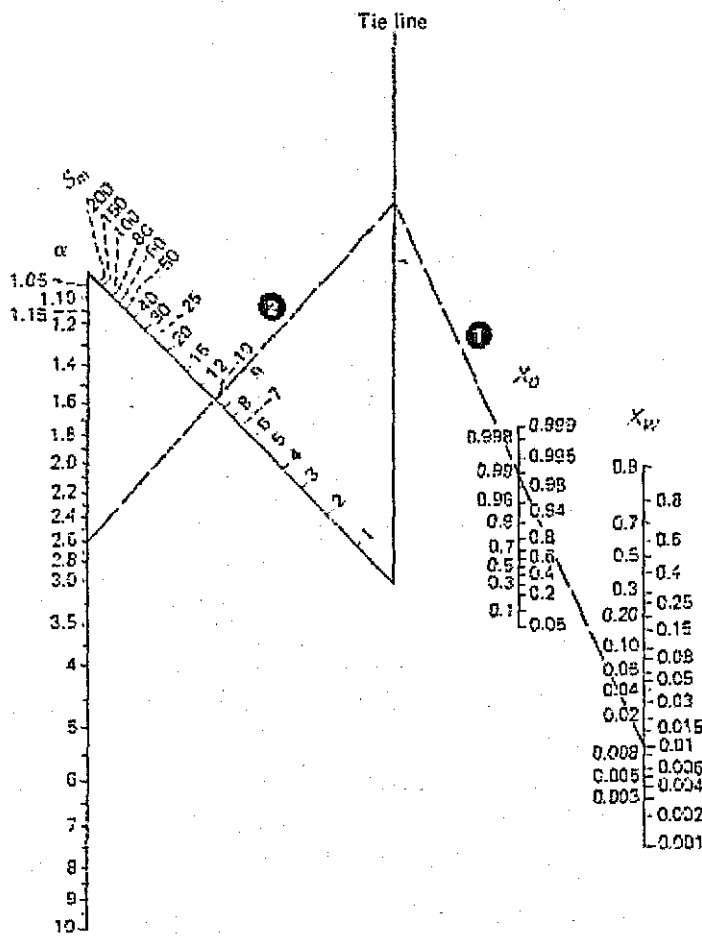
Fig. 2 – Minimum number of trays at total reflux

4.   Number of Trays at a Given Reflux Ratio.

This is determined using a diagram developed by Erbar and Maddox (Fig. 3), using values of R/(R+1) and $R_m/(R_m+1)$ to determine S, the theoretical number of plates at reflux.
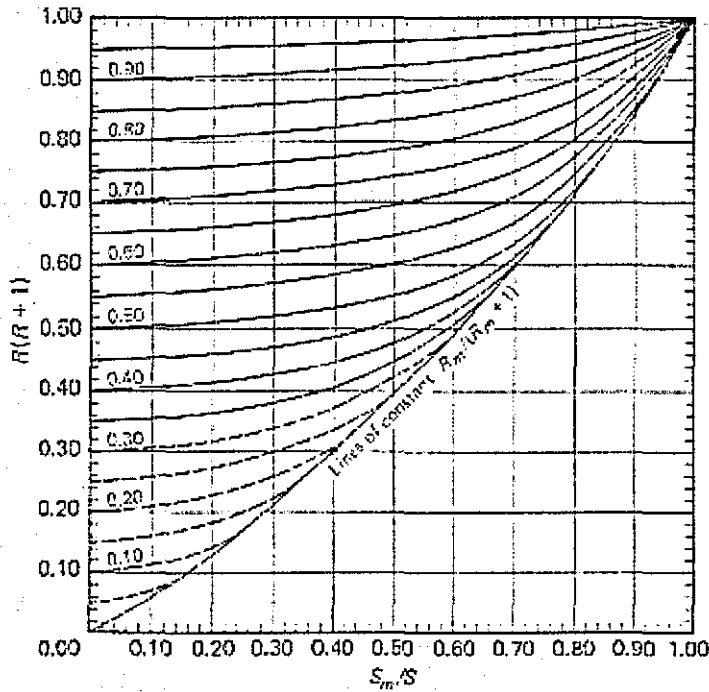
Fig. 3 – Number of theoretical plates

5.   Actual number of plates

This depends on the tray efficiency. For a first estimate, tray efficiency is estimated at 70% so that the number of plates N=S/0.7.

6.   Column Diameter

This uses the Brown-Smoulders method. It is based on the relationship

$$G = C\left[\rho_v\left(\rho_l - \rho_v\right)\right]^{0.5}$$

Where:

G = Allowable Vapour Velocity, lb/(h)(ft^2)

C = Coefficient, = 600, dimensionless

ρ_l = Density of Liquid, lb/ft^3

ρ_v = Density of Vapour, lb/ft^3

From this we can then calculate the cross-sectional area

$$A = \frac{V}{G}$$

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A = Cross sectional area, ft^2

V = Vapour Flow Rate, lb/h

Since V = L+D and R=L/D we can re-write this equation as

$$A = \frac{D(R+1)}{G} = 0.785d^2$$

L = Reflux, lb/h

D = Distillate rate lb/h

d = Column diameter, ft.

Re-arranging gives $d = \left[\dfrac{D(R+1)}{0.785G} \right]^{0.5}$

Column Height

From the number of stages the column height can be calculated.

Assume a Plate spacing of 0.5m

Height of Column = 0.5N

Packed Columns

For packed columns (calculating the number of stages from the McCabe-Thiele method [48]), it will be very hard to obtain data for the height of an equilibrium stage for a particular system at this stage of the design project. Data for the height of an equivalent theoretical plate (HETP) for Pall rings of varying sizes is found in [48]. These values are reproduced in table 4:

Size of packing, mm	HETP, m
25	0.4-0.5
38	0.6-0.75
50	0.75-1.0

Table 4 – Height of an Equivalent Theoretical Plate for Pall Ring packings

These values should be used to estimate column size, though it must be realised that they only apply for Pall rings. The values for Raschig rings and saddles will be higher than these. As a first approximation add 50% to these values to compensate for this.

Also, a factor must be added to the column height to account for the disengagement space and liquid sump. As a first approximation assume that this compromises 15% of the total column height [9]

Column height = 0.5N/(1-0.15) = 0.59N

For packed columns the diameter can be estimated from the economic gas flowrates in [40]. This quotes the economic gas flowrate for a variety of packings and sizes. From this and the volumetric gas flowrate the column diameter can be calculated.

3.2.2   Liquid Inventory

The biggest question that must be answered so far as liquid inventory is concerned is how to represent the changing composition of the liquid in the column – the liquid in the bottom of the column will be different to the liquid in the top of the column. For towers in which the solution is two chemicals with similar hazards – flammability, explosiveness, toxicity –then the varying composition is not as important. This is applicable for the separation of two hydrocarbons. However, for non-similar mixtures, where the substances have different hazards for example hydrocarbon-water a method must be developed that takes into account the varying composition. This is done by dividing the column into 2 sections:

Top section (above the feed point) – Liquid and vapour composition = Top product composition

Bottom section (below the feed point) – Liquid and vapour composition = Bottoms product composition

The feed point can be determine either from the McCabe-Thiele diagram, or from the equation derived by Kirkbride [48]:

$$\log \frac{N_r}{N_s} = 0.206 \log \left[\left(\frac{B}{D} \right) \left(\frac{x_{f,HK}}{x_{f,LK}} \right) \left(\frac{x_{b,LK}}{x_{d,HK}} \right)^2 \right]$$

N_r = Number of stages above the feed

N_s = Number of stages below the feed

B = Bottoms product flowrate, kmol/h

D = Distillate flowrate, kmol/h

$x_{f,HK}$ = Concentration of heavy key in the feed

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$x_{f,LK}$ = Concentration of light key in the feed

$x_{d,HK}$ = Concentration of heavy key in the top product

$x_{b,LK}$ = Concentration of light key in the bottom product

The total liquid inventory is equal to the liquid hold-up on the trays plus liquid sump in the column. There should be an allowance of 15% of plate section height for disengagement space and liquid sump [48]. So therefore we will assume the liquid sump in the column is equal to 7.5% of plate section height, and the vapour disengagement space will be equal to 7.5% of plate section height.

Hold-up on a Tray = $\dfrac{\pi}{4}d^2 * 0.88 * w_H$ [48]

Where w_H = Weir height, assume = 50mm = 0.05m

The 0.88 multiplication factor is due to the downcomer area – the downcomer area is approximately equal to 12%, so the area of plate is therefore 88% of column cross sectional area.

Top Product Liquid Inventory = $N_r * \dfrac{\pi}{4}d^2 * 0.88 * 0.05$

$= 0.044\dfrac{\pi}{4}N_r d^2$

Bottom Section Liquid Inventory

The bottom section also has the liquid sump, which we have assumed as being 7.5% of the total column height.

So Bottom Section Inventory = Plate Hold-up + Liquid Sump

$= 0.044\dfrac{\pi}{4}N_s d^2 + 0.075 * 0.59\dfrac{\pi}{4}Nd^2$

$= 0.044\dfrac{\pi}{4}N_s d^2 + 0.044\dfrac{\pi}{4}Nd^2 = 0.044\dfrac{\pi}{4}d^2\left(N_s + N\right)$

3.2.3   Vapour Inventory

Total Vapour Inventory = Column volume – total liquid inventory

$$= 0.59N\dfrac{\pi}{4}d^2 - 0.088\dfrac{\pi}{4}Nd^2$$

$$= 0.50 \frac{\pi}{4} N d^2$$

The ratio of the top product vapour bottoms product vapour on the plates (that is, the total vapour volume less the disengagement space) will be equal to the ratio of the number of plates above the feed to the number of plates below the feed

Vapour disengagement space $= 0.075 * 0.59 \frac{\pi}{4} N d^2 = 0.044 \frac{\pi}{4} N d^2$

So $v_b + v_d + 0.044 \frac{\pi}{4} N d^2 = 0.50 \frac{\pi}{4} N d^2$

Where: v_b = Volume of vapour on plates in stripping section, m^2

v_d = Volume of vapour on plates in rectifying section, m^2

And $\frac{v_d}{v_b} = \frac{N_r}{N_s}$

Since $\frac{N_r}{N_s}$ will be known from either the Kirkbride equation or a McCabe-Thiele diagram, these equations can be solved for v_b and v_d.

So the bottom section vapour inventory $= v_b$

Top section vapour inventory $= v_d + 0.044 \frac{\pi}{4} N d^2$

Nomenclature

B = Bottoms product flow rate, kmol/h

C = Factor that depends on tray spacing and surface tension in allowable vapour = 600

d = Column diameter, m

D = Distillate flow rate, kmol/h

F = Feed flow rate, kmol/h

G = Allowable vapour rate in column, lb/hft^2

L = Liquid flow rate above feed plate, kmol/h

L' = Liquid flow rate below feed plate, kmol/h

L$_w$ = Liquid flow rate above feed plate, kg/s

L'$_w$ = Liquid flow rate below feed plate, kg/s

$L_{w,max}$ = Maximum liquid flow rate in column, kg/s

m = Molar mass, g/mol

N = Actual number of plates

N_m = Minimum number of plates at maximum reflux ratio

N_T = Theoretical number of plates at given reflux

P_x = Partial pressure of substance x, Pa

q = Heat required to vaporise one mole of feed/molar latent heat

Q_{cond} = Cooling duty in condenser, kW

Q_{reb} = Heating duty in reboiler, kW

R = Reflux ratio

R_m = Minimum Reflux Ratio

V = Vapour flow rate above feed plate, kmol/h

V' = Vapour flow rate below feed plate, kmol/h

w_h = Weir height, 50mm

W_w = Cooling water flow rate in condenser, kg/h

W_s = Steam flow rate in reboiler, kg/h

x_B = Mole fraction of light fraction in bottoms product

x_D = Mole fraction of light fraction in distillate

x_F = Mole fraction of light fraction in feed

α = Relative Volatility

λ_v = Latent heat of vaporisation of distillate vapour, Btu/lb

ρ_v = Vapour density, kg/m^3 (lb/ft^3 in Zomosa's method)

ρ_l = Liquid density, kg/m^3 (lb/ft^3 in Zomosa's method)

σ = Surface Tension, N/m

3.3   Liquid Extraction

There are many methods for calculating the number of stages required for an extraction, each method varying in time required, degree of complexity and accuracy. Of major importance to us is speed and ease of use. Therefore iterative procedures are unsuitable, as are methods that require the drawing of numerous graphs. The method that best suits our criteria is the use of the Kremser

equations. These are relatively simple equations that relate the number of stages to parameters that are known or are easy to calculate. The height of the column can then be calculated by multiplying the number of stages by the height of a transfer stage. The diameter can be determined through calculation of the flooding velocity in the column

The biggest obstacle to be overcome is in the calculation of column height. For this we require mass transfer coefficients and the specific interfacial surface area between liquids per unit volume of column. However these parameters can only be determined with any degree of certainty by experimental procedures. There has only been limited success in developing correlations to predict these parameters from basic principles. As in packed column distillation an assumption shall have to be made as to HETP values for different packing sizes.

3.3.1   Short-Cut Method for the Design of Liquid-Liquid Extraction Columns [42]

The first assumption that must be made is that the rates of flow of feed solvent, F' and the rate of flow of extraction solvent, S' are constant. Then the solute concentrations are given by the weight ratio of solute to feed solvent X and the weight ratio of the solute to extraction solvent Y. The concentrations on this plot will essentially give a straight operating line for stages 2 through r-1 in Fig. 4.
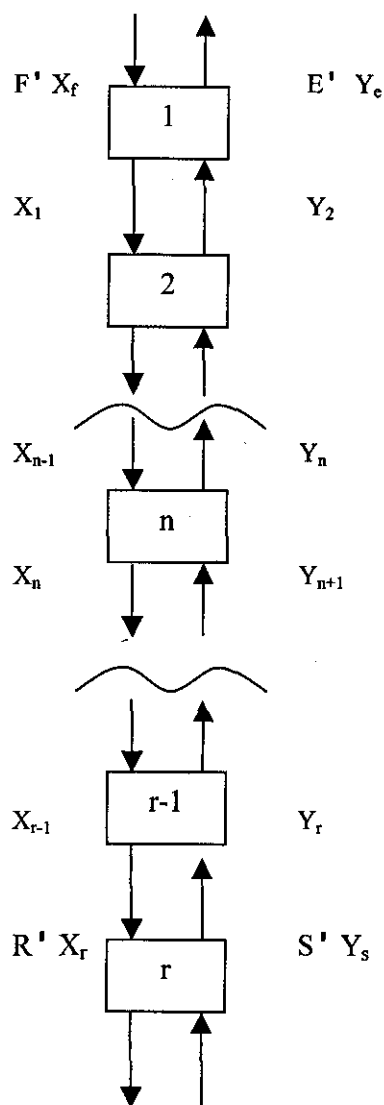
Fig. 4 – Countercurrent liquid extraction

3.3.2   Short-cut design method

Case A – Immiscible Solvents

Rate of feed solvent in feed stream = rate of feed solvent in raffinate stream

Rate of extraction solvent in extraction solvent = rate of extraction solvent in extract stream

Hence $S'/F' = E'/R'$

A material balance can be written around the feed end of the extractor to stage n, and then rearranged to a McCabe-Thiele type of operating line with a slope of F'/S'.

$$Y_{n+1} = \frac{F'}{S'}X_n + \frac{E'Y_e - F'X_f}{S}$$

The same operating line can be derived for the raffinate end up to stage n.

$$Y_n = \frac{F'}{S'} X_{n-1} + \frac{S'Y_s - R'X_r}{S'}$$

So the overall material balance is

$$Y_e = \frac{F'X_f + S'Y_s - R'X_r}{E'}$$

If we further assume that the equilibrium line and operating lines are straight and the intercept of the equilibrium line is zero then the number of theoretical stages, N can be determined through the use of one of the Kremser equations. If the intercept of the equilibrium line is not zero then Y_s/K'_s should be used instead of Y_s/m, where K'_s is the partition ratio in Bancroft coordinates Y_s

Kremser Equations

Extraction factor, $\xi \neq 1.0$

$$N = \frac{In\left[\left(\frac{X_f - Y_s/m}{X_r - Y_s/m} \right)\left(1 - \frac{1}{\xi} \right) + \frac{1}{\xi} \right]}{In\xi}$$

When $\xi = 1.0$

$$N = \frac{X_f - Y_s m}{X_r - Y_s m} - 1$$

Where m is the slope of the operating line. At low concentrations this is equal to K'. ξ is calculated by dividing the slope of the equilibrium line by the slope of the operating line:

$$\xi = mS'/F'$$

The solute concentration in the raffinate X_r can be evaluated as the result of changing the ratio of solvent to feed:

Extraction factor, $\xi \neq 1.0$

$$\frac{X_r - Y_s/m}{X_f - Y_s/m} = \frac{\xi - 1}{\xi^{N+1} - 1}$$

When $\xi = 1.0$

$$\frac{X_r - Y_s/m}{X_f - Y_s/m} = \frac{1}{N+1}$$

When the equilibrium line is not straight then the geometric mean of the equilibrium line at the concentration leaving the feed stage m_1 and at the raffinate concentration leaving the raffinate stage m_r should be used.

$$m = \sqrt{m_1 m_r}$$

Case B – Partially miscible solvents

In this case we assume that the feed stream dissolves extraction solvent only in the feed stage and then retains that amount throughout the extractor. Likewise, the extraction solvent is assumed to dissolve feed solvent only in the raffinate stage. The primary extraction-solvent rate in the extractor is assumed to be S', and the primary feed-solvent rate is assumed to be F'. The extract rate E' will be less than S', and the raffinate rate R' will be less than F' due to solvent solubilities.

The slope of the operating line will be F'/S', as before but only stages 2 to r-1 will fall on the operating line. By definition, X_1 will be on the equilibrium line in equilibrium with Y_e. We can also calculate the pseudo feed concentration X^B_f that will fall on the operating line and $Y_{n+1} = Y_e$.

$$X_f^B = X_f + \frac{S'-E'}{F'} Y_e$$

In the same way Y_r will be on the equilibrium line with X_r. We can therefore calculate a pseudo concentration of solute in the inlet extraction solvent Y^B_s that will fall on the operating line where $X_{n-1} = X_r$

$$Y_s^B = Y_s + \frac{F'-R'}{S'} X_r$$

These values can then be used in the Kremser equation together with X_r and ξ to calculate the number of theoretical stages required.

3.3.3   Number of Mass Transfer Units

For differential contactors the concept of a mass transfer unit better represents the operation inside the extractor. The Kremser equation can be modified to represent this. With the same assumptions – a straight operating line, and a straight equilibrium line with an intercept of zero – the Kremser equation for number of mass transfer units based on raffinate stage compositions becomes:

When $\xi \neq 1$

$$N_{OR} = \frac{In\left[\left(\dfrac{X_f - Y_s/m}{X_r - Y_s/m}\right)\left(1 - \dfrac{1}{\xi}\right) + \dfrac{1}{\xi}\right]}{1 - 1/\xi}$$

When $\xi = 1$ the number of mass transfer units is equal to the number of theoretical stages

When $\xi = 1$

$$N_{OR} = N = \frac{X_f - Y_s/m}{X_r - Y_s/m} - 1$$

The response of the solute concentration in the raffinate to the solvent to feed ratio S'/F' for a

constant N_{OR} can be represented by

When $\xi \neq 1$

$$\frac{X_r - Y_s/m}{X_f - Y_s/m} = \frac{1 - 1/\xi}{e^{N_{OR}(1 - 1/\xi)} - 1/\xi}$$

When $\xi = 1$

$$\frac{X_r - Y_s/m}{X_f - Y_s/m} = \frac{1}{N_{OR} + 1}$$

3.3.4   Column Height and Diameter

Once we have calculated N_{OR} we can calculate the column height, Z from

$$Z = H_{OR} N_{OR}$$

Where H_{OR} is the height of a mass transfer unit. As with the HETP for distillation columns it is highly

unlikely that this will be known at this stage.

Packed bed depths for varying packing sizes and number of transfer units per bed are quoted in Table 5

from [48]. This could be used to estimate the packed height required.

	Packing Size		
Transfer Units per Bed	1 inch	1.5 inches	2 inches
1.5	4.4	5.3	6.2
2.0	7.2	8.6	10.1
2.5	9.9	11.9	14.0

Table 5 – Packed bed depth for liquid extraction columns [48]. (Packed bed depths in feet)

The column diameter can be determined from the empirical relationship determined by

Crawford and Wilke [48]. This is a function relating to the Reynolds number of the continuous and

dispersed phase, $\dfrac{\rho_c}{a_p \mu_c}\left(V_c^{0.5} + V_d^{0.5}\right)^2$ to the expression $\left(\dfrac{\mu_c}{\Delta\rho}\right)\left(\dfrac{\sigma_i}{\rho_c}\right)^{0.2}\left(\dfrac{a_p}{\varepsilon}\right)^{1.5}$. By calculating

the value of this expression from the physical data and the liquid flowrate the liquid phase velocities

can be determined from Fig. 5.
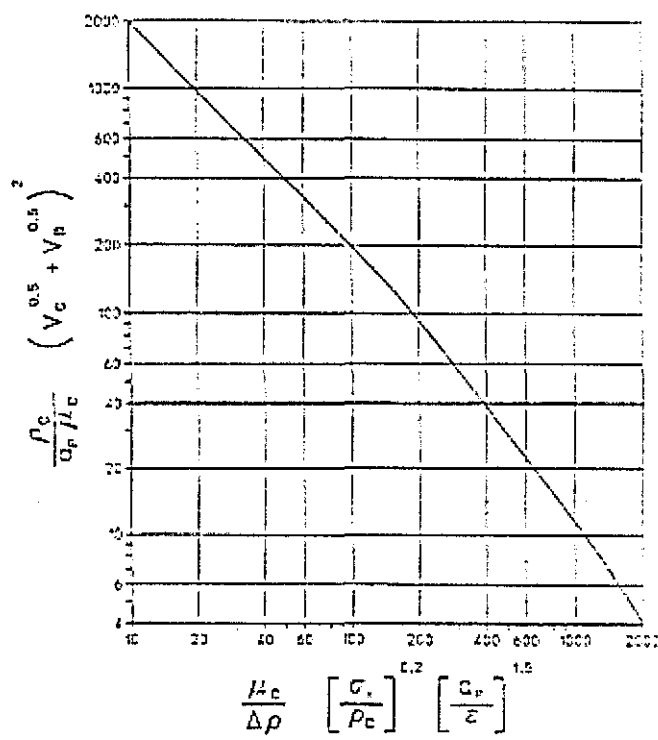
Fig. 5 – Flooding velocity in packed columns

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3.3.5   Liquid-Liquid Packed Column Inventory h^t of packed section.

We have packing of diameter d, and height, Z. As in distillation columns there will also be a

volume in the column both above and below the packing to allow for disengagement space. As in

distillation columns we will assume 15%.

The volume of the column, $V = 1.15 \frac{\pi}{4} d^2 Z$

If the voidage fraction of the packing is ε then:

Liquid volume in vessel, $V_1 = \frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z$

The compositions of the extract and raffinate stages will change throughout the length of the column,

as we are dealing with a differential contactor. Therefore, we will have to make an assumption as to

the compositions involved. We will assume that the composition changes halfway along the length of

the column – so from Fig. 4 we can say that in the top half of the column we will deal with two liquid

inventories, one with a composition equal to that of the feed composition, and another of equal

composition to the extract composition. Likewise, in the bottom of the column we will assume

compositions equal to the extract solvent and raffinate compositions.

Liquid volume in top of column, $V_{lt} = 0.5 \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$ $\frac{\pi d^2}{4} Z \varepsilon$

Liquid volume in bottom of column, $V_{lb} = 0.5 \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$

The volumes of the individual phases will be a ratio of the volumetric flow rates of the phases in that

half of the column.

The volumetric flow rates the individual streams will be:

$Feed = \frac{F}{\rho_F A_t}$

$Extract = \frac{E}{\rho_E A_t}$

$Raffinate = \frac{R}{\rho_R A_t}$

$$\text{Extract Solvent} = \frac{S}{\rho_S A_t}$$

Therefore, the individual inventories in the column will be:

$$\text{Feed} = \left[\left(\frac{F}{\rho_F A_t} \right) \middle/ \left(\left(\frac{E}{\rho_E A_t} \right) + \left(\frac{F}{\rho_F A_t} \right) \right) \right] * 0.5 \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$$

$$= 0.5 \left(\frac{F \rho_E}{E \rho_F + F \rho_E} \right) \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$$

$$\text{Extract} = 0.5 \left(\frac{E \rho_F}{E \rho_F + F \rho_E} \right) \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$$

$$\text{Raffinate} = 0.5 \left(\frac{R \rho_S}{R \rho_S + S \rho_R} \right) \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$$

$$\text{Extract Solvent} = 0.5 \left(\frac{S \rho_R}{R \rho_S + S \rho_R} \right) \left[\frac{\pi}{4} d^2 Z \varepsilon + 0.15 \frac{\pi}{4} d^2 Z \right]$$

Nomenclature

d = Column diameter, m

F = Mass flow rate of feed, kg/h

F' = Mass flow rate of feed solvent alone in feed, kg/h

S = Mass flow rate of extraction solvent stream kg/h

S' = Mass flow rate of extraction solvent alone in extraction solvent stream kg/h

R = Mass flow rate of raffinate, kg/h

R' = Mass flow rate of feed solvent alone in raffinate, kg/h

E = Mass flow rate of extract, kg/h

E' = Mass flow rate of extraction solvent alone in extract, kg/h

X_f = Weight solute/weight feed solvent in feed

X_r = Weight solute/weight feed solvent in raffinate

Y_e = Weight solute/weight extraction solvent in extract

Y_s = Weight solute/weight extraction solvent in extraction solvent

K' = Partition coefficient in Bancroft (weight ratio) coordinates, Dimensionless

K'_s = Partition coefficient in Bancroft coordinates at Y_s, Dimensionless

A_t = Cross-sectional area of tower, m^2

a = Specific interfacial surface between liquids per unit volume of tower, m^2/m^3

k_r = Mass transfer coefficient in raffinate phase $kg/s.m^2$

k_e = Mass transfer coefficient in extract phase, $kg/s.m^2$

H_e = Height of transfer unit attributed to driving force in extract phase, m

H_r = Height of transfer unit attributed to driving force in raffinate phase, m

H_{or} = Height of transfer unit based on overall driving force in raffinate concentrations, m

N = Number of theoretical stages

Z = Height of Column, m

N_{or} = Number of mass transfer units based on overall driving force in raffinate concentrations

ξ = Extraction factor, Dimensionless

3.4   Gas Absorption

There are two main stages to the design of gas absorption columns. Firstly the column height must be calculated, by determining the number of transfer units required to carry out the desired operation and the height of each of those transfer units. Coburn's chart enables the rapid calculation of the number of transfer units. The column diameter can be estimated from Morris and Jackson [40], which give an economic gas flow rate for a variety of packing types. Using this value along with the volumetric gas flow rate allows calculation of column diameter.
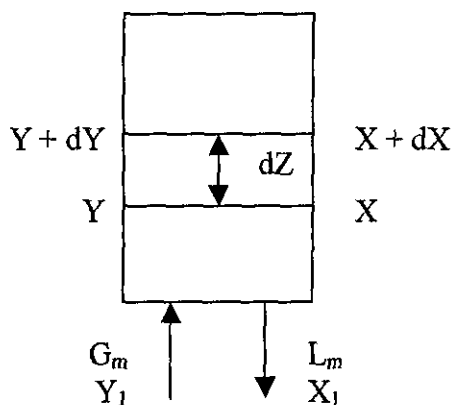
Fig. 6 - Gas absorption

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3.4.1   Coburn's Chart [42]

If we assume that the system is dilute, $x \approx X_1$ and $y \approx Y_1$, then:

$$G'_m\left(y_1 - y_2\right) = L'_m\left(x_1 - x_2\right)$$

Where G'_m and L'_m are the gas and liquid molar flowrates per unit area on a solute free basis.

If we take a material balance between the top and some location where the mole fractions are x and y then:

$$G'_m\left(y - y_2\right) = L'_m\left(x - x_2\right)$$

If we assume that the solvent is solute free, then $x_2 = 0$:

$$x = \frac{G'_m}{L'_m}\left(y - y_2\right)$$

The number of overall transfer units in terms of gas phase concentrations, N_{OG} is given by:

$$N_{OG} = \int_{y_1}^{y_2} \frac{dy}{y_e - y}$$

Dilute concentrations, $y = mx$, so:

$$N_{OG} = \int_{y_1}^{y_2} \frac{dy}{\dfrac{mG'_m}{L'_m}\left(y - y_2\right) - y}$$

$$= \int_{y_1}^{y_2} \frac{dy}{\left[\dfrac{mG'_m}{L'_m} - 1\right]y - \dfrac{mG'_m}{L'_m}y_2}$$

Solving this integral yields:

$$N_{OG} = \frac{1}{1 - \dfrac{mG'_m}{L'_m}} In\left[\left(1 - \frac{mG'_m}{L_m}\right)\frac{y_1}{y_2} + \frac{mG'_m}{L'_m}\right]$$

Colburn, 1939 plotted this equation as a graph that is reproduced in Fig. 7
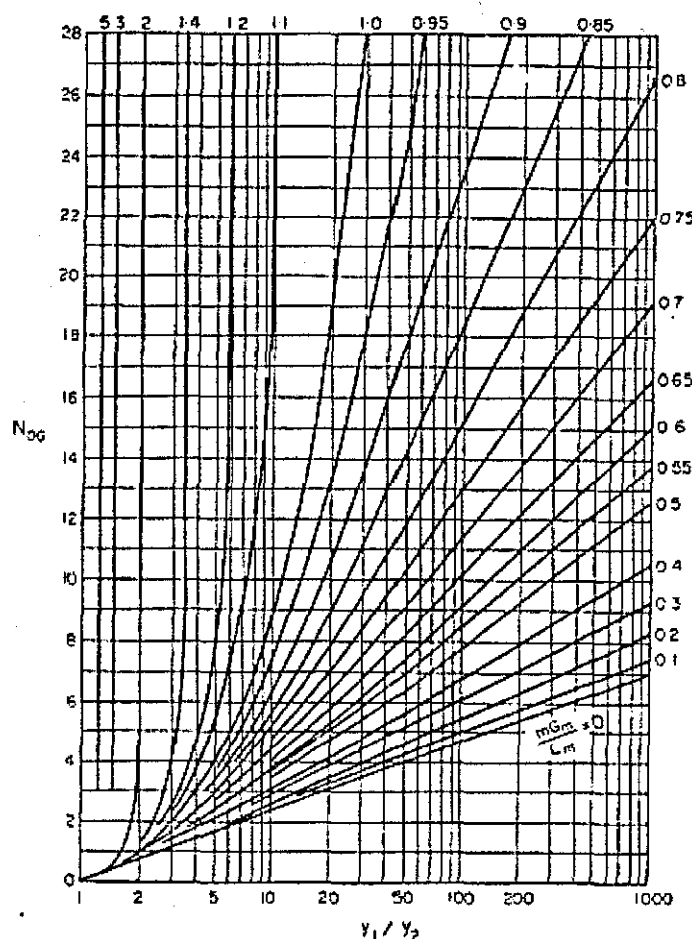
Fig.8 – Coburn's chart for gas absorption columns

From this plot the number of transfer units can be quickly established.

3.4.2   Design Methodology

In order to calculate the liquid flowrate and the slope of the equilibrium curve, *m*, the liquid equilibrium concentration must be calculated from the activity coefficients. This would correspond to the minimum liquid flowrate. From this the liquid flowrate can be found, and the number of mass transfer units determined from the chart. The method is as follows:

1. Calculate the activity coefficient at the top and bottom of the column. There are many different equations that can be used for this purpose, for example the Van Laar equation could be used. Constants for use in the equations can be found from a variety of sources, for example Ghmeling and Onken [15], or Landolt-Bornstein [33].

2. Taking the highest value of the activity coefficient (as this corresponds with the worst case scenario) the liquid exit composition at equilibrium with the inlet gas is: $x_e = \dfrac{P}{\gamma P^o} y$

3. The minimum liquid flowrate can then be calculated from $\left(\dfrac{L}{G}\right)_m = \dfrac{y_1 - y_2}{x_1 - x_2}$. Since the liquid, L will usually be assumed to be fresh feed, $x_2 = 0$. The outlet gas composition y_2 will be known from the design statement. Usually the column will be designed for 99% removal of the required component.

4. The actual liquid flowrate is taken as 1.4*minimum flowrate

5. The actual outlet liquid concentration will be $x_1 = \dfrac{y_1 - y_2}{\left(L / G\right)}$

6. $\dfrac{y_1}{y_2}$ will be known from the original design statement.

7. Calculate the slope of the equilibrium curve, $m = \dfrac{\gamma P^o}{P}$

8. The number of transfer units can now be determined from Fig. 7.

9. The height of the packed column can then be calculated from:

$$Z = N_{OG} * H_{OG}$$

Where Z = Height of column, m

H_{OG} = Height of transfer unit in gas phase concentrations, m.

As in Liquid-Liquid extraction calculations H_{OG} is difficult to calculate as it depends on a number of variables. Data on height of transfer units can also be found in Sinnot [48]. Other references for the height of a transfer unit can be found in that text.

10. Using the economic gas flowrate for the type of packing under consideration from Morris and Jackson [40], calculate the column diameter.

3.4.3   Inventory in Gas Absorption Columns

In order to calculate the liquid inventory in the column we must calculate the liquid hold-up. There are two ways of doing this.

The following correlation that can be used to estimate the total liquid hold-up [45]:

$$H_{OW} = 0.143 \left(\frac{L'}{d_p} \right)^{0.6}$$

Where: L' = Liquid flowrate (kg/m^{2}s)

d_p = Equivalent diameter of the packing, mm

H_{OW} = Liquid hold-up, (m^3 of liquid/m^3) of column.

Piche et al. have also developed a computer programme, freely available for download from the Internet, for calculating packed bed properties. This program requires data on liquid and gas properties and uses neural network correlations to calculate the liquid hold-up, as well as other variables in packed tower operation. The program can be downloaded from http://www.gch.ulaval.ca/~flarachi. This can also be used to calculate liquid hold-up in a packed column.

In order to take into account the changing composition in the column we will assume that the composition of the gas and liquid streams changes at a point half-way up the column – so that half of the liquid inventory will be of composition X_1 and the other half of composition X_2, and likewise for the gas inventory.

Using this information the liquid inventory in the column will be:

Liquid Inventory, composition X_1 = $0.5 H_{ow} \dfrac{\pi d^2}{4} Z$

Liquid Inventory, composition X_2 = $0.5 H_{ow} \dfrac{\pi d^2}{4} Z$

The Gas Inventory will be the total volume of the column less the liquid inventory and the packing volume. Now, the total volume less the packed volume is equal to the voidage fraction times the column volume, so:

Total Gas Inventory = $\varepsilon \dfrac{\pi d^2}{4} Z - H_{ow} \dfrac{\pi d^2}{4} Z = \dfrac{\pi d^2}{4} Z (\varepsilon - H_{ow})$

But there must also be an allowance for column space for vapour disengagement, and likewise for distillation columns we will assume that this is equal to 15% of packed volume.

$$\text{Total Gas Inventory} = \frac{\pi d^2}{4} Z(\varepsilon - H_{OW}) + 0.15 \frac{\pi d^2}{4} Z = \frac{\pi d^2}{4} Z(\varepsilon - H_{OW} + 0.15)$$

$$\text{Gas Inventory, composition } Y_1 = 0.5 \frac{\pi d^2}{4} Z(\varepsilon - H_{ow} + 0.15)$$

$$\text{Gas Inventory, composition } Y_2 = 0.5 \frac{\pi d^2}{4} Z(\varepsilon - H_{ow} + 0.15)$$

Nomenclature

d = Column diameter, m

d_p = Equivalent diameter of packing, mm

G'_m = Gas molar flowrate per unit area on a solute free basis, kmol/m^{2}s

H_{OG} = Height of an overall transfer unit based on gas phase concentrations, m

H_{OW} = Liquid Hold-up in column, m^3/m^3

L' = Liquid mass flowrate per unit area, kg/m^{2}s

L'_m = Liquid molar flowrate per unit area on a solute free basis, kmol/m^{2}s

m = Slope of the equilibrium line, Dimensionless

N_{OG} = Number of overall transfer units based on gas phase concentrations

P = Pressure, kN/m^2

P^o = Vapour pressure of solute A at the operating temperature, kN/m^2

x = Mol fraction of A in liquid phase, Dimensionless

X = Moles of solute gas A per moles of solvent in liquid phase, Dimensionless

y = Mol fraction of A in gas phase, Dimensionless

Y = Moles of solute gas A to inert gas B in gas phase, Dimensionless

Z = Column Height, m

ε = Voidage fraction of packing, dimensionless

γ = Activity coefficient, Dimensionless

3.5   Adsorbers

The design of an adsorber requires knowledge of the amount of adsorbent required to remove the contaminant. This information can be determined from isotherm data. A variety of isotherms have been developed – for example, the Langmuir, BET and Freundlich isotherms. Of these, the Freundlich isotherm has found the most widespread use, and so this is the isotherm we shall use in our method. The Freundlich isotherm was originally developed for adsorption from liquids [45] but has also been used for gases [53]. The amount of adsorbent required for adsorption can be estimated by using single component isotherm data. This data can be obtained from adsorbent suppliers, or from texts such as [8] or [54]. Liquid phase isotherms are more widely available than vapour phase isotherms in the literature.

3.5.1   The Freundlich Isotherm

$$\frac{x}{m} = KC^{1/n}$$

Where:

x = Mass of contaminant adsorbed

m = Mass of adsorbent

C = Concentration of solute in solution in equilibrium with that on the solid (mg/L in liquid phase, kPa in vapour phase)

K = A Constant

n = A Constant

3.5.2   Design Methodology

1) The engineer will decide – based on the throughput and concentration of material to be adsorbed – whether a regenerable system is required, or if the adsorbent will be changed after a set time.

2) For a regenerable system, assume a cycle time of 8h so that a new adsorption run commences at the start of each shift. Two adsorbers must be used, so that one adsorber is in operation whilst the other is regenerating.

3) For a non-regenerable system, the engineer should assume some changeover time. Depending on the system this could be anything up to 3 months.

4) Calculate the amount of material to be adsorbed for each component during the previously determined time period.

5) Using the Freundlich isotherm data, calculate the amount of adsorbent required for each contaminant.

6) The minimum total adsorbent required will be the sum of the individual adsorbent requirements calculated in step 5.

7) A factor must be added to that value calculated in step 6, because of the nature of the isotherm data. Many times, especially in manufacturers literature these are batch isotherms used only to show that the given adsorbent can remove the desired contaminant. The working capacity may be less because of other constituents present – for example, Total Organic Carbon (TOC) in the case of water, and also because of non-instantaneous adsorption kinetics. Therefore, a factor must be added as a safety factor, and this may be anything from 20% to 100% [53]. We will take a value of 50%, as a safety factor to account for deficiencies in the method.

The inventory of chemicals present will be the amount of adsorbed material at the end of each cycle (this is when the inventory will be highest and as such represents the most hazardous time period in which the adsorber is operating) calculated in step 4, and the amount of adsorbent required calculated in step 7. The gas inventory can be neglected as it will be extremely small in comparison to those inventories (in the case of an 8h cycle the adsorbed material will be present for 8h whilst the gas will only have a residence time a fraction of this – less than a minute. Therefore the gas is present in insignificant quantities when compared to the other components present).

It can be seen that one of the major parameters to determine inventory – and hence inherent safety – in adsorbers is the cycle or changeover time. A smaller cycle time will result in smaller vessels, but greater regeneration costs. Shorter changeover times for non-regenerable systems will also result in smaller and more inherently safe vessels but this must also be balanced against the cost of changeover, and also more frequent shutdowns to maintain and replace the adsorbent. This in itself is

also an inherently unsafe operation as the risk of accident is highest during shutdown and start-up.

This is a trade-off the engineer must be aware of.

3.6   Heat Exchangers

We will assume the use of a single pass counter-current shell and tube heat exchanger. These

can be used for all applications [48] so are suitable for any general case. Counter-current flow will be

assumed, as with this type of flow it is possible to utilise a greater amount of the heat content of the

heating fluid. Therefore it is felt that this type of contact is most likely to be found in industry. Other

types of heat exchangers, for example printed circuit heat exchangers are finding greater use in industry

and may have smaller inventories. However they tend to be designed for specific applications. Shell

and tube heat exchangers may not be the most efficient or the most inherently safe design but they are

suitable for most applications. It may also be argued that since they would tend to have a larger

inventory than other types of heat exchanger the assumption of their use is pessimistic and therefore

has an added safety factor.

The area required for heat exchange, A, can be calculated from

$$Q = mC\Delta T$$

$$Q = UA\Delta T_{lm}$$

Where:

m = Mass flowrate of stream, kg/s

C = Heat capacity, kJ/kg°C

ΔT = Temperature of fluid out – Temperature of fluid in

U = Overall heat transfer coefficient, W/m²°C

A = Heat exchange area, m²

ΔT_{lm} = Log mean temperature difference across heat exchanger

Values for U can be estimated from [48] depending on the fluids involved.

Next an assumption must be made of the dimensions of the tubes in the exchanger. The

diameter of the tubes depends on the nature of the fluids involved – the corrosiveness, and the fouling.

The engineer should use his or her best judgement. The engineer should also make an assumption as to the length of a tube. The preferred lengths of tubes are 6ft, 8ft, 12ft, 16ft, 20ft and 24ft. [48]

From this information, the number of tubes can be calculated from:

$$N_t = \frac{A}{\frac{\pi}{4}d_o^2}$$

no $$Nt = \frac{A}{L \cdot \pi d}$$

From this the shell diameter can be calculated from:

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{1/n_1}$$

Where:

d_o = Outside tube diameter, m

N_t = Number of tubes

D_b = Bundle diameter, m

K_1 = A constant. Assuming a single pass, for square pitch K_1=0.215, for triangular pitch K_2= 0.319

n_1 = A constant. For square pitch $n_1 = 2.207$, for triangular pitch $n_1 = 2.142$

From the bundle diameter, D_b the shell diameter D_s can be obtained from charts in Sinnot [48]

Inventory

Tube side inventory, m³ = Volume in tubes + volume in shell heads

$$\frac{\pi}{4}d_i^2 L_t N_t + \frac{4\pi}{3}D_s^3$$

Where:

d_i = Tube inside diameter, m

$Nt \propto \frac{A}{d}$ $V \propto$ $Nt \propto \frac{A}{d}$

Shell side inventory

Shell side inventory, m³ = $\frac{\pi}{4}D_s L_t - \frac{\pi}{4}d_i^2 L_t N_t = \frac{\pi}{4}L_t\left(D_s - d_i^2 N_t\right)$

This is only applicable for heating and cooling of process streams. Due to the density difference along the length of condensers and vaporisers this method is not applicable, and without a detailed examination into this area together with practical data from plants it would be difficult to develop a method for calculating inventory in vaporisers and condensers. At present therefore the inventory in these equipment items cannot be calculated.

Cooler-condensers, where an uncondensable gas is present are extremely hard to design due to the changing heat transfer coefficient along the length of the exchanger. This makes it very hard to calculate the dimensions of the exchanger. In these situations it is more appropriate to use vapour pressure data to calculate the amount of vapours condensed in order to estimate the composition of the outlet streams. There is at present no method available to calculate inventory.

3.7   Quench Columns

The design of quench columns, where a gas stream is cooled by direct contact with liquid in a packed tower is a complicated procedure. The design must take into account both the heat transfer and mass transfer within the column, as each factor influences the other. Therefore the column must be designed iteratively to determine the changing composition in the liquid and gas phase, and also the gas and liquid temperatures in each section of the column. Although the calculations are basic engineering equations the number of calculations that must be carried out in the design is so large it leads to a very lengthy procedure.

By neglecting mass transfer in the column, and designing the column only on the basis of heat transfer the design is greatly simplified. The time required for sizing can be reduced from hours, if not days to only a few minutes. The column will probably be undersized due to neglecting the latent heats of vaporisation, however from a sample calculation comparing this short-cut to a detailed calculation, the difference in size is not excessively great (AD.3). The diameter can be calculated from the economic flowrates, in the same way as for other packed columns.

The equation for heat transfer between the gas and liquid phases (neglecting that due to mass transfer) is:

$$LCdT_l = UA(T_g - T_l)Z$$

Where:

L = Mass flowrate of liquid per m^2 per hour

C = Heat capacity of liquid, kJ/kg^{o}C

dT_l = Temperature difference between the liquid into and liquid out of the column

U = Overall heat transfer coefficient

T_g = Temperature of gas in, ^{o}C

T_l = Temperature of liquid out, ^{o}C

Z = Height of column, m

3.8   Decanters

A precise size of a decanter would be unknown, because the droplet size would be unavailable at this stage. An estimate of the size of a decanter can be made by assuming a 5-minute residence time in the vessel [48].

3.9   Gas-Solids Separation

A design of a cyclone for the separation of solids from a gas stream shows that size of the vessel is such that the inventory in this item of equipment is minor in comparison to the inventory of the solids storage. It is therefore felt that the sizing of these vessels is of minor importance in a route selection study.

3.10   Pipeline Inventory

As noted earlier, the inventory in process pipelines may have a large effect on overall inventory. An estimation of pipeline diameter can be made from the velocity of fluid in a pipeline. In industry the pipe diameter would be calculated on an economic basis, with the diameter of pipeline chosen that minimises capital and pumping costs. The normal range for fluid velocities in pipelines is 1-3 m/s for liquids, and 15-30 m/s for gases [48]. By selecting the lowest value in this range an

estimate of pipe diameter can be made. The lowest value of fluid velocity is chosen as this corresponds to the largest diameter, and hence the largest inventory.

The length of the pipeline must also be known, however this is where major uncertainties arise. The site layout is only known after the detailed design has been performed, so at this stage it is very difficult to make any estimation of pipe length. One possible method would be to take some factor of the minimum distance between vessels, but this has problems that would prohibit its use. Firstly it is highly improbable that vessels will be at a convenient distance from one another that can be represented in terms of the minimum distance. The distance between equipment items will depend on factors such as the type of upstream and downstream equipment, the location of the upstream and downstream equipment, the contents of surrounding vessels, plant access etc. Also, although the ground distance between vessels will be the major factor in deciding pipe length other factors will influence the pipe length, such as the requirement for elevating pipes for road access. Also the height of equipment – both the elevation and physical height – will result in longer pipelines. This would be especially important in very tall vessels, such as fractionating columns in oil refineries.

It can be seen that this is an area that requires much work. With no data or experience from industry, or site plan from a detailed design study it is extremely difficult to estimate pipe inventory. It is felt that the pipe length has such a large effect on inventory any method derived that does not have a basis in empirical results would be so inaccurate as to prove completely unsuitable. A possible way to proceed would be to consider only the pipes between major process items, and attempt to estimate the length between them based on a rough siting study based only on the type of process being undertaken in each processing step, and the relationship between the different steps. This is an area that requires careful examination from someone who has experience with plant site layout and pipeline design.

4.0   Case Studies

In order to assess the suitability of using short-cut methods to calculate vessel inventory these methods must be compared to some benchmark to determine their accuracy. It was decided that IChemE design studies would be used as the benchmark. These studies use detailed calculations to design process plant to the level of accuracy required for manufacturing activities to begin and as such yield highly accurate results. Two design studies were considered, that of the production of Methyl Ethyl Ketone (MEK) from 2-Butanol [1] and the production of acetic anhydride from acetone [20]. The short-cut design will use the same route for manufacturing the desired product as the IChemE design study. Although in reality the engineer would study all the available options for manufacturing a chemical the purpose of this exercise is to compare the results of short-cut calculations with detailed design methods. In order to be able to draw any conclusions about the accuracy of the short-cut calculations the same unit operations must be used to enable a like for like comparison.

Once the route has been identified the major equipment items are selected using the guidelines in Section 2. A mass balance is performed to calculate the flows through each equipment item. The items can then be sized through short-cut methods. The methods used are those described in Section 3, unless a literature search provides a suitable alternative. For example, a literature review in the MEK design study yielded the 'Height of a Reactor Unit' concept, which was used to size the reactor. The equipment sizes calculated through the short-cut method are then compared with those calculated through the detailed IChemE study. This will enable a comparison of the short-cut methods with detailed methods, to determine whether or not they give an acceptable level of accuracy. A comparison with cost estimates will be used to decide what constitutes an acceptable level of accuracy. Cost estimates in the early stages of the design process tend to be accurate to 40% [9]. This is the value that will therefore be used to determine acceptability of the short-cut methods. The inventory of each equipment item will be calculated for the short-cut design, to demonstrate how this is done. The methods used for calculating the equipment inventories are those given in Section 3. The inventory of each equipment item will not be given for the detailed IChemE study. This is because the inventory of the equipment is a function of the vessel size. Using the same calculation for the short-cut method and the detailed design would not yield any further information that could be used in comparison or help in assessing the suitability of the short-cut method.

4.1   Methyl Ethyl Ketone Production

This case study is the design of a plant to produce 10,000 tonnes/year of Methyl Ethyl Ketone (MEK) from 2-Butanol. The 2-Butanol is reacted at high temperature (400-500°C) on a zinc oxide catalyst forming MEK and Hydrogen:

$$2 - \text{Butanol} \longrightarrow \text{MEK} + \text{Hydrogen}$$

$$C_4H_{10}O \rightarrow C_4H_8O + H_2$$

The services available are:

Dry saturated steam at 140°C

Cooling water at 24°C

Flue Gases at 540°C

Process:

The 2-Butanol will come from feed at 25°C, and will be heated, vaporised and superheated to reach the inlet reactor temperature of 500°C. The reactor products will be condensed to separate the MEK and 2-Butanol from the Hydrogen. However, a significant portion of MEK will be lost with the Hydrogen stream, so it will be necessary for further separation to recover as much MEK as possible. This will be done by firstly absorbing the MEK with water. Separating MEK and water is a difficult separation, so liquid-extraction shall be used with a 1,1,2-Trichloroethane (TCE) solvent. The water will be recycled back to the absorber. The TCE and MEK will then be separated in a distillation column. The MEK from this column will still contain some 2-Butanol, so it will be combined with the stream from the condenser and the MEK separated from the 2-Butanol in a distillation column. The 2-Butanol will be recycled back to the reactor, and the MEK removed as product. The flowchart for this process is shown in Figure 7.

The short-cut methods will be compared with values from a detailed Institute of Chemical Engineering design study, 'The Manufacture of Methyl Ethyl Ketone from 2-Butanol' [1].
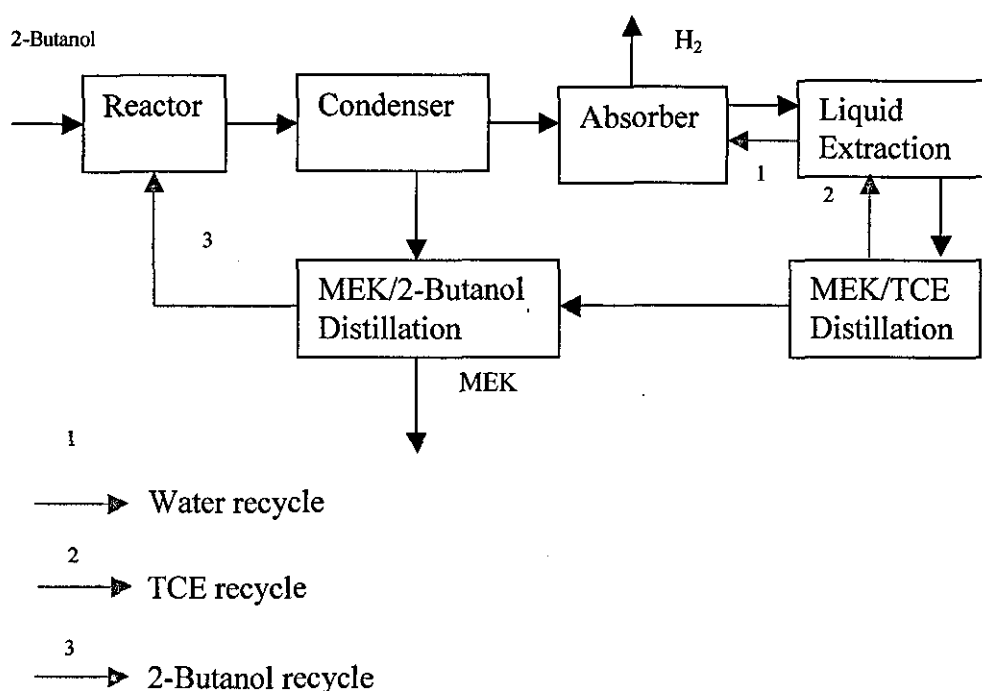
Fig. 8 Flowchart showing major equipment items for MEK production

4.1.1   Reactor

The reactor is sized by the 'Height of a Reactor Unit' from Perona and Thodos [41]. This is a short cut method that enables the calculation of the length of a reactor tube by calculating the length of tube required for the reaction to reach equilibrium.

The 'Height of a Reactor Unit' method does not consider mass transfer effects, heat transfer and catalyst activity. These will have a significant effect on the length of tube required. Therefore the IChemE method is a much more detailed method that uses a computer programme to calculate the temperature and conversion profiles throughout the reactor, and this data enables the engineer to determine the reactor size required.

The reactor converts 2-Butanol to Methyl Ethyl Ketone and Hydrogen according to the reaction:

$$C_4H_{10}O \longrightarrow C_4H_8O + H_2$$
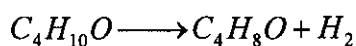
Mass Balance

	In (kg/h)	Out (kg/h)
2-Butanol	1541.67	154.17
MEK	1.42	1351.42
Hydrogen	0	37.5
Total	1543.09	1543.09

Equipment size

	Reactor length (m)	Cross-sectional area (m^2)
IChemE design	3.0	0.123
Short-cut design	1.3	0.119

Equipment Inventory

Chemical	Mass (kg)
MEK	0.053
2-Butanol	0.122
Hydrogen	0.002
Total	**0.177**

So the total inventory is 0.177 kg of a mixture of 68.9% 2-Butanol, 29.9%MEK

The reactor designed is a plug flow reactor. It is cylindrical in shape, with a length of 1.3m and a cross-sectional area of 0.119m^2.

It can be seen that the IChemE design provides for a reactor over twice the size of the one designed through short-cut methods. This is because the short-cut reactor sizing method is based only on the reaction, and not on the heat transfer characteristics. Once these are taken into account it is found that in order to provide suitable heat exchange in the reactor tubes of 3m in length are required.

This is an appreciable error, however the effects of this margin of error are lessened because of the low inventory in the vessel. The total inventory is only 0.177 kg, and taking into account the

extra length of the IChemE designed reactor the inventory will increase to approximately 0.5 kg (The first 1.3m will be filled with catalyst; next 1.7m will be empty tube). This is still a very low value, especially when considering the total flowrate into the equipment so it is considered the short-cut method is sufficient in calculating the order of magnitude of the hazard posed by the vessel contents.

4.1.2   Condenser

It proved impossible to calculate the inventory in the condenser. Uncertainties in the calculation of condenser size and the content of condensate in the condenser prevented the estimation of inventory. This has been identified as a major area of concern and one that requires much work.

4.1.3   Gas Absorber

The purpose the absorber is to separate the uncondensed 2-Butanol and MEK from Hydrogen. They are still present in such high amounts that it is necessary to recover them.

The column diameter was calculated by the same method for both the short-cut design and the detailed IChemE design study. For the short-cut method column height was calculated using the method described in section 3.4. The detailed design study calculates the column height on the basis of the overall mass transfer coefficient, the interfacial area and the driving force. The mass transfer coefficient is calculated by two different methods. The first uses well-established correlations for calculating the gas and liquid film mass transfer coefficients. The second uses correlations developed by Othmer and Scheibel who studied the absorption of MEK from air to water using a packed column [1]. The mean of the values obtained from the two methods is used to calculate the mass transfer coefficients, and from this column height.

Mass Balance

	Gas In, kg/h	Liquid In, kg/h	Gas Out, kg/h	Liquid Out, kg/h
2-Butanol	28.86	0	0	28.86
MEK	242.64	0	2.43	240.21
Hydrogen	37.5	0	37.5	0
Water Vapour	0	0	10.82	0
Water	0	2172.71	0	2161.89
Total	309	2172.71	50.75	2430.96

Equipment Size

	Packed Height	Column diameter
IChemE design	5.0	0.5
Short-cut design	8.0	0.5

Liquid Inventory

Water	23.0 kg
10% MEK Solution	22.4 kg

So the total liquid inventory is 45.4 kg of a 4.9% solution of MEK

Gas Inventory

MEK	0.288 kg
2-Butanol	0.033 kg
Hydrogen	0.096 kg
Water Vapour	0.015 kg
Total	0.432 kg

The total gas inventory is 0.432 kg of a gas mixture containing 66.6%w/w MEK, 7.6% 2-Butanol and 22.2% Hydrogen.

The column is a cylindrical packed column. The height of the packed section of the column is 8m. The width of the column is 0.5m.

The size of the column corresponds well to that found through the IChemE method. The method used to calculate column size was the same in both methods, but the column height was acceptably close to that found through a detailed design.

4.1.4   Liquid Extraction

The relative volatility of the system MEK-Water is such that it cannot be distilled. Therefore it is necessary to extract the MEK with some other material so that it may be separated by distillation. 1,1,2 Trichloroethane can be used for this purpose. [42]

The method discussed in section 3.3 was used for the short cut design of the liquid extraction column. The IChemE study uses both capital and operating cost data to calculate the solvent required. Using this the column height is calculated using the overall mass transfer coefficient, the interfacial area and the overall mean driving force. It must be pointed out that the columns designed in the short-cut method and the detailed IChemE method are different. The short-cut design method assumes the use of a packed column whilst the IChemE method assumes the use of a Rotating Disc Contactor.

Mass Balance

	In		Out	
	Feed, kg/h	**Solvent, kg/h**	**Extract, kg/h**	**Raffinate, kg/h**
MEK	240.21		230.08	10.13
2-Butanol	28.86		28.86	0
Water	2161.89			2161.89
1,1,2 Trichloroethane		1070	1070	
	2430.96	1070	1328.94	2172.02

Equipment Size

	Packed Height, m	Diameter, m
IChemE design	2.5	0.2
Short-cut	6	0.2

Equipment Inventory

	2-Butanol, kg	MEK, kg	TCE, kg	Water, kg	**Total, kg**
Feed	0.7	5.9		53.1	59.7
TCE Feed			30.5		30.5
Extract	0.7	5.6	25.8		32.1
Raffinate		0.3		62.7	63.0
Total	1.4	11.8	56.3	115.8	**185.3**

So from the above table it can be seen that the inventory of the column will be 185.3 kg of liquid, with composition 30.4% TCE and 6.4% MEK.

The liquid extraction unit is a cylindrical packed column. The height of the packed section is 6m, and the diameter is 0.2m.

The short-cut method sizes a column well over twice as big as that found in the detailed design. Although the magnitude of the error is slightly concerning, the fact that it errs on the safe side tends to alleviate those concerns. It is always better to overestimate rather than underestimate properties that would give rise to increased hazards, such as inventories. This demonstrates one possible disadvantage with the short-cut methodology in that the use of only a limited range of equipment can be assumed. At this stage the use of more efficient technologies, such as the rotating disc contactor, cannot be taken into account.

4.1.5   Solvent Recovery

The solvent extraction still separates the Methyl Ethyl Ketone and 2-Butanol from the 1,1,2 Trichloroethane. The TCE is then recycled to the liquid extraction column.

　　　The sizing of the distillation column required for solvent recovery was not calculated using Zomosa's method (3.1). This is because one of the underlying assumptions of Zomosa's method is that the equilibrium curve can be approximated by a straight line. An examination of the equilibrium data for the MEK-TCE system shows that this is not the case. Therefore it is assumed that the column is a packed column rather than a plate column, with the column height being calculated by the McCabe-Thiele method. The column diameter is calculated in the same manner as the gas absorption design, using the economic flowrates from Morris and Jackson [40].

　　　The IChemE method uses the same method for calculating column diameter. The column height is calculated through evaluation of the integral

$$Z = \frac{G}{K_y a} \int_{y_2}^{y_1} \frac{dy}{y^* - y}$$

Where:　G = Molar flowrate, kmol/m²s

　　　　K_y = Mass transfer coefficient

　　　　a = Interfacial area per meter height of column, m²/m

　　　　y = Mol. Fraction of MEK in vapour

　　　　y^* = Equilibrium mol. Fraction of MEK in vapour.

Mass Balance

	In	Out	
	Feed, kg/h	Distillate, kg/h	Bottoms Product, kg/h
MEK	230.08	227.74	2.34
2-Butanol	28.86	17.61	11.25
TCE	1070		1070
Total	1328.94	245.36	1083.58

Equipment Inventory

	Packed Height, m	Diameter
IChemE design	7.3	0.44
Short-Cut design	6.6	0.40

Liquid Inventory

	MEK	2-Butanol	TCE	Total
Distillate	3.4	0.26		3.66
Bottoms	0.05	0.26	25.2	25.5
Total	3.45	0.52	25.2	**29.2**

Giving a liquid inventory of 29.2 kg of 86.3% TCE and 11.8% MEK

Gas Inventory

	MEK	2-Butanol	TCE	Total
Distillate vapour	0.74	0.06		0.80
Bottoms vapour	Negligible	0.01	1.12	1.13
Total	0.74	0.07	1.12	**1.93**

So there is a total gas inventory of 1.93 kg, with the gas composed of 38.3% MEK, 58.0% 1-1-2 Trichloroethane.

It can be seen that the short-cut design is in good agreement with the detailed design. The short-cut design is slightly smaller, but is well within the margin of accuracy stipulated for acceptability.

4.1.6   MEK Purification

The liquid flow from the condenser and the distillate product from the solvent extraction still are combined and sent to a distillation column, where MEK is separated from the 2-Butanol as final product.

An examination of the equilibrium data suggested that Zomosa's method was applicable in this instance. This was therefore used in the short-cut method.

The detailed IChemE method calculated the number of theoretical stages from a McCabe-Thiele diagram. The plate efficiency was calculated using a method published by the American Institute of Chemical Engineers [1]. From these values the column height was determined. The column diameter was calculated by determining the maximum vapour velocity through the bubbling area of a plate. This diameter was confirmed by verifying that the flooding was less than half the plate spacing and the residence time in the downcomer was not excessive.

Mass Balance

	In	Out	
	Feed, kg/h	**Distillate, kg/h**	**Bottoms Product, kg/h**
MEK	1336.52	1335.31	1.21
2-Butanol	142.92	13.84	129.08
Total	1479.44	1349.15	130.29

Equipment Size

	Number of plates	Diameter
IChemE design	35	1.0
Short-Cut design	28	0.7

Liquid Inventory

	MEK	2-Butanol	Total
Distillate	98.3	1.0	99.3
Bottoms Product	5.3	583.3	588.6
Total	103.6	584.3	**687.9**

So the liquid inventory is 492.5 kg of a solution with composition 86.6% 2-Butanol, 13.4% MEK

Gas Inventory

	MEK	2-Butanol	Total
Distillate	4.7	Negligible	4.7
Bottoms Product	0.1	8.4	8.5
Total	4.8	8.4	**13.2**

Vapour inventory of 8.7 kg of a 33.3% MEK, 66.7% 2-Butanol.

I can be seen that the short-cut method under predicts the size of the distillation column required. The short-cut design is approximately 40% of the size of the detailed design. This is still within an order of magnitude accuracy, although the under prediction may give cause for concern.

4.2   Acetic Anhydride Plant Design

The case study is for the design of a plant to manufacture 20000 tonnes per year of acetic anhydride. The product is to be of 95% w/w purity.

Acetic anhydride is produced from the reaction of acetic acid and ketene:

$$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O$$

Ketene   Acetic Acid   Acetic Anhydride

The there are two main feedstocks into the process. Acetone, used to create the ketene in the reactor vessel, and acetic acid. The acetic acid is used to cool the reactor products in a quench column. The gases are then further cooled. As they condense the acetic acid and ketene react to form acetic anhydride.

The ketene is produced on site from the thermal cracking of acetone at 650°C to 800°C:

$$(CH_3)_2CO \rightarrow CH_4 + CH_2CO$$
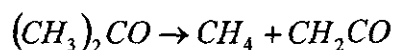
Acetone → Methane + Ketene

Other side reactions are present in this reaction, which are discussed in section 4.2.1. Researchers have found that the economic conversion for this reaction is 25%. In order to minimise the decomposition of ketene the gases must be rapidly cooled. This is done by quenching the gases with a mixture of liquid acetic acid and acetic anhydride. This is then passed to packed quench tower for further cooling, and also to ensure that there is sufficient acetic acid in the gas stream for reaction with the ketene.

The vapours are passed to a condenser, where the reaction of acetic acid with ketene takes place. As the vapours condense they react with each other forming acetic anhydride. The design of this vessel is for 90% conversion of the ketene present. The condensed liquor comprising acetone, acetic acid and anhydride is passed to the acetone recovery column, where the acetone is separated by distillation and recycled back to the reactor. The bottoms product from this column containing a

mixture of acetic acid and acetic anhydride is passed to a further distillation column where the acetic

anhydride is removed as product. The flowchart for this process is shown in Figure 10.

The short-cut methods will be compared with values from a detailed Institute of Chemical

Engineering design study, 'The Manufacture of Acetic Anhydride' [20].
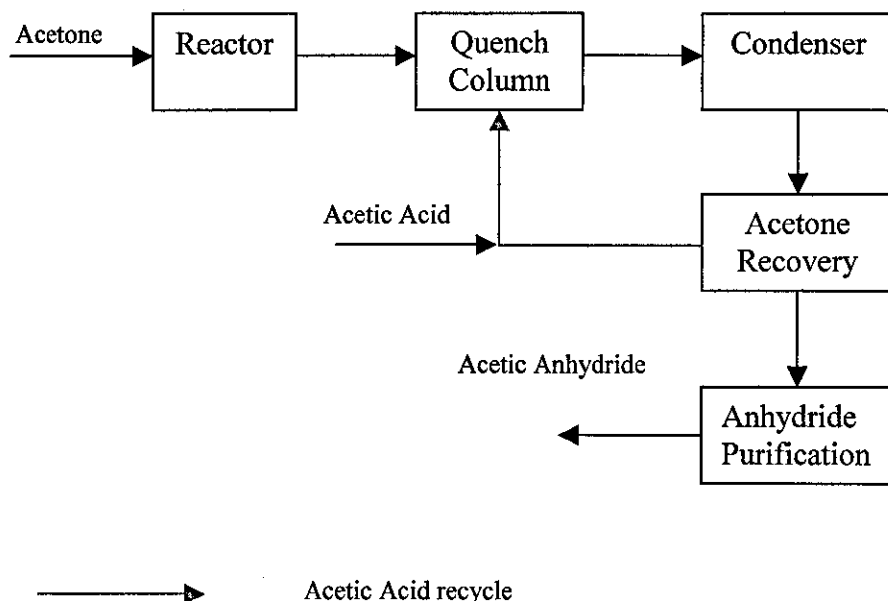
Fig. 9 Flowchart showing major equipment items for acetic anhydride production.

4.2.1   Reactor

The main reaction is the thermal decomposition of acetone to methane and ketene:
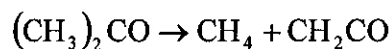
$$(CH_3)_2 CO \rightarrow CH_4 + CH_2 CO$$

However, two unwanted side reactions also take place. The first is the decomposition of ketene to

ethene and carbon monoxide:

$$2CH_2 CO \rightarrow C_2 H_4 + 2CO$$
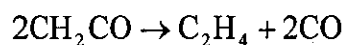
And the second is the dehydrogenation of acetone, forming hydrogen, carbon monoxide and carbon

(coke):
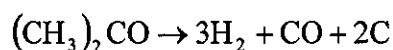
$$(CH_3)_2 CO \rightarrow 3H_2 + CO + 2C$$

Mass Balance

	In		Out	
	kg/h	kmol/h	kg/h	kmol/h
Acetone	8773	151.3	6580	113.4
Ketene			1112	26.5
Methane			592	137.0
Ethene			172	4.4
Carbon Monoxide			292	10.4
Carbon Dioxide			21	0.5
Hydrogen			4	2
Total	8773	151.3	8773	194.2

The reaction takes place in a furnace. The reaction section will only be a minor part of the furnace. The heat transfer in the furnace will require a much larger volume in order to preheat and vaporise the acetone, provide heat of cracking and provide superheat. The design of a furnace is complex, requiring knowledge of flame temperature, heat transfer coefficients, skin temperature and other thermodynamic properties. Attempts to develop short-cut methods for calculating furnace inventory failed to give results of sufficient accuracy. The size and inventory in this section is therefore not given as it will not be representative of the actual size of the furnace.

4.2.2   First Liquid Quench

The liquid quench is not used for inventory estimation purposes. Injecting a liquid spray into the reactor outlet gases in the pipework is the method for the first quench, so that the inventory would only be that in the pipes.

4.2.3   Quench Column

The design of the quench column is such that the gases exit at a temperature suitable for entering the condenser and that the amount of acetic acid in the outlet gas is equimolar with the ketene for reaction in the condenser.

The short-cut design uses the methodology in section 3.7, with the column height being calculated only on the basis of the heat transfer coefficient. The detailed IChemE design uses both heat and mass transfer coefficients to calculate the column height. This uses a series of iterative calculations to calculate the gas compositions and temperatures at different points throughout the column, and from this the packed height can be determined.

Mass Balance

	Gas In kg/h	Liquid In, kg/h	Gas Out, kg/h	Liquid Out, kg/h
Acetone	6580		6580	
Ketene	1112		1112	
Methane	592		592	
Ethene	172		172	
Carbon Monoxide	292		292	
Carbon Dioxide	21		21	
Hydrogen	4		4	
Acetic Acid	2772	22259	1590	23441
Acetic Anhydride	2772	22259	1298	23733
Total	14317	44518	11661	47174

Equipment Size

	Packed Height, m	Diameter, m
IChemE design	2.0	1.4
Short-cut design	2.0	1.8

Liquid Inventory

Total liquid inventory of the quench column will be 151.3 kg of a 50% mixture of acetic acid and acetic anhydride

Gas Inventory

	Bottom section, kg	Top section, kg	**Total, kg**
Acetone	2.4	1.7	4.1
Ketene	0.4	0.3	0.7
Methane	0.2	0.2	0.4
Ethene	0.1	0.1	0.2
Carbon Monoxide	0.1	0.1	0.2
Carbon Dioxide	Negligible	Negligible	Negligible
Hydrogen	Negligible	Negligible	Negligible
Acetic Acid	1.0	0.4	1.4
Acetic Anhydride	1.0	0.3	1.3
Total	5.2	3.1	**8.3**

The total gas inventory is 8.3 kg of a mixture including 49.3% acetone, 16.9% acetic acid, 15.7% acetic anhydride and 8.4% ketene.

The vessel is a cylindrical packed column of height 2.0m and diameter 1.8 m.

The detailed calculation involves a complex iterative procedure that takes into account both heat transfer and mass transfer characteristics. The short-cut method only takes into account heat transfer and so does not require iterative calculations. As can be seen this does not result in an unacceptable increase in error. In fact the column height is the same in both instances. The only difference is in column diameter as a result of a different form of packing resulting in a different economic gas flowrate.

4.2.4   Condenser

As in the Methyl Ethyl Ketone study there is presently no method for determining the inventory in a condenser

4.2.5   Absorber

There is a considerable amount of acetone still remaining in the gas stream exiting the condenser. It is therefore necessary to recover this acetone to recycle back to the reactor to make the process as efficient as possible. The acetone is recovered by absorption in acetic acid.

The short-cut design uses the method given in section 3.4. The detailed IChemE design differs in that a plate column with interstage cooling is used, because of the high heat of absorption of acetone. Without cooling the temperature of the liquid will increase greatly, thus reducing the absorption rate. The detailed design derives an equation for the number of theoretical plates from first principles. The plate efficiency is calculated using O'Connell's method [20]. From this the total number of plates can be calculated. Next the heat load on the absorber is calculated and from this the number of heat exchangers required in the column can be determined. The column diameter is determined by taking the mean of the minimum and maximum plate diameters, calculated using the gas flowrates in the column.

Mass Balance

	Gas In, kg/h	Gas Out, kg/h	Liquid In, kg/h	Liquid Out, kg/h
Acetone	1126	11		1115
Acetic Acid	155	155	3021	2868
Acetic Anhydride	103	103		260
Ketene	107			
Methane	592	592		
Ethene	172	172		
Carbon Monoxide	292	292		
Carbon Dioxide	21	21		
Hydrogen	4	4		
Total	2572	1350	3021	4243

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Equipment Size

	Packed Height	Diameter
IChemE design	*	1.07
Short-Cut design	9.2	1.0

Liquid Inventory

	First section, kg	Second section, kg	Total, kg
Acetone		18.4	18.4
Acetic Acid	64.0	47.1	111.1
Acetic Anhydride		4.2	4.2
Total, kg	64.0	69.7	**133.7**

There is a total liquid inventory of 133.7kg of a solution of 83.1% acetic acid, 13.8% acetone.

Gas Inventory

	First section, kg	Second section, kg	Total, kg
Acetone	1.4	0.0	1.4
Acetic Acid	0.2	0.3	0.5
Acetic Anhydride	0.1	0.2	0.3
Ketene	0.1	0.0	0.1
Methane	0.8	1.0	1.8
Ethene	0.2	0.3	0.5
Carbon Monoxide	0.4	0.5	0.9
Carbon Dioxide	0.0	0.0	Negligible
Hydrogen	0.0	0.0	Negligible
Total	3.2	2.3	**5.5**

So there is a total gas inventory of 5.5kg of a 25.5% acetone, 32.7% methane mixture.

The column designed as part of the IChemE design study was a plate column with 12 plates, with a plate spacing of 20 inches so that the total column height is 6.0m. The reason for the selection of a plate column was due to the heat given out by the absorption of acetone in acetic acid, necessitating cooling within the column. This is something not taken into account in the short-cut design. However, it is felt that this would not affect the inventory to any great extent. The packed column is taller than the plate column, but this is offset by the lower liquid hold-up in a packed column. By neglecting the cooling requirement the actual column would have an inventory of cooling water which is not taken into account here. However the hazard posed by cooling water itself is very low so there is minimal adverse effect on safety.

4.2.6   Acetone Recovery

The short-cut design uses Zomosa's method to size the column. The IChemE design uses a plate-to-plate analysis to calculate the temperature and compositions on each theoretical plate in the column, and from this the total number of theoretical plates can be determined. This trial and error calculating procedure is necessary because of the complexities of separating a multi-component mixture. The column diameter is calculated using the same method as the gas absorber.

Mass Balance

	Feed kg/h	Distillate, kg/h	Bottoms product, kg/h
Acetone	6569	6523	46
Acetic Acid	2868	37	·2831
Acetic Anhydride	3896	51	3845
Total	13333	6611	6722

Equipment Size

	Number of plates	Column diameter, m
IChemE design	16	1.83
Short-cut design	35	1.05

Liquid Inventory

	Top section, kg	Bottom section, kg	**Total, kg**
Acetone	838.5	13.2	851.7
Acetic Acid	4.2	794.8	799.0
Acetic Anhydride	6.8	1079.8	1086.6
Total, kg	849.5	1887.8	**2737.3**

There is a total liquid inventory of 2737.3 kg/h of a mixture containing 39.7% acetic anhydride, 29.2% acetic acid and 31.1% acetone.

Gas Inventory

	Top section, kg	Bottom section, kg	**Total, kg**
Acetone	17.1	0.1	17.2
Acetic Acid	0.1	7.6	7.7
Acetic Anhydride	0.1	10.3	10.4
Total, kg	17.3	18.0	**35.3**

Total gas inventory of 35.3 kg of a mixture containing 29.5 % acetic anhydride, 21.8% acetic acid, 48.7% acetone.

The equipment is a plate column with 16 plates and a diameter of 1.83m.

The difference in column height is a slight cause for concern, as the column is less than twice the height of the detailed design method. However this is offset by the increase in column diameter so that the overall volume is similar between the two designs. In fact the short-cut design has a volume that is 25% greater than the detailed design. However, it cannot be relied on that two very different dimensions will offset each other.

The relative volatility is very high at 9.66. It is possible that this is indicative of a failure of one of the underlying assumptions of Zomosa's method, that is the equilibrium curve being

approximated by a straight line. In this instance it may be more appropriate to calculate the column height through the McCabe-Thiele method.

4.2.7   Acetic Acid Purification

The acetic acid purification column is designed using the same methods as the acetone recovery column for both the short-cut and IChemE designs.

Mass Balance

	Feed, kg	Distillate, kg	Bottoms Product, kg
Acetone	30	30	0
Acetic Acid	1875	1755	120
Acetic Anhydride	2547	99	2448
Total	4452	1884	2568

Equipment Size

	Number of plates	Column diameter, m
IChemE design	19	1.22
Short-cut design	26	1.05

Liquid Inventory

	Top section, kg	Bottom section, kg	Total, kg
Acetone	8.6		8.6
Acetic Acid	501.9	61.2	563.1
Acetic Anhydride	28.0	1240.2	1268.2
Total	538.5	1301.4	1839.9

Total liquid inventory of 1839.9 kg of a mixture of 30.6% acetic acid and 68.9% acetic anhydride.

Gas Inventory

	Top section, kg	Bottom section, kg	Total, kg
Acetone	0.3		0.3
Acetic Acid	16.8	0.5	17.3
Acetic Anhydride	0.9	10.5	11.4
Total	18.0	11.0	**29.0**

Total gas inventory of 29 kg of a mixture of 59.7% acetic acid, 39.3% acetic anhydride.

The equipment is a plate column with 19 plates and a diameter of 1.22m.

The column dimensions are similar in both design methods. The difference between them is felt to be acceptable.

4.3 Conclusions from Case Studies

Analysis of Results

	MEK, kg	2-Butanol, kg	Hydrogen, kg	Water, kg	TCE, kg
Reactor	0.053	0.122	0.002		
Gas Absorber	2.5	0.0	0.1	43.2	2.5
Liquid Extraction	11.8	1.4		115.8	56.3
Solvent Recovery	4.2	0.6	0.0	0.0	26.3
MEK Purification	108.4	592.7			
Total, kg	127.0	594.8	0.1	159.0	82.6

Table 8 – Summary of total inventory of equipment items in MEK case study

	Acetone, kg	Ketene, kg	Methane, kg	Ethene, kg	CO, kg	CO$_2$, kg	H$_2$, kg	Acetic Acid, kg	Acetic Anhydride, kg
Quench Column	4.1	0.7	0.4	0.2	0.2	0	0	58.9	58.8
Absorber	19.8	0.1	0.8	0.5	0.9	0	0	111.6	4.2
Acetone Recovery	868.9	0	0	0	0	0	0	806.7	1097
Acid Purification	8.9	0	0	0	0	0	0	580.4	1279.6
Total, kg	901.7	0.8	1.2	0.7	1.1	0	0	1557.6	2439.6

Table 9 – Summary of total inventory of equipment items in Acetic Anhydride case study

It can be seen from the tables 8 and 9 that there is a large variation in the inventories in different equipment items. The gas inventory of the system is negligible in comparison with the liquid inventory. This is to be expected for two reasons:

1) Lower residence times associated with gas processing
2) The density of gases in comparison to liquids

The table also shows that there are large differences in the inventories in different types of equipment items. It can be seen that the plate columns have an inventory greatly in excess of that found in packed columns. In the two case studies the inventory in the plate columns dominates the total inventory. In the MEK study, 73% of the total inventory is associated with one plate column and in the anhydride case study 95% of the process inventory is accounted for by two plate columns.

Not all of the major process items in process plant have sized in these studies. Heat exchangers and condenser have not been sized. Also, in the acetic anhydride study the reactor has not been sized. This would have a negligible effect on total inventory, because the reaction takes place in a furnace. As can be seen from the MEK case study gas phase reactions have a comparatively low process inventory.

This is not to say that the equipment items that possess comparatively low inventories can be neglected, or have a low effect on overall process safety. Inventory is only one component of the total hazard associated with a vessel. The physical and chemical properties of the chemicals involved will be of the utmost importance, as will the operating conditions of the equipment item. The hazard posed by each equipment item must be assessed separately, and the engineer must critically assess each item to reduce the hazard of the plant as far as is reasonably practicable. What the above study does show however is that there are key items of a process plant that can pose a significantly hazard due to the inventory of hazardous material that they contain. With this information the engineer can examine ways to reduce the inventory of those items, for example by alternate reaction schemes or different separation technologies.

Storage Tanks

No analysis was performed on any storage units in a plant. Intermediate storage inventory will most likely be found in any given process, with the reason given by engineers being that these inventories are essential in order to make the process easier to control and to minimise any fluctuations in flows and compositions. However it is felt that the engineer should critically assess whether or not the intermediate storage is necessary, rather than accept that it will exist. The effect of intermediate storage on total plant inventory can quickly be seen from the acetic anhydride case study. A storage tank situated just before acetone recovery with a ten-minute hold-up time would have an inventory of over 2200kg (Appendix E) making it one of the largest inventories in the plant.

The inventory in storage tanks is not calculated because it is readily apparent that they have a much greater inventory than would be found in the processing part of the plant. A 1-day storage of the fresh feed of acetone required would have an inventory of 54 tonnes, far in excess of the total plant inventory. It is also a simple matter to size storage tanks on the basis of hold-up time.

Areas for Improvement

Some areas of concern arose out of this study. It proved very difficult to size a cooler-condenser using a short-cut method. It would be inappropriate to assume some value of the overall

heat transfer coefficient and size the condenser using that value, as the nature of a cooler-condenser means the heat transfer coefficient will change greatly over the length of the condenser. It would be difficult to justify the selection of some heat transfer coefficient.

Calculating the inventory of condensers and vaporisers is also an area of uncertainty. Any inaccuracy in determining the ratio of liquid and vapour will lead to a large change in the total inventory.

Equipment Sizes

	IChemE Design Case Study	Short-Cut
Reactor		
Tube length (l)	3.0	1.3
Total cross-sectional area (m^2)	0.123	0.119
Shell Diameter (m)	0.438	0.266
Gas Absorber		
Diameter (m)	0.5	0.5
Packed Height (m)	5.0	8
Liquid Extraction		
Diameter (m)	0.2	0.2
Packed Height (m)	2.5	6
Solvent Recovery		
Diameter (m)	0.44	0.4
Packed Height (m)	7.3	6.6
MEK Purification		
Number of Plates	35	28
Diameter (m)	1.0	0.7

Table 6 – Summary of Equipment Sizes for MEK Case Study

	IChemE Design Case Study	Short-Cut
Quench Column		
Diameter (m)	1.4	1.8
Packed Height (m)	2.0	2.0
Gas Absorber		
Diameter (m)	1.07	1
Packed Height (m)	N/A – Uses Plate Column	9.8
Acetone Recovery		
Diameter (m)	1.83	1.05
Number of Plates	16	35
MEK Purification		
Diameter (m)	1.22	1.05
Number of Plates	19	26

Table 7 – Summary of Equipment Sizes of Acetic Anhydride Case Study

The results from these case studies were encouraging. The equipment sizes were comparable with that which would be found through detailed design. From tables 6 and 7 it can be seen that for the most part the volume of the equipment sized was within approximately +/- 50% of that found in the IChemE study, which is comparable with the margin of error of a cost appraisal at this stage [9]. A significant exception is the liquid extraction column in the MEK case study, which is sized by short-cut methods to be over twice as large than that designed in the IChemE design study. This is because the IChemE design uses a rotating disc contactor, whilst the short-cut design uses a packed column. This is a disadvantage of short-cut methodology – the use of more efficient technology cannot be taken into account. However this is the exception, and the other results are acceptable. On the basis of these results it is concluded that it is possible to obtain satisfactory results from an inventory estimation study and that these results could be applied in an inherent safety study for the purposes of route selection.

5.0   Discussion

The field of inventory estimation is extremely important to furthering inherent safety techniques. Without knowing approximately how much hazardous material will be present in a particular process plant in the early design stages it is impossible to ascertain how inherently safe that process is, and therefore any attempt to select a route based on inherent safety would fail. It is therefore of the utmost importance to develop a method for estimating inventory. The most important factor in developing such a method is time. Since there may be many different routes under consideration a lengthy method would give rise to delays and cost penalties that would make such a method unusable. The other key factor is data availability. Whilst it is possible to obtain as much data as is necessary, the time taken to compile this data is key. It is obviously not feasible to commission laboratory experiments to obtain this data due to the time and costs involved. The data used in an inherent safety analysis must be readily obtainable or else the analysis will not be suitable in the early design stage.

Since the method will be used early in the design process it is not to be expected that the method will be very accurate. An order of magnitude would be sufficient, to give an idea of the amount of material involved. Also since most inherent safety indexes use a step function, where each score corresponds to a range of the variable under consideration any inventory estimation only has to place the inventory within that range. A good indication of the accuracy that may be expected comes from cost estimation carried out at the same stage. According to Douglas [9] the accuracy of a cost estimate in the early design stage would be +/- 40%. From tables 6 and 7 it can be seen that the case studies indicate that the accuracy of the short-cut methods is comparable with this range. Since the inventories are calculated on the basis of vessel geometry it is expected the accuracy of the inventory estimation will also lie within this range.

Pipeline Inventory

It has been stated that due to uncertainties in the method it would be impossible to predict the inventory that would be present in pipelines. However it is necessary to make some estimate of the inventory that may be present in pipelines compared to that present in equipment items in order to

decide whether it is prudent to ignore pipeline inventory, or if the inventory is such that it is essential that further research be carried out in this area.

The method described here is rudimentary. It is intended only as a rough estimate of the pipeline inventory. As stated in section 3.10 the fluid velocity can be estimated to be 1m/s for liquids, and 15m/s for gases. From these values and the volumetric flowrate, which is known the pipe cross-sectional area can be calculated. The pipeline inventory can then be found by multiplying by pipe length. For our purposes an arbitrary value of 20m has been chosen. A value based on the minimum spacing distance would not be acceptable due to a variety of reasons. Firstly, not all equipment items will be at the minimum spacing or some convenient multiple of this spacing from the upstream or downstream equipment. Secondly, the height of tall equipment items would have a significant effect on pipe lengths. In petrochemical plants fractionating columns can be extremely tall items of equipment, and the top product from such a column would have to travel down the equipment – adding a significant amount to the overall length. Thirdly the requirement of moving pipes (through elevation, for example) for vehicle and pedestrian access would add to the overall length, although this would be minor in comparison to the first two points.

The value of twenty meters has been chosen as it is felt to be of the same order of magnitude of pipeline lengths that could be found in process plant. This is the same order of magnitude of minimum equipment spacings from [38]. It must be pointed out that pipe lengths may exceed this value by a sizeable margin, for example in pipe runs to and from storage facilities and in very large equipment (for example in petrochemical plants where the primary fractionators may far exceed 20m in height). However the storage facilities themselves lie outside the scope of this investigation because it is readily apparent they will have a large inventory, so it seems also prudent that the pipe runs to and from storage may also be neglected for the most part. Also the pipe runs from very large columns will for the most part be the exception to pipe lengths. Applying these pipe lengths to all vessels will give a gross distortion of the inventories, especially for small plants.

MEK	Pipes (In), kg	Pipes (Out), kg	Total (kg)	Vessel (Tot), kg
Reactor	0.6	0.6	1.1	0.2
Gas Absorber				
Gas	0.1	0.0	0.2	0.4
Liquid	12.1	12.00	24.1	45.4
Liquid Extraction	18.0	19.5	37.405	185.3
Solvent Recovery	7.4	7.4	14.8	31.1
MEK Purification	8.2	8.2	16.4	701.1
Acetic Anhydride				
Reactor	3.2	3.24	6.5	0.52
Quench Column				
Gas	5.3	4.34	9.6	8.3
Liquid	247.3	247.34	494.6	114.9
Gas Absorption				
Gas	1.0	0.5	1.5	5.5
Liquid	16.8	23.6	40.4	122.8
Acetone Recovery	74.1	74.1	148.1	2772.6
Anhydride Purification	24.7	24.7	49.5	1868.9

Table 10 – Estimate of pipeline inventories

Table 10 is a summary of the inventory in the pipes to and from equipment items compared to the inventory in the equipment items in each of the case studies in Section 4. It must be pointed out that this effectively double counts the inventory since the same inventory will be considered in both the flow out from one equipment and the flow into the next piece of equipment. The reason for this is that these inventories are used only to compare with vessel inventories, not the actual plant inventory.

It is apparent that there is not a simple correlation between equipment inventory and pipe inventory. This is expected due to the wide difference in flowrates and equipment types. For gas pipelines the inventory exceeds the vessel inventory. This is again expected due to the low hold-up times inherent to gas processing equipment. In the above examples this is not a major problem, since the inventories are so low with respect to the liquid inventories the overall increase in hazard taking into account pipeline inventory is minimal. This would hold true for most process plants, where liquid phase processing can be expected. However for plants that rely for the most part on gas phase processing failure to take into account pipeline inventories would lead to results that bear little relation to real world values.

For the most part the liquid inventories in pipelines lie below that in the equipment items to which they connect. With only one exception the pipeline inventories are under 50% of the equipment inventories,

with the large pipeline inventory in this case being as a result of a very large liquid flowrate. It can also be seen that with packed columns (MEK Gas Absorption, liquid extraction and solvent recovery columns and Acetic Anhydride quench column and absorption column) the pipeline inventory is more important than when compared with plate columns (MEK purification column and Acetic Anhydride acetone recovery and anhydride purification columns) – the large hold-ups in plate columns far outweigh that in the pipes. The sizing of liquid pipelines is an area of major concern – although the data above is limited in both scope and accuracy the impact on total inventory, especially for packed columns would be significant.

It can therefore be seen that pipeline inventory is important in any inventory estimation study. The major problem to be overcome with regards to pipeline inventory is that of pipe length. To calculate the pipeline inventory the length of the pipeline must be known. But the major question that must be asked is how is it possible to calculate pipe length when the space between vessels is unknown? This is something that could only be known from a study of the siting of the plant and individual equipment items – however, this is something that only happens after the detailed design. It would be almost impossible to express the actual length of pipeline as a multiple of the minimum distance being equipment items (data of minimum vessel spacings can be found from a variety of sources). Analysing data from existing plants may compensate for these uncertainties. If data on pipe lengths can be obtained from industrial sources it may enable a more accurate prediction of lengths between particular equipment items in inventory estimation.

Phase Change

The other main point that has came out of this research is the uncertainty in calculating inventory in those equipment items that require a phase change – for example, condensers and vaporisers. Firstly the sizing of a condenser-cooler that contains an uncondensable gas is a complex, laborious process. Due to the changing flow regime in the condenser and the varying heat transfer coefficients that arise as a result of this the only way to design a condenser is the Colburn-Hougen method, a complex, iterative method. The next problem is one shared with condensers and reboilers – due to the changing phases it is very difficult to estimate the mass of material in such a vessel. Since the density of liquid is much higher than that of gases, the ratio of the volume of gas to condensate will

have a large effect on the total inventory. In the case of a total condenser it may be argued that there is a linear gradient along the length of the condenser, so that the volume of condensate and gas is equal. However, this would not be the case in a partial condenser, where the uncondensable gas must be taken into account. For vaporisers it could be argued that the equipment inventory should be considered to be fully liquid with no vapour as this is a worst-case scenario in the event of failure of the heating fluid. However this does not pertain to condensers, and would lead to an inconsistency in the design.

6.0   Conclusions

Although there are still improvements to be made the method gives adequate results. The time taken to perform the assessments is not great and for an engineer with design experience it should take only a few days to perform an assessment for one route. Research has found that inherently safer techniques and technologies tend to give cost savings, both in capital cost and running cost [16]. A slight delay in the overall design process may therefore not result in increased overall costs.

The accuracy of the study is also felt to be sufficient. The aim was to obtain a level of accuracy consistent with that found in cost estimations at a similar stage. With regards to equipment volume the margin of error of the short-cut methods was approximately +/- 50%, compared with detailed design studies. It must be remembered however that an extra margin of error will be added in estimating the inventory. This error will arise from the assumptions in calculating the inventory from the equipment dimensions. It must be pointed out however that the calculation of inventory in a functioning plant may use a similar procedure (or identical) to that in a design study – using the same assumptions in calculating inventory from equipment dimensions. Therefore even if detailed information on process plant was available this error could be impossible to quantify.

There will also be an error from the simplifications in calculating inventory composition; however again it may prove impossible to calculate the actual composition in process plant. This is because the problem of varying composition in an equipment item will be present regardless of whether or not the study is done during a design stage or in a functioning plant.

There are other mitigating factors. As stated before chemically similar materials will have comparable hazards, so the composition will be less important. Also worst-case assumptions would be used at the engineer's judgement. For example if the composition of a mixture was close to, but outside the flammable limit calculation of hazard would be done at the flammable limit in order to account for uncertainties.

The results therefore will not be accurate, but they will be representative. High levels of accuracy are not required, as the step scoring of index methods requires only an accuracy of an order of magnitude.

Overall the results are promising and show good potential. It must be accepted that they have only been calculated with respect to two processes, with two different final products. This limited sample cannot be said to be indicative of the process industry as a whole. Also the two routes fall into the category of bulk chemicals and may not represent what would be found in the pharmaceutical and fine chemicals industry. Many more studies are required – with different products but also with different routes to the same product. Until this is done it cannot be said definitively that this method of estimating inventory is a success.

The objective of this project was to determine the feasibility of using short-cut methods to estimate inventory. From a study of two routes it has been found that it is indeed feasible to do this. The accuracy of the results is acceptable, and the time required not excessive. It is hoped that this will lead to further research into this topic and this will lead to a method that can be used with confidence by process engineers, in order to design plants with safety the first and foremost consideration.

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Appendix A – Sample Calculations

A1.1   Distillation

Sample Calculation for determining the parameters required for inventory calculations in distillation columns.

Assume that a distillation column will be required to separate a Methanol-Water stream, with a flow rate of 5000kg/h and a methanol molar feed composition of 30%. The top product will have a molar composition of methanol of 99%, and the bottoms product will have a molar composition of methanol of 1%

Zomosa's method.

From previous calculations α =3.752

$X_F = 0.3$

$$R_m = \frac{1}{(\alpha - 1)x_f} = 1.211$$

Reflux ratio, R = 1.3R_m = 1.575

From Fig. 2 minimum number of theoretical plates = 7.2

From Fig. 3, Erbar-Maddox correlation the number of theoretical plates = 13.8

70% plate efficiency, total number of plates = 20

Column diameter

$$G = C\left[\rho_v\left(\rho_l - \rho_v\right)\right]^{0.5}$$

C = 600

ρ_v = 1.15 kg/m^3 = 0.0718 lb/ft^3

ρ_l = 751 kg/m^3 = 46.883 lb/ft^3

$$G = 600\left[1.15\left(751 - 1.15\right)\right]^{0.5} = 1100 \text{ lb/(h)(ft}^2)$$

$$d = \left[\frac{D(R+1)}{0.785G}\right]^{0.5} = 3.73 \text{ ft} = 1.12\text{m}$$

For ease of construction we would let the column diameter be equal to 1.10 m.

A1.2   Liquid-Liquid Extraction

860kg/h of a solution of acetic acid in water containing 10% acid is to be extracted with 1220 kg/h methyl isobutyl ketone (MIBK) to reduce the concentration to 0.1%. The extract is to contain 6.5% acid. Assume the MIBK is 100% pure.

$F = 860kg/h$

$F' = 860(1-0.1) = 774kg/h$

$X_f = 0.1/0.9 = 0.111$ kg acetic acid/kg water

$X_r = 0.001/0.999 = 0.001$ kg acetic acid/ kg water

MIBK is pure, $S = S' = 1220$ kg/h

$Y_s = 0$

Assume R'=F' and E'=S'

$$Y_e = \frac{774(0.111) + 1220(0) - 774(0.001)}{1220} = 0.0698$$

Correlation of Liquid-Liquid Equilibrium Data for Water-Acetic-MIBK

[42]

X	Y	$0.93X^{1.1}$	$1.27X^{1.29}$
0.0299	0.0196	0.0195	
0.1364	0.1039	0.1039	
0.2708	0.2354	0.2210	0.2355
0.3864	0.4039		0.3725
0.5964	0.6525		0.6519
0.8065	0.9492		0.9624

From this we see that for $0.03 < X < 0.25$, $Y = 0.93X^{1.1}$

$Y_e = 0.0698$,

$X_1 = (0.0698 / 0.93)^{1/1.1} = 0.0950$

$m = dY/dX = d(0.93X^{1.1})/dX = 1.023X^{0.1}$

$X = 0.0950, m = 0.808$

$X < 0.03, m = K'$. From [42], $K' = 0.656$

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$m_r = K' = 0.656$

$$\xi = \sqrt{m_l m_r}\left(\frac{S'}{F'}\right) = \sqrt{0.656 * 0.808}\left(\frac{1220}{774}\right) = 1.15$$

Kremser Equation,

$$N_{OR} = \frac{In\left[\left(\frac{0.111 - 0//656}{0.001 - 0/0.656}\right)\left(1 - \frac{1}{1.15}\right) + \frac{1}{1.15}\right]}{1 - \frac{1}{1.15}} = \frac{2.718}{0.129} = 21$$

Height of Column, $Z = H_{OR}N_{OR}$

$H_{OR} = H_r + H_e/\xi$

$$= \frac{R}{A_t k_r a} + \frac{R}{A_t k_e a} \cdot \frac{1}{\xi}$$

$$= \frac{R}{A_t a}\left(\frac{1}{k_r} + \frac{1}{k_e \xi}\right)$$

$R' = 774$ kg/h, $X_r = 0.001$,

$R = 774.8$ kg/h

The values of a, k_r and k_e should be obtained either via laboratory calculation or a correlation. The individual engineer should select the most appropriate correlation in his or her own view to determine these variables.

A1.3   Gas Absorption

Example of the inventory estimation of a gas absorber can be found in the MEK and Acetic Anhydride case studies.

A1.4   Adsorber

From USACE [53]

Design of an Adsorber for Removing Volatile Organic Chemicals (VOCs) from an air steam.

Activated Carbon is used to remove benzene, toluene, trichloroethylene (TCT) and perchloroethylene (PCE) from an airstream. The air enters the adsorber at 1 m^3/s. The adsorber operates at 1 atm and 25°C. The carbon bed is changed every 3 months, and the contaminant concentrations are as follows:

PCE: 15ppm

TCE: 14ppm

Toluene: 5ppm

Benzene: 9ppm

Solution:

First, we must calculate the partial pressure of each contaminant in the feed stream. The partial pressure, $P = xP_t$, where

P = Partial pressure, kPa

P_t = Total pressure, kPa

X = Concentration

$P_{PCE} = 15*10^{-6}*101.3 = 1.52*10^{-3}$ kPa

$P_{TCE} = 14*10^{-6}*101.3 = 1.42*10^{-3}$ kPa

$P_{Tol} = 5*10^{-6}*101.3 = 0.51*10^{-3}$ kPa

$P_{Ben} = 9*10^{-6}*101.3 = 0.91*10^{-3}$ kPa

We can now calculate the mass of contaminant absorber per unit mass of carbon by using the Freundlich isotherm relationship:

$$\frac{x}{m} = KC^{\left(\frac{1}{n}\right)}$$

K and (1/n) values for the different contaminants can be obtained from adsorption equilibrium data, for example that published in Dobbs and Cohen [8].

Contaminant	Temp, K	K	C, $*10^{-3}$ kPa	1/n	x/m
PCE	298	1.0	1.52	0.144	0.393
TCE	298	0.95	1.42	0.263	0.169
Toluene	298	0.565	0.51	0.111	0.244
Benzene	298	0.388	0.91	0.131	0.155

$$\text{Molar flowrate of air} = \frac{PV}{RT} \approx \frac{101.3 * 1}{8.34 * 10^{-3} * 298} = 40.8 gmol / s = 2.45 \text{ kgmol/min}$$

Contaminant flowrates

Flowrate of PCE = 2.45 * (15ppm PCE/1*10^6 ppm air) = $3.68*10^{-5}$ kgmol / min

TCE = $3.43*10^{-5}$ kgmol/min

Toluene = $1.23*10^5$ kgmol/min

Benzene = $2.21*10^{-5}$ kgmol/min

Now we must calculate the amount of contaminant that must be removed in three months assuming constant flow, and 30 days to a month

PCE = $3.68*10^{-5}$*166(kg/kgmol)*1440(min/day)*30*3 = 792 kg

TCE = $3.43*10^{-5}$*137.5*1440*30*3 = 611.2 kg

Toluene = $1.23*10^{-5}$*92*1440*30*3 = 147 kg

Benzene = $2.21*10^{-5}$*78*1440*30*3 = 223kg

Carbon Requirements

PCE = 792/0.393 = 2015 kg

TCE = 611.2/0.169 = 3617 kg

Toluene = 147/0.244 = 602 kg

Benzene = 223/0.155 = 1439 kg

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Appendix B – Physical Data Calculation

The physical data for the compounds involved in this design have been calculated or estimated from varying correlations found in texts. If a value has been taken from a text, that text will be referenced. If not referenced it has been calculated through the following procedures

Density [42]

Density of Organic Liquids can be calculated from the equation:

$$\rho = \frac{C_1}{C_2^{\left[1+\left(1-\frac{T}{C_3}\right)^{C_4}\right]}}$$

	C_1	C_2	C_3	C_4
MEK	0.93767	0.25035	535.5	0.29964
2-Butanol	0.966	0.26064	536.05	0.2746
Acetone	1.4486	0.25892	591.95	0.2529
Acetic Anhydride	0.86852	0.25187	606	0.31172
Acetic Anhydride	1.2332	0.25886	508.2	0.2913

In the absence of any data on the variation with temperature on the density of 1,1,2 Trichloroethane it will be assumed to be constant at 1450 kg/m³ (From Material Safety Data Sheet)

ρ = Density, kg/kmol

T = Temperature in Kelvin's

Densities of Vapours are calculated from

$$\rho = \frac{MP}{RT}$$

M = Molecular Weight, g/mol

P = Pressure, Nm⁻²

R = Ideal Gas Constant, 8.314

T = Temperature, K

ρ = Density, g/m³

Heat Capacities (Vapours) [42]

Heat Capacities of Organic and Inorganic compounds can be calculated from:

$$C_P = C_1 + C_2 \left[\frac{C_3}{T} / \sinh\left(\frac{C_3}{T} \right) \right]^2 + C_4 \left[\frac{C_5}{T} / \cosh\left(\frac{C_5}{T} \right) \right]^2$$

	C_1	C_2	C_3	C_4	C_5
MEK	$0.784*10^5$	$2.1032*10^5$	$1.5488*10^3$	$1.1855*10^5$	693
2-Butanol	$0.8202*10^5$	$2.522*10^5$	$1.601*10^3$	$1.5864*10^5$	-704.15
Hydrogen	$0.2762*10^5$	$0.0956*10^5$	$2.466*10^3$	$0.0376*10^5$	567.6
Acetone	57040	163200	1607	96800	731.5
Methane	33300	79930	2086.9	41600	991.96
Ethylene	33380	94790	1596	55100	740.8
Carbon Monoxide	29110	8770	3085.1	8460	1538.2
Carbon Dioxide	29370	34540	1428	26400	588
Acetic Acid	40200	136750	1262	70030	569.7
Acetic Anhydride	71300	222200	1620.3	167600	746.5

C_P = Heat Capacity, kJ/kmolK

The heat capacity of ketene is given by [47]:

$C_p = 4.792 + (22.594*10^{-3})T - (7.187*10^{-6})T^2$

Where is T the temperature in Kelvins, and the heat capacity is expressed as calories per gram.

Heat Capacity of Liquids [42]

The heat capacities of liquids are given by the equation $C_1 + C_2T + C_3T^2 + C_4T^3 + C_5T^4$

	C_1	C_2	C_3	C_4	C_5
Acetone	135600	-177	0.2837	0.000659	0
Acetic Acid	139640	-320.8	0.8985	0	0
Acetic Anhydride	36600	511	0	0	0
MEK	132300	200.87	-0.9597	0.00195	0
2-Butanol	19120	-730.4	2.2998		0

Latent Heat of Vaporisation [42]

These can be calculated from the correlation

$$H_v = C_1 * (1 - T_r)^{C_2 + C_3*T_r + C_4*T_r^2}$$

H_v = Latent heat of vaporisation, J/kmol

T_r = Reduced Temperature = T/T_c

T = Temperature, K

T_c = Critical Temperature, K

	C_1	C_2	C_3	C_4	T_c
MEK	$4.622*10^7$	0.355	0	0	535.5
2-Butanol	$7.256*10^7$	0.4774	0	0	536.05
Acetone	4.22E+07	0.3397			508.2
Acetic Acid	2.03E+07	0.11911	-1.3487	1.4227	591.95
Acetic Anhydride	6.35E+07	0.3986			606

There is no correlation for the variation of the latent heat of vaporisation of 1,1,2-Triochloroethane

with temperature, so it will be assumed constant at $34.82*10^3$ kJ/kmol (Handbook of Physical

Constants)

Vapour Pressure

Vapour pressure of Organic and Inorganic Liquids can be found from

$$\text{Vapour Pressure (Pa)} = e\left[C_1 + \left(\frac{C_2}{T} \right) + C_3 \ln T + C_4 * T^{C_5} \right]$$

	C_1	C_2	C_3	C_4	C_5
MEK	72.698	-6413.6	-7.5779	$5.6476*10^{-6}$	2
2-Butanol	152.54	-11111	-19.025	$1.0426*10^{-5}$	2
H_2O	73.649	-7258.2	-7.3037	$4.1653*10^{-6}$	2
Acetone	69.006	-5599.6	-7.0985	6.22E-06	2
Acetic Acid	53.27	-6304.5	-4.2985	8.89E-18	6
Acetic Anhydride	100.95	-8873.2	-11.451	6.13E-06	2

Viscosity [42]

The viscosity of hydrocarbon liquids can be calculated from:

$$\log \mu = B\left(\frac{1}{T} - \frac{1}{T_o} \right) - 3.0$$

μ = Viscosity, Pa sec

T_o is calculated from $N^* = N + \sum_i \Delta N_i$

N = Number of Carbon Atoms in the Molecule

$N^* <20$ $T_o = 28.86 + 37.439N^* - 1.3547N^{*2} + 0.02076N^{*3}$

$N^* >20$ $T_o = 8.146N^* + 238.59$

B is calculated from $B = B_a + \sum_i \Delta B_i$

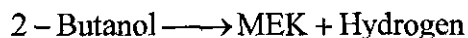$N^* <20$ $B_a = 24.79 + 66.885N^* - 1.3173N^{*2} - 0.00377N^{*2}$

$N^* >20$ $B_a = 530.59 + 13.74N^*$

ΔN_i and ΔB_i depend on the type of groups found on the hydrocarbon molecule, and can be obtained

from [42].

Appendix C – Methyl Ethyl Ketone Design

Design of a Plant to Produce 10,000 tonnes/year of Methyl Ethyl Ketone (MEK) from 2-Butanol. The 2-Butanol is reacted at high temperature (400-500°C) on a zinc oxide catalyst forming MEK and Hydrogen:

$$2 - \text{Butanol} \longrightarrow \text{MEK} + \text{Hydrogen}$$

The services available are:

Dry saturated steam at 140°C

Cooling water at 24°C

Flue Gases at 540°C

Process:

The 2-Butanol will come from feed at 25°C, and will be heated, vaporised and superheated to reach the inlet reactor temperature of 500°C. The reactor products will be condensed to separate the MEK and 2-Butanol from the Hydrogen. However, a significant portion of MEK will be lost with the Hydrogen stream, so it will be necessary for further separation to recover as much MEK as possible. This will be done by firstly absorbing the MEK with water. Separating MEK and water is a difficult separation, so liquid-extraction shall be used with a 1,1,2-Trichloroethane (TCE) solvent. The water will be recycled back to the absorber. The TCE and MEK will then be separated in a distillation column. The MEK from this column will still contain some 2-Butanol, so it will be combined with the stream fro the condenser and the MEK separated from the 2-Butanol is a distillation column. The 2-Butanol will be recycled back to the reactor, and the MEK removed as product.
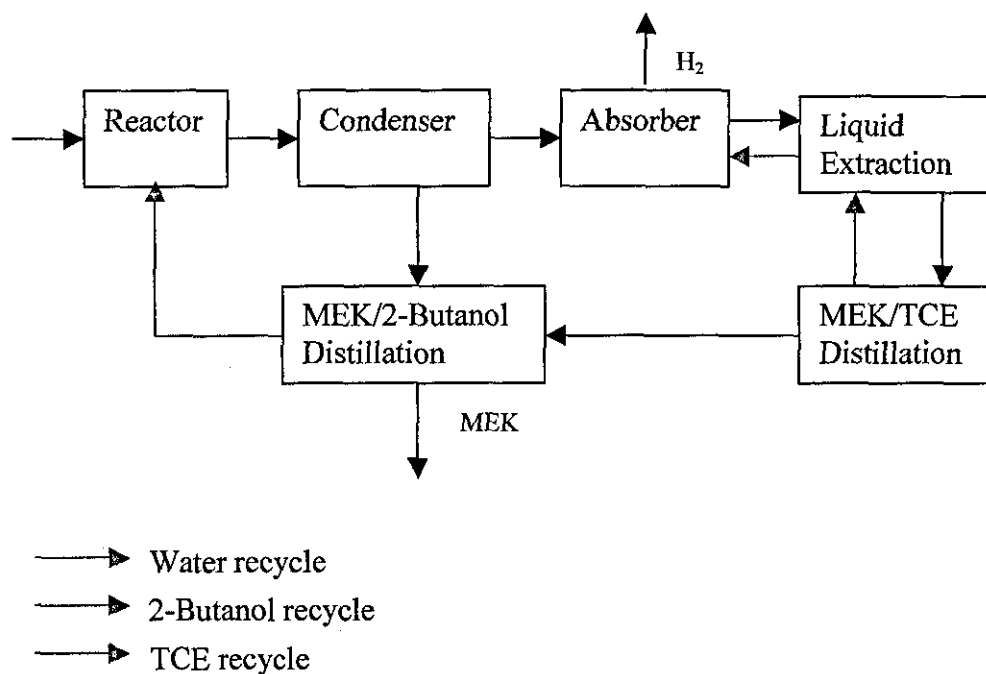
Fig. 8 Flowchart showing major equipment items for MEK production

AC.1 Reactor

$$C_4H_{10}O \longrightarrow C_4H_8O + H_2$$
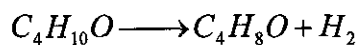
Production rate of MEK from plant = 10,000 tonnes/year.

Assuming continuous production the number of working hours in a year = 8000

Hourly MEK Production rate = 10000000/8000 = 1250 kg/h

Adding 8% to account for leaks and losses, design for an MEK rate from the reactor of 1350 kg/h, or

18.75 kmol/h (Mol. wt MEK = 72)

In order to produce this amount of MEK from 2-Butanol at a conversion of 90% the total flow of 2-

Butanol into the reactor should be $(18.75 * 74) \big/ 0.9 = 1541.67$ kg/h

(Mol. wt 2-Butanol = 74)

The amount of 2-Butanol converted is 1541.67*0.9 = 1387.5 kg/h, so the amount of unreacted 2-

Butanol leaving the reactor is 154.17kg/h

Now, assuming that the final MEK product is 99% pure, then $\dfrac{1350}{0.99} - 1350 = 13.63$ kg/h of 2-Butanol will leave in the product stream.

So the 2-Butanol recycle back to the reactor will be 1541.67-1387.5-13.63 = 140.54 kg/h (Assuming no other losses at this point).

This comes from the MEK distillation column. Assuming a 99% bottoms product purity, this will contain 1.42 kg/h of MEK

From the stoichiometric equation it can be seen that 18.75 kmol of H_2 will be formed, which is equal to 37.5 kg/h.

Mass Balance

	In (kg/h)	Out (kg/h)
2-Butanol	1541.67	154.17
MEK	1.42	1351.42
Hydrogen	0	37.5
Total	1543.06	1543.09

	In (kmol/h)	Out (kmol/h)
2-Butanol	20.83	2.08
MEK	0.02	18.77
Hydrogen		18.75
Total	20.85	39.60

Reactor Design

The reactor rate equation is given as part of the basis for the design problem, and is taken from [41]:

$$r_A = \frac{C\left(P_{A,i} - P_{K,I}P_{H,I}/K\right)}{P_{K,i}\left(1 + K_A P_{A,i} + K_{AK}P_{A,i}/P_{K,I}\right)}$$

$$\log C = -\frac{5964}{T_i} + 8.464$$

$$\log K_A = -\frac{3425}{T_i} + 5.231$$

$$\log K_{AK} = \frac{486}{T_i} - 0.1968$$

$$\log K = -\frac{2790}{T_i} + 1.59 \log T_i + 1.871$$

$P_{A,i}$, $P_{K,i}$ and $P_{H,I}$ are the interfacial partial pressures of the alcohol, the MEK and the hydrogen respectively.

The reaction takes place at 2 bar. The will take place in a series of tubes at a temperature of 400-500°C.

From [41] the length of a tube in the reactor can be estimated by using the Height of a Reactor Unit concept:

$$HRU = 224.9G/(140.89T - 86168)^{5/6}$$

$$Z = HRU * \ln\left[\frac{(p_{a1} - p_a^*)}{((p_{a2} - p_a^*))}\right]$$

Where:

HRU = The height of a reactor unit, m

T = Temperature in reactor, K

Z = Reactor length

p_{a1} = Partial pressure of 2-Butanol at reactor inlet

p_{a2} = Partial pressure of 2-Butanol at reactor outlet

p_a^* = Partial pressure of 2-Butanol at equilibrium

From the modified Reynolds number we can say that $\mathrm{Re}' = \dfrac{D_p G}{\mu(1 - \varepsilon)}$

Assuming the use of 0.32cm cylinders as the catalyst, $\varepsilon = 0.393$

The viscosity = $1.905 * 10^{-5} \mathrm{Nm^{-2}}$, and the Reynolds Number is assumed to be 1000.

G = 3.604 kg/m^{2}s

$$HRU = 224.9 * 3.604/(140.89T - 86168)^{5/6} = 0.425m$$

T = Temperature in tubes = 400°C

If we let the interfacial temperature equal 400°C, then K=99

The length of the reactor tube can be determined by calculating the length when the reaction has reached equilibrium, that is r_a =0.

From the rate equation it can be seen that this will take place when $p_a - \dfrac{p_k p_h}{K} = 0$

For a reactor pressure of 2 bar

$$p_h = p_h = \frac{2x}{1+x} \text{ and } p_a = \frac{2(1-x)}{1+x}$$

Inserting these into $p_a - \dfrac{p_k p_h}{K} = 0$ and solving we find that the equilibrium conversion, $x_e = 0.99$

Then $p_a^{\cdot} = \dfrac{2(1-0.99)}{1+0.99} = 0.01$ and $p_K = p_H = \dfrac{2*0.99}{1+0.99} = 0.9949$

From the problem statement, x = 0.90, so $p_{A2} = \dfrac{2(1-0.9)}{(1+0.9)} = 0.105$

$$Z = 0.425 * \ln\left[\frac{(2-0.01)}{(0.105-0.01)}\right] = 1.3\,m$$

The diameter of the reactor tubes is unimportant as all that is required is the cross sectional area of the reactor.

G = 3.604 kg/m²s

Total flow into the reactor is 1543.09 kg/h = 0.429 kg/s

A = 0.429/3.604 = 0.119 m²

Reactor Inventory

Total volume of the reactor, V = 1.3*0.119 = 0.115m³

For 0.32 cm cylinders the gas volume is 0.115*(1-0.393) = 0.094m³

To calculate the inventory, divide the reactor into 2 sections, one with composition equal to inlet composition and one with composition equal to outlet composition.

Inlet composition:

MEK: $\dfrac{0.02}{20.85}*0.094/2 = 45.08*10^{-6}\,\text{m}^3$

Alcohol: $\dfrac{20.83}{20.85}*0.047 = 0.047\,\text{m}^3$

Outlet

MEK: $\dfrac{18.77}{39.60}*0.047 = 0.022\,\text{m}^3$

Alcohol: $\dfrac{2.08}{39.60}*0.047 = 0.002\,\text{m}^3$

Hydrogen: $\dfrac{18.75}{39.60}*0.047 = 0.022\,\text{m}^3$

Average reactor temperature = 450°C

$$\rho = \frac{PM}{RT}$$

$\rho_H = 0.07\,\text{kg/m}^3$

$\rho_A = 2.49\,\text{kg/m}^3$

$\rho_M = 2.43\,\text{kg/m}^3$

Inventory:

MEK = 0.022*2.43 = 0.053 kg/h

2-Butanol = (0.047+0.002)*2.49 = 0.122 kg/h

Hydrogen = 0.022*0.07 = 0.002 kg/h

Reactor Mass Inventory	Mass (kg)
MEK	0.053
2-Butanol	0.122
Hydrogen	0.002
Total	0.177

AC.2 Condenser

Mass Balance

	kg/h	Wt. fraction	kmol/h	Mol. fraction
2-Butanol	154.17	0.100	2.08	0.053
MEK	1351.42	0.876	18.77	0.474
Hydrogen	37.5	0.024	18.75	0.473
Total	1543.09	1.00	39.6	1.00

The gas product from the reactor is used to vaporise the 2-butanol feed to the reactor. The heat of the gas feed to the condenser can be determined through calculation of the heat transferred to the 2-butanol.

Mass flowrate of 2-butanol 1547.67 kg/h (from reactor mass balance)

Latent heat of vaporisation of 2-butanol at its atmospheric boiling point, 373K = 555.5 kJ/kg

Heat transferred to 2-butanol = 1547.67*555.5 = $859.7*10^3$ kJ/kg

Without knowing the average temperature of the feed to the condenser it is impossible to determine the average heat capacity. Therefore, there will be an assumption as to the average temperature in the vaporiser. This first assumption will be 300K. If the average temperature is calculated to be vastly different to this, the calculation will be repeated.

Heat capacity at 300K of:

MEK, $C_{p(MEK)} = 2.199$ kJ/kgK

2-Butanol $C_{p(2-Bu\tan ol)} = 2.450$ kJ/kgK

Hydrogen $C_{p(Hydrogen)} = 14.661$ kJ/kgK

Heat capacity of mixture = (0.1*2.450+0.876*2.199+0.024*14.661) = 2.523 kJ/kgK

$$Q = mC_p \Delta T$$
$$859.7*10^3 = 1543.09 * 2.523 * \Delta T$$
$$\Delta T = 221\,K$$

Outlet temperature = 400-221 = 179°C

Average temperature = (400+179)/2 = 290 K. This is close enough to the original assumption of 300K.

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From the flow into the condenser it can be seen that the amount of non-condensables in the inlet stream is very high (47.3% of the volume of the inlet gas), complicating the design significantly. The design of a cooler-condenser with more than two materials present is a very complicated iterative procedure. In order to simplify matters the amount of material condensed will be estimated from the vapour pressures. Then the amount of heat required to cool and condense this material will be calculated, and from this the heat-transfer area estimated.

The gas enters at 179°C and will be cooled to 30°C.

Vapour pressure of MEK at 30°C = $15.4*10^3 \, kN/m^2$

Since the condenser operates at atmospheric pressure, the inert pressure of the gas (that is, the partial pressure of the hydrogen) will be $1.01*10^5 - 15.4*10^3 = 85.6*10^3$

Amount of MEK in outlet gas = $18.75 * \dfrac{15.4*10^3}{85.6*10^3} = 3.37 \, kmol/h$

It will be assumed that the ratio of 2-Butanol in the outlet gas will be equal to the ratio of 2-Butanol to MEK in the feed.

Amount of 2-Butanol in outlet gas = $3.37 * 0.1 / 0.876 = 0.385 \, kmol/h$

Mass Balance Out

Uncondensed Gas	kg/h	kmol/h
2-Butanol	28.86	0.39
MEK	242.64	3.37
Hydrogen	37.5	18.75
Total	309.0	22.51

Condensate	kg/h	kmol/h
MEK	1108.78	15.40
2-Butanol	125.31	1.69
Total	1234.09	17.09

AC.3 Gas Absorber

Gas Absorption

Mass In	kg/h	Wt. fraction	kmol/h	Mol. fraction
2-Butanol	28.86	0.094	0.39	0.017
MEK	242.64	0.785	3.37	0.150
Hydrogen	37.5	0.121	18.75	0.833
Total	309.0	1.000	22.51	1.000
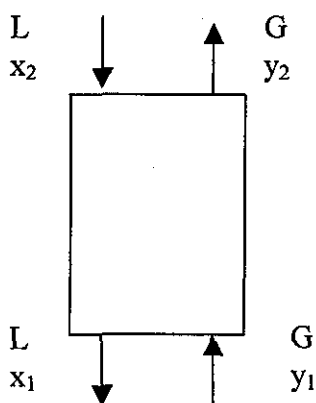
The solvent entering will be fresh feed of water, i.e. $x_2 = 0$

The absorber will be designed for a 99% w/w removal of MEK, so that the MEK leaving in the gas will

be $0.01*242.64 = 2.43$ kg/h

There will be an assumption of total absorption of 2-Butanol, due to the relatively small amount

present.

Also leaving in the gas stream will be water vapour. This can be calculated by calculating the

Humidity in the exit gas.

Mass flowrate of dry gas out $= 2.43 + 37.5 = 39.93$

Molar flowrate of dry gas out $= \dfrac{2.43}{72} + \dfrac{37.5}{2} = 18.78$

Therefore, the molecular weight of the gas out is $39.93/18.78 = 2.13$ kg/kmol

From [42], the vapour pressure of water at 25°C is $3.142*10^3$ N/m^2. If the column operates at

atmospheric pressure the humidity of the gas out is:

$$H = \frac{3.142*10^3}{1.01*10^5 - 3.142*10^3}\left(\frac{18}{2.13}\right) = 0.271 \text{ kg water/kg dry gas}$$

So the mass flowrate of water vapour from the column is $0.271*39.93 = 10.82$ kg/h

Mass Balance of Gas Out

	kg/h	Wt. fraction	kmol/h	Mol. fraction
2-Butanol	0	0	0	0
MEK	2.43	0.048	0.034	0.002
Hydrogen	37.5	0.739	18.75	0.967
Water Vapour	10.82	0.213	0.60	0.031
Total	50.75	1.000	19.38	1.000

To calculate the liquid flowrate it is necessary to determine the liquid concentrations in equilibrium with the vapour concentrations. This is done by determining the activity coefficient of the mixture. However, this is calculated from the liquid concentrations. Therefore the activity coefficient will be calculated at the minimum liquid composition (at the top of the column, where the solution is very dilute), and at the maximum concentration, limited by the design.

The absorption column feeds the liquid extraction unit. The system MEK/Water/1-1-2 Trichloroethane forms an isopicnic at 11% w/w MEK. Therefore it is necessary to set to ensure that the MEK from the absorption column to the liquid extraction column does not exceed 10% w/w (this value is the maximum outlet concentration for MEK). (It must be noted that this concentration cannot be reached through the absorption of MEK gas in water).

The activity coefficients can be calculated from the Van Laar equation

$$\ln \gamma_1 = A_{12} \left(\frac{A_{21} x_2}{A_{12} x_1 + A_{21} x_2} \right)^2$$

From Ghmeling and Onken, 1977

$A_{12} = 3.3726$

$A_{21} = 1.8346$

(Subscript 1 refers to MEK; subscript 2 refers to water)

At the minimum concentration, infinite dilution $x_1 = 0$, $x_2 = 1$

$$\ln \gamma_1 = 3.3726 \, ,$$

$$\gamma_1 = 29.2$$

At the maximum concentration, the mass fraction of MEK = 10%. Neglecting 2-Butanol due to the low concentration, this corresponds to a molar composition of:

$$x_1 = \frac{0.1/72}{0.1/72 + 0.9/18} = 0.027$$

$x_2 = 0.973$

$$\ln \gamma_1 = 3.3726 \left(\frac{1.8346 * 0.973}{(3.3726 * 0.027) + (1.8346 * 0.973)} \right)^2 = 3.031$$

$$\gamma_1 = 20.7$$

It can be seen that the activity coefficient will be relatively constant over the length of the column.

The vapour composition is related to the liquid composition by:

$$y = \frac{\gamma * P^o}{P} x$$

Where P^o is the vapour pressure of MEK at 25°C

P = Total pressure of the column = $1.01 * 10^5$ N/m²

From [42]

$P^o = 12227$ N/m²

Taking the highest value of γ throughout the column:

At the base of the column, $y_1 = 0.150$

$$x_1 = \frac{1.01 * 10^5}{12227 * 29.2} * 0.150 = 0.042$$

A mass balance over the column gives:

$$\left(\frac{L}{G} \right)_m = \frac{y_1 - y_2}{x_1 - x_2} = \frac{0.150 - 0.0018}{0.042} = 3.53$$

The liquid flowrate is usually taken as 1.4 times the minimum value

$$\frac{L}{G} = 1.4 * 3.53 = 4.94$$

And the concentration of liquid out at this flowrate will be:

$$x_2 = \frac{0.150 - 0.0014}{4.96} = 0.030$$

Thus it can be seen that it will be possible to design a column that will give a 10% MEK solution.

$$\frac{y_1}{y_2} = \frac{0.150}{0.0018} = 83.3$$

$$m = \frac{\gamma * P^o}{P} = \frac{29.2 * 12227}{1.01 * 10^5} = 3.53$$

$$m\frac{G'_m}{L'_m} = 3.53 * \frac{1}{4.96} = 0.71$$

From Fig.5 $N_{OG} = 12.8$

It will be assumed that the packing used will be 3.8cm Raschig Rings. From [48] for random packings of 3.8 cm the HTU will be of the magnitude 0.5-0.75m. Taking an average of 0.625m the height of the column,

$$Z = 12.8 * 0.625 = 8\,m$$

From [40] the economic gas flow rate in a column with 3.8cm packing is between 1850-2900m³/m²h, so take an average of 2375m³/m²h. This is a value for air, and must be corrected for other gases with the factor of:

(Density of air at RTP/Density of Gas)$^{0.33}$

If the average temperature in the column is 25°C, then the densities are:

$$\rho_{Air} = \frac{29 * 1.01 * 10^5}{8.314 * 298} = 1182.2\,g/m^3 = 1.18\,kg/m^3$$

$$\rho_{gas} = \frac{11.42 * 1.01 * 10^5}{8.314 * 298} = 465.5\,g/m^3 = 0.47\,kg/m^3$$

Gas flowrate, G' $= 2375\left(\frac{1.18}{0.47}\right)^{0.33} = 3218\,m^3/m^2h$

The gas flowrate in is 21.65 kmol/h. This has a molar volume of:

$$V = \frac{nRT}{P} = \frac{8.314 * 298}{1.01 * 10^5} = 0.0245\,m^3/mol = 24.5\,m^3/kmol$$

So G = 21.65*24.5=530.4 m³/h

$$A = \frac{530.4}{3218} = 0.165 \text{ m}^2$$

d = 0.46m say 0.5m.

Mass Balance Out

Liquid Flow Out

From the equilibrium relationships it can be seen that it is possible to obtain a 10%MEK solution from the column.

If 99%w/w of the incoming MEK is removed, then 242.64*0.99 = 240.21 kg/h of MEK is absorbed.

In order to make a 10% solution, the amount of water required must therefore be:

(240.21/0.1) – 240.21 = 2161.89 kg/h

Also in this solution will be 28.86 kg/h of 2-Butanol

Liquid Flow In

2161.89 kg/h of water leave the column in solution with the MEK, and 10.82 kg/h leaves the column as water vapour, so total flow into the column = 10.82+2161.89 = 2172.71 kg/h

Mass Balance

	Gas In, kg/h	Liquid In, kg/h	Gas Out, kg/h	Liquid Out, kg/h
2-Butanol	28.86	0	28.86	0
MEK	242.64	0	2.43	240.21
Hydrogen	37.5	0	37.5	0
Water Vapour	0	0	10.82	0
Water	0	2172.71	0	2161.89
Total	309	2172.71	79.61	2402.10

	Gas In, kmol/h	Liquid In, kmol/h	Gas Out, kmol/h	Liquid Out, kmol/h
2-Butanol	0.39	0	0.39	0
MEK	3.37	0	0.03	3.34
Hydrogen	18.75	0	18.75	0
Water Vapour	0	0	0.60	0
Water	0	2172.71	0	120.11
Total	22.51	120.71	19.77	123.45

Inventory

Liquid Hold-up

$$H_{OW} = 0.143 \left(\frac{L'}{d} \right)^{0.6}$$

Cross-Sectional Area, $A = \frac{\pi}{4} d^2 = 0.196 \, m^2$

Liquid mass flow rate, $L = 2402.10 \, kg/h$

$$L' = \frac{2402.10}{0.196 * 3600} = 3.40 \, kg/m^2 s$$

$$H_{OW} = 0.143 \left(\frac{3.40}{38} \right)^{0.6} = 0.03$$

Liquid Inventory

Assuming that the column can be divided into two sections, one half solely composed of water and one

half solely composed of a 10% MEK solution

$$H_2O \, \text{Inventory} = 0.5 * \frac{\pi}{4} d^2 * 7.8 * 0.03 = 0.023 \, m^3$$

With ρ_{H20} at 25oC = 1000 kg/m^3

Water Inventory = 23.0 kg

Inventory of 10% MEK soln. = 0.023 m^3

Density H_2O = 1000 kg/m^3

Density MEK = 805 kg/m^3

Density 2-Butanol = 808 kg/m^3

density not estimate

Density of Solution = $(0.100 * 805) + (0.894 * 1000) + (0.006 * 808) = 975 \, \text{kg/m}^3$

Mass of Solution = 975*0.023 = 22.4 kg

Gas Inventory

With 38mm Raschig Rings, the voidage fraction = 0.73

So Gas Inventory = $\frac{\pi}{4} d^2 * 7.8(0.73 - 0.03 + 0.15) = 1.30 \, \text{m}^3$

Gas In:

MEK = 0.150*1.30/2 = 0.098 m^3

2-Butanol = 0.017*1.30/2 = 0.011 m^3

Hydrogen = 0.833*1.30/2 = 0.541 m^3

Gas Out

MEK = 0.002*1.30/2 = Negligible

H_2 = 0.967*1.30/2 = 0.629 m^3

H_2O = 0.033*1.30/2 = 0.021 m^3

Gas Densities at 25oC

$\rho_{MEK} = 2.935 \, \text{kg/m}^3$

$\rho_{2-But} = 3.016 \, \text{kg/m}^3$

$\rho_{H_2} = 0.082 \, \text{kg/m}^3$

$\rho_{H_2O} = 0.734 \, \text{kg/m}^3$

Inventory

MEK = 0.098*2.935 = 0.288 kg

2-Butanol = 0.011*3.016 = 0.033 kg

Hydrogen = (0.541+0.629)*0.082 = 0.096 kg

Water Vapour = 0.021*0.734 = 0.015 kg

Liquid Inventory

Water	23.0
10% MEK Solution	22.4

So the total liquid inventory is 45.4 kg of a 4.9% solution of MEK

Gas Inventory

MEK, kg	0.288
2-Butanol, kg	0.033
Hydrogen, kg	0.096
Water Vapour, kg	0.015
Total, kg	0.432

The total gas inventory is 0.432 kg of a gas mixture containing 66.6%w/w MEK, 7.6% 2-Butanol and

22.2% Hydrogen.

AC.4   Liquid Extraction

Liquid In

	kg/h	Wt. fraction	kmol/h	Mol. fraction
2-Butanol	28.86	0.012	0.39	0.003
MEK	240.21	0.099	3.34	0.027
Water	2161.89	0.889	120.11	0.970
Total	2430.96	1.000	123.84	1.000

The first assumption for simplicity will be that the MEK and 2-Butanol is one material

$x_f = 0.099+0.012 = 0.111$

It is necessary to assume a concentration of MEK and 2-Butanol in the raffinate, assume 0.5%

From the distribution curve $\dfrac{Solvent}{Feed} \approx \dfrac{E}{R} = \dfrac{0.111-0.005}{0.48-0} = 0.22$

Minimum solvent rate = 0.22*2430.96 = 534.8 kg

Assuming a solvent rate of twice the minimum = 1069.6 kg, say 1070 kg/h

$$X_f = \frac{0.111}{1-0.111} = 0.125$$

$$X_r = \frac{0.005}{1-0.005} = 0.005$$

Fresh solvent, $Y_s = 0$

F' = 2161.89

S = S' = 1070 kg/h

R' = F'

E' = S'

$$Y_e = \frac{F'X_f + S'Y_s - R'X_r}{E'} = \frac{2161.89(0.125-0.005)}{1070} = 0.242$$

Mass Balance Out:

Y_e = Weight Solute/Weight Solvent in extract phase

Weight of solute = 0.242*1070 = 258.94 kg/h

Assuming all of the 2-Butanol is recovered:

Weight of MEK in extract phase = 258.94-28.86 = 230.08 kg/h

Weight of MEK in raffinate = 240.21-230.08 = 10.13 kg/h

Mass Balance Out

	Extract		Raffinate	
	Kg/h	Wt. Fraction	Kg/h	Wt. fraction
MEK	230.08	0.173	10.13	0.005
2-Butanol	28.86	0.022		
Water			2161.89	0.995
TCE	1070	0.805		
Total	1328.94	1.00	2172.02	1.000

$$N = \frac{\ln\left[\left(\frac{X_f - Y_s/m}{X_r - Y_s/m}\right)\left(1 - \frac{1}{\varepsilon}\right) + \frac{1}{\varepsilon}\right]}{\ln \varepsilon}$$

From liquid extraction data $m_r = 3.44$, $m_l = 1.92$

$$\varepsilon = m\frac{S}{F} = \sqrt{1.92 * 3.44} * \frac{1070}{2430.96} = 1.131$$

$$N = \frac{\ln\left[\left(\frac{0.125}{0.005}\right) * \left(1 - \frac{1}{1.131}\right) + \frac{1}{1.131}\right]}{\ln 1.131} = 10.8$$

$$N_{OR} = \frac{N \ln \varepsilon}{1 - \frac{1}{\varepsilon}} = 11.5$$

Say 12 transfer units

In the absence of data pertaining to HTU values for this system, assume HTU = 0.5m

Z = 12*0.5 = 6.0m

The column diameter can be calculated from the flooding chart in Strigle [49]. This plots

$$\left(\frac{\mu_c}{\Delta\rho}\right)\left(\frac{\sigma_i}{\rho_c}\right)^{0.2}\left(\frac{a_p}{\varepsilon}\right)^{1.5} \text{ against } \frac{\rho_c}{a_p\mu_c}\left(V_c^{0.5} + V_d^{0.5}\right)^2 .$$

Where

μ_c = Viscosity of continuous phase, cP

ρ_c = Density of continuous phase, lb/ft^3

$\Delta\rho$ = Difference in density between continuous and dispersed phase

σ_I = Interfacial Tension, dyne/cm

a_p = Surface area of packing, ft^2/ft^3

ε = Voidage fraction

V_c = Continuous phase superficial velocity, ft/h

V_d = Dispersed phase continuous velocity, ft/h

Assume the use of 1 inch Raschig Rings

$a_p = 58 \text{ m}^2/\text{m}^3$

$\varepsilon = 0.714$

From the predicative method in [48] the viscosity of 1,1,2 trichloroethane at 25°C = 1.733cP

The surface tension of hydrocarbon streams can be approximated as 20 dyne/cm [48]

$\rho_c = 1450 \text{ kg/m}^3 = 90.52 \text{ lb/ft}^3$

$\rho_d = 960.8 \text{ kg/m}^3 = 59.98 \text{ lb/ft}^3$

$\Delta\rho = 30.54 \text{ lb/ft}^3$

$$\left(\frac{\mu_c}{\Delta\rho}\right)\left(\frac{\sigma_i}{\rho_c}\right)^{0.2}\left(\frac{a_p}{\varepsilon}\right)^{1.5} = \left(\frac{1.733}{30.54}\right)\left(\frac{20}{90.52}\right)^{0.2}\left(\frac{58}{0.74}\right)^{1.5} = 0.0567 * 0.739 * 638.9 = 29.1$$

From Fig 4 $\dfrac{\rho_c}{a_p\mu_c}\left(V_c^{0.5} + V_d^{0.5}\right)^2 = 600$

$\left(V_c^{0.5} + V_d^{0.5}\right)^2 = 666$

$\left(V_c^{0.5} + V_d^{0.5}\right) = 25.8$

Volumetric flowrate of continuous phase = 1070/1450 = 0.738 m³/h = 26.0 ft³/h

Volumetric flowrate of dispersed phase = 2430.96/960.8 = 2.53 m³/h = 89.1 ft³/h

$$\frac{V_c}{V_d} = \frac{26.0}{89.1} = 0.292$$

$V_c = 82.0$ ft/h

$V_d = 280.7$ ft/h

Cross-sectional area, A = 89.1/280.7 = 0.317 ft²

d = 0.64ft = 0.19m

So the diameter of the column, d = 0.2m

Total volume of liquid in column =

$$\varepsilon\frac{\pi}{4}d^2 Z + 0.15\frac{\pi}{4}d^2 Z = \left(0.74 * \frac{\pi}{4}0.2^2 * 6\right) + \left(0.15\frac{\pi}{4} * 0.2^2 * 6\right) = 0.168 \text{ m}^3$$

Dividing the column up into two sections, the top section will have an inventory a mixture of the fresh solvent and raffinate and the bottom section will have an inventory that is a mixture of the extract and feed streams.

$$\rho_{H_2O} = 1000 \, \text{kg/m}^3$$

$$\rho_{TCE} = 1450 \, \text{kg/m}^3$$

$$\rho_{2-BUT} = 808 \, \text{kg/m}^3$$

$$\rho_{MEK} = 805 \, \text{kg/m}^3$$

$$\rho_{FEED} = (0.099 * 805) + (0.012 * 808) + (.889 * 1000) = 978 \, \text{kg/m}^3$$

$$\rho_{RAF} = \text{Mostly water, therefore } 1000 \text{kg/m}^3$$

$$\rho_{EXT} = (0.173 * 805) + (0.022 * 808) + (0.805 * 1450) = 1394 \, \text{kg/m}^3$$

Volumetric flowrates

$$Q_{FEED} = 2430.96 / 978 = 2.486 \, \text{m}^3/\text{h}$$

$$Q_{EXT} = 1328.94 / 1394 = 0.953 \, \text{m}^3/\text{h}$$

$$Q_{RAF} = 2172.02 / 1000 = 2.172 \, \text{m}^3/\text{h}$$

$$Q_{TCE} = 1070 / 1450 = 0.738 \, \text{m}^3/\text{h}$$

Again the column is to be divided into two sections – in one section the inventory will be comprised of the feed Trichloroethane and the raffinate, and in the other it shall be comprised of the feed 10%MEK solution and the extract

The ratio of the inventory of TCE:Raffinate will be equal to the ratio of their volumetric feed rates

$$\frac{V_{TCE}}{V_{RAF}} = \frac{0.738}{2.172} = 0.340$$

And the total volume will be half of the column volume, $V_{TCE} + V_{RAF} = 0.084$

Solving $V_{TCE} = 0.021 \, \text{m}^3$

Mass of TCE = 0.018*1450 = 30.5 kg

$V_{RAF} = 0.063 \, \text{m}^3$

Mass of water = 63 kg

$$V_{EXT} + V_{FEED} = 0.084 \quad , \quad \frac{V_{FEED}}{V_{EXT}} = \frac{2.486}{0.953} = 2.609$$

$V_{FEED} = 0.061 \text{ m}^3$

Mass of 10% MEK solution = 0.061*978 = 59.7 kg

$V_{EXT} = 0.023 \text{ m}^3$

Mass of extract = 0.023*1394 ≈ 32.1 kg

From this information and the mass balances on each stream, the mass of each individual component may be calculated in the following table.

Inventory

	2-Butanol, kg	MEK, kg	TCE, kg	Water, kg	**Total, kg**
Feed	0.7	5.9		53.1	59.7
TCE Feed			30.5		30.5
Extract	0.7	5.6	25.8		32.1
Raffinate		0.3		62.7	63.0
Total, kg	1.4	11.8	56.3	115.8	185.3

So from the above table it can be seen that the inventory of the column will be 154.9kg of liquid, with composition 31.3% TCE and 6.4% MEK.

AC.5   Solvent Recovery

Mass Balance In

	Kg/h	Wt. fraction	kmol/h	Mol. fraction
MEK	230.08	0.173	3.196	0.275
2-Butanol	28.86	0.022	0.39	0.034
TCE	1070	0.805	8.015	0.691
Total	1328.94	1.000	11.601	1.000

For this system the 2-Butanol is present in such low quantities that we will assume the system is a binary one, so that the only separation is between MEK and TCE, and that all the 2-Butanol leaves with the top product. From the equilibrium data of the system MEK and TCE we will choose operating characteristics of the column such that $x_d = 0.93$ and $x_b = 0.004$

Mass balance of MEK: $0.93D + 0.004B = 3.196$

Mass Balance of TCE: $0.996B + \left(1 - 0.93 - \dfrac{0.39}{D}\right)D = 8.015$

(Assuming total recovery of the 2-butanol, the composition of 2-butanol in the distillate will be 0.39/D)

Solving these equations we find:

$D = 3.401$ kmol/h

$B = 8.200$ kmol/h

Mass Balance Out

Top

	Kg/h	Wt. Fraction	Kmol/h	Mol. fraction
MEK	227.74	0.928	3.163	0.93
2-Butanol	17.61	0.072	0.238	0.07
TCE				
Total	245.36	1.000	3.401	1.00

Bottom

	Kg/h	Wt. Fraction	Kmol/h	Mol. fraction
MEK	2.34	0.002	0.033	0.004
2-Butanol	11.25	0.010	0.152	0.018
TCE	1070	0.987	8.015	0.978
Total	1083.58	1.000	8.200	1.000

From the equilibrium data of this the system MEK-TCE it can be seen that the shape of the equilibrium curve is such that a short-cut method like Zomosa's will be too inaccurate to gain reasonable estimates with regards to the Reflux rate and the number of plates. In this case a better approach is to plot the

McCabe-Thiele diagram. The McCabe-Thiele diagram can be used to determine the number of plates

for plate columns, or the number of ideal transfer stages for packed columns [48].

Assumptions:

Feed enters at it's bubble point such that $q = 1$.

$R = 1.3 R_{MIN}$

Equilibrium Data

Temperature	Mol. fraction of MEK in liquid	Mol. fraction of MEK in Vapour
112	0.04	0.217
107.1	0.085	0.380
100.2	0.161	0.560
95.6	0.234	0.660
92.3	0.308	0.724
89.7	0.369	0.779
86.4	0.475	0.819
84.5	0.560	0.847
83.2	0.631	0.867
82.0	0.714	0.885
80.9	0.848	0.92
80.4	0.928	0.952

From the McCabe-Thiele diagram (Fig. 10) it is found that the number of stages, $N = 11$.
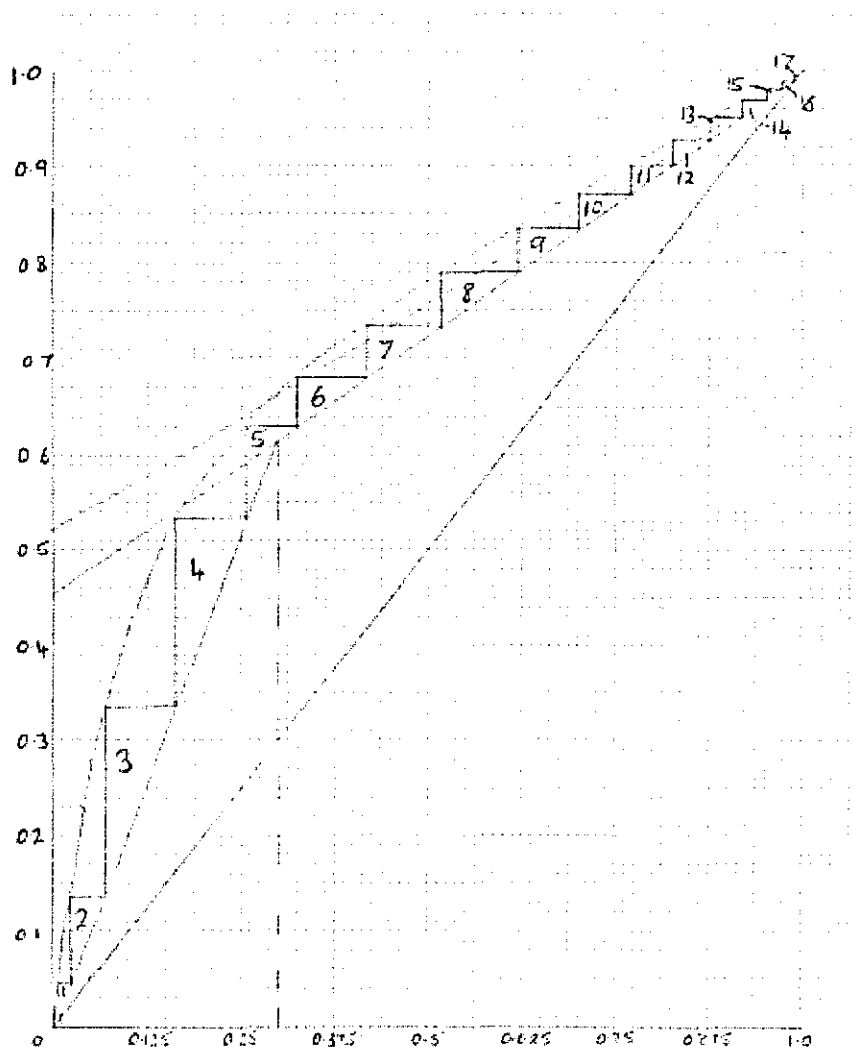
Fig. 10 – McCabe-Thiele diagram for MEK – TCE system

To determine the diameter of the column the economic gas flow rate. Assuming the use of 1 inch

Raschig Rings as packing, the economic gas flow rate from Morris and Jackson [40] is 1825 m^3/m^2h.

Correcting for density we get:

$$G' = 1825 \left(\frac{\rho_{Air}}{\rho_g} \right)^{0.33}$$

Where ρ_g = Density of vapour in column.

In the top section of the column, the temperature = 353K

$$\rho_{Air} = 1.182 \, kg/m^3$$

The molecular weight of the vapour is 72.9, so $\rho_g = 2.509 \, kg/m^3$

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Economic gas flowrate = 1424 m^3/m^2h

Now, D = 3.401 kmol/h

Vapour rate in top of column, $V = D(R+1)$

From McCabe-Thiele diagram R = 0.68, so V = 5.714 kmol/h

Volumetric flowrate, G = 5.714*22.4*$\dfrac{353}{273}$ =165.5 m^3/h

$A = \dfrac{G}{G'} = \dfrac{165.5}{1424} = 0.116\,m^2$

So d = 0.38m

So let the column diameter = 0.4m

For Pall Rings of 1 inch diameter the Height of an Equivalent Transfer Plate = 0.4-0.5m [45]. For Raschig Rings this will be slightly higher, so in the absence of other data assume an HETP of 0.6m.

Z = 11*0.6 = 6.6m

Inventory

Above the feed the inventory will be assumed to be of composition equal to the distillate composition, and below the feed the inventory will be assumed to be equal to the bottoms product inventory. The feed is located on the nth stage.

Liquid Hold-Up, $H_{OW} = 0.143\left(\dfrac{L'}{d}\right)^{0.6}$

d = 1 inch = 25 mm

Above the feed point, $L=V-D$ = 5.714-3.401 = 2.313 kmol/h

Molecular weight = 72.9 so mass flowrate = 168.6 kg/h

A = 0.126 m^2, L' = 168.6/0.126*3600 = 0.372 kg/m^2s

$H_{OW(T)} = 0.143\left(\dfrac{0.372}{25}\right)^{0.6} = 0.011\,m^3/m^3$ of column

Below the feed the slope of the operating line (from the McCabe-Thiele diagram), L/V= 2.55 and B = $L-V$. Solving with B = 8.200 kmol/h, V = 5.290 kmol/h and L = 13.490 kmol/h. The molecular weight of the liquid is 133.3 so the mass flow of the liquid = 133.3*13.490 = 1798.2 kg/h

L' = 1798.2/0.126*3600 = 3.964 kg/m^2s

$$H_{OW\{B\}} = 0.143\left(\frac{3.964}{25}\right)^{0.6} = 0.047$$

Top Product Inventory

From the McCabe-Thiele diagram the number of stages above the feed = 6

$$\text{Liquid Inventory} = \frac{6}{11}\cdot\frac{\pi}{4}d^2ZH_{OW(T)} = \frac{6}{11}\cdot\frac{\pi}{4}*0.4^2*6.6*0.011 = 4.976*10^{-3}\,m^3$$

Voidage fraction of packing = 0.714

$$\text{Gas Inventory} = \frac{6}{11}\cdot\frac{\pi}{4}d^2Z\varepsilon = \frac{6}{11}\cdot\frac{\pi}{4}*0.40^2*6.6*0.714 = 0.323\,m^3$$

Bottom Product Inventory

$$\text{Liquid Inventory} = \frac{5}{11}\cdot\frac{\pi}{4}d^2ZH_{OW(B)} = \frac{5}{11}\cdot\frac{\pi}{4}*0.4^2*6.6*0.047 = 0.0177\,m^3$$

$$\text{Gas Inventory} = \frac{5}{11}\cdot\frac{\pi}{4}d^2Z\varepsilon = \frac{5}{11}\cdot\frac{\pi}{4}*0.4^2*6.6*0.714 = 0.269\,m^3$$

At the top of the column, the temperature is 353K

Densities of liquids

$$\rho_{MEK} = 735\,kg/m^3$$

$$\rho_{2-But} = 746\,kg/m^3$$

$$\rho_D = (0.928*735)+(.072*746) = 736\,kg/m^3$$

Liquid mass inventory = $736*4.976*10^{-3}$ = 3.66 kg

Gas Inventory

$$\rho_{MEK} = 2.478\,kg/m^3$$

$$\rho_{2-But} = 2.547\,kg/m^3$$

$$\rho_{D(Vapour)} = (0.928*2.478)+(0.072*2.547) = 2.483\,kg/m^3$$

Vapour mass inventory = $0.323*2.483$ = 0.80 kg

At the Bottom of Column the temperature is 385K

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$$\rho_{MEK} = 695 \, \text{kg/m}^3$$

$$\rho_{TCE} = 1450 \, \text{kg/m}^3$$

$$\rho_B = 709 \, \text{kg/m}^3$$

$$\rho_B = (0.002*695)+(0.01*709)+(0.988*1450) = 1441 \, \text{kg/m}^3$$

Liquid mass Inventory = 0.0177*1441 = 25.5 kg

Vapour Inventory

$$\rho_{MEK} = 2.272 \, \text{kg/m}^3$$

$$\rho_{2-But} = 2.335 \, \text{kg/m}^3$$

$$\rho_{TCE} = 4.212 \, \text{kg/m}^3$$

$$\rho_{B(Vapour)} = (0.002*2.272) + (0.01*2.335) + (0.988*4.212) = 4.189 \, \text{kg/m}^3$$

Mass Inventory = 4.189*0.269 = 1.13 kg

Liquid Inventory

	MEK, kg	2-Butanol, kg	TCE, kg	Total, kg
Distillate	3.4	0.26		3.66
Bottoms	0.05	0.26	25.2	25.5
Total, kg	3.45	0.52	25.2	29.2

Giving a liquid inventory of 29.2 kg of 86.3% TCE and 11.8% MEK

Gas Inventory

	MEK, kg	2-Butanol, kg	TCE, kg	Total
Distillate vapour	0.74	0.06		0.80
Bottoms vapour	Negligible	0.01	1.12	1.13
Total	0.74	0.07	1.12	1.93

So there is a total gas inventory of 1.93 kg, with the gas composed of 38.3% MEK, 58.0% 1-1-2

Trichloroethane.

Condenser and Reboiler

Condenser

Vapour Flow in Top section of column = 5.714 kmol/h

Distillate Flow Rate = 3.401 kmol/h

Liquid to be Condensed = 2.313 kmol/h

Latent Heats of Vaporisation at 353K

$$H_{V(MEK)} = 31.54*10^3 \text{ kJ/kmol}$$

$$H_{V(2-But)} = 43.44*10^3 \text{ kJ/kmol}$$

Latent Heat of Vaporisation $H_v = (0.93*31.54)+(0.07*43.44) = 32.37*10^3 \text{kJ/kmol}$

$$Q = L*H_v = 2.313*32.37*10^3 = 74.87*10^3 \text{ kJ/h} = 20.80 \text{ kJ/s}$$

U = 500 W/m²°C

$$\Delta T_{lm} = \frac{(80-24)-(80-40)}{\ln\left(80-24\middle/80-40\right)} = 47.6 \,^{\circ}\text{C}$$

$$A = \frac{20.8*10^3}{500*47.6} = 0.874 \,\text{m}^2$$

This is a small heating duty, so smaller tubes shall be used. Try 1/4inch outside diameter (6.35 mm)

and 8ft length (2.44 m)

Heat transfer area of one tube = $\pi d l = \pi*6.35*10^{-3}*2.44 = 0.0487 \,\text{m}^2$

Number of Tubes, N = 0.874/0.0487 = 18 tubes

Bundle diameter,

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{1/n_1} = 15.875\left(\frac{18}{0.319}\right)^{1/2.142} = 104 \,\text{mm}$$

Shell clearance = 50mm

Shell diameter, D_s = 154 mm

Reboiler

From McCabe-Thiele diagram L/V = 2.55, and B=L-V

B = 8.200 kmol/h

L = 13.490 kmol/h

V = 5.290 kmol/h

Latent Heats at 385K

$$H_{V(MEK)} = 29.45 \, \text{kJ/kmol}$$

$$H_{V(TCE)} = 34.82 \, \text{kJ/kmol}$$

$$H_V = (0.004 * 29.45) + (0.018 * 39.64) + (0.978 * 34.82) = 34.89 * 10^3 \, \text{kJ/kmol}$$

Q = 5.290*34.89*10³ = 184.6*10³ kJ/h = 51.28 kJ/s

Heating medium is steam at 140°C

$$\Delta T_{lm} = 28$$

$$A = \frac{51.28 * 10^3}{28 * 900} = 2.035 \, \text{m}^2$$

This is a small heating duty, so smaller tubes shall be used. Try 1/4inch outside diameter (6.35 mm) and 8ft length (2.44 m)

Heat transfer area of one tube = $\pi d l = \pi * 6.35 * 10^{-3} * 2.44 = 0.0487 \, \text{m}^2$

Number of Tubes, N = 2.035/0.0487 = 42

Bundle diameter,

$$D_b = d_o \left(\frac{N_t}{K_1} \right)^{1/n_1} = 15.875 \left(\frac{42}{0.319} \right)^{1/2.142} = 155 \, \text{mm}$$

Shell clearance = 50mm

Shell diameter = 155+50 = 205mm

AC.6   Methyl Ethyl Ketone Purification

The top product from the solvent extraction still is combined with the condensate from item the

condenser.

Flow From Condenser

	kg/h	Wt. fraction	kmol/h	Mol. fraction
MEK	1108.78	0.898	15.400	0.901
2-Butanol	125.31	0.102	1.693	0.099
Total	1234.09	1.000	17.093	1.000

Flow From Solvent Extraction Still

	Kg/h	Wt. fraction	Kmol/h	Mol. fraction
MEK	227.74	0.928	3.163	0.930
2-Butanol	17.61	0.072	0.238	0.070
TCE				
Total	245.35	1.000	3.401	1.000

Mass Balance In

	Kg/h	Wt. fraction	Kmol/h	Mol. Fraction
MEK	1336.52	0.894	18.563	0.906
2-Butanol	142.92	0.103	1.931	0.094
Total	1479.44	1.000	20.494	1.000

Assuming that $x_D = 0.99$ and $x_B = 0.01$

Mass balance on MEK $0.99D + 0.01B = 18.563$

Mass balance on 2-Butanol $0.01D + 099B = 1.931$

Solving these equations $D = 18.733$ kmol/h, $B = 1.761$ kmol/h

Distillate Flow

	Kg/h	Wt. fraction	Kmol/h	Mol. fraction
MEK	1335.31	0.990	18.546	0.99
2-Butanol	13.84	0.010	0.187	0.01
Total	1349.15	1.000	18.733	1.00

Bottoms Flow

	Kg/h	Wt. fraction	Kmol/h	Mol. fraction
MEK	1.21	0.009	0.017	0.010
2-Butanol	129.08	0.991	1.744	0.990
Total	130.29	1.00	1.761	1.000

Column Design

Calculation of relative volatility

The relative volatility can be calculated from the vapour pressures of MEK and 2-Butanol at the temperatures on the top and bottom plates.

Top plate temperature 80°C

V.P MEK = 115052 Nm^{-2}

V.P. 2-Butanol = 46803 Nm^{-2}

α_{80} = 115052/46803 = 2.458

Bottom plate temperature = 99oC

V.P. MEK = 209349 Nm^{-2}

V.P. 2-Butanol = 103190 Nm^{-2}

α_{99} = 2.029

$\alpha_{AV} = \sqrt{\alpha_{80}\alpha_{99}} = 2.233$

$$R_m = \frac{1}{(\alpha-1)x_F} = \frac{1}{1.233 * 0.906} = 0.90$$

$$R = 1.3R_m = 1.3 * 0.90 = 1.17$$

The density of the distillate vapour, $\rho_{V(D)} = 2.476\,\text{kg/m}^3 = 0.155\,\text{lb/ft}^3$

$$\rho_{L(D)} = 735.3\,\text{kg/m}^3 = 46.030\,\text{lb/ft}^3$$

$$G = 600\left[\rho_V\left(\rho_L - \rho_V\right)\right]^{0.5} = 1600\ \text{lb/ft}^2\text{h}$$

$$d = \left[\frac{D(R+1)}{0.785G}\right]^{0.5} = \left[\frac{2.2*1349.15*2.17}{0.785*1600}\right]^{0.5} = 2.265\ \text{ft} = 0.69\text{m}$$

Say d = 0.70m

From Fig.1 $N_m = 10$.

And from fig.2 $N = 2N_m = 20$

70% efficiency, N = 20/0.7 = 29

Therefore there are N-1 = 28 plates in the column, and with a plate spacing of 0.5m the column height,

Z = 14m.

Since the feed point is located near the top of the column the column will be divided into two sections

for inventory, one above the feed point one below the feed.

$$\text{Feed point location} \log\frac{N_r}{N_s} = 0.206\log\left[\left(\frac{B}{D}\right)\left(\frac{x_{f,hk}}{x_{f,lk}}\right)\left(\frac{x_{b,lk}}{x_{d,hk}}\right)^2\right]$$

$$\log\frac{N_r}{N_s} = 0.206\log\left[\left(\frac{1.951}{18.768}\right)\left(\frac{0.1}{0.9}\right)\left(\frac{0.01}{0.01}\right)^2\right]$$

$$\frac{N_r}{N_s} = 0.4$$

$N_r + N_s = 28$

$N_s = 20$

$N_r = 8$

Top product liquid inventory = $0.044 * 8 * \dfrac{\pi}{4} * 0.7^2 = 0.135\,\text{m}^3$

Bottom product liquid inventory (including liquid sump)

$$= 0.044 * \frac{\pi}{4} * 0.7^2 * (20 + 28) = 0.813 \, \text{m}^3$$

Vapour Inventory = Inventory on top plates + Inventory on Bottom Plates + Inventory in

Disengagement Space

$$v_B + v_D + 0.044 \frac{\pi}{4} N d^2 = 0.50 \frac{\pi}{4} N d^2$$

and $\dfrac{v_B}{v_D} = \dfrac{20}{8} = 2.5$

Solving these equations

$$v_D = 1.404 \, \text{m}^3$$

$$v_B = 3.510 \, \text{m}^3$$

Bottom product vapour inventory = 3.510 m³

Top product vapour inventory = $v_D + 0.044 \frac{\pi}{4} N d^2 = 1.878 \, \text{m}^3$

Top Product Liquid Inventory, at 353K

$$\rho_D = 735.3 \ \text{kg/m}^3$$

Mass Inventory = 0.135*735.3 = 99.3 kg

Top Product Vapour Inventory

$$\rho_{MEK} = 2.478 \, \text{kg/m}^3$$

$$\rho_{2-But} = 2.547 \, \text{kg/m}^3$$

$$\rho_{D(Vapour)} = (0.99*2.478)+(0.01*2.547) = 2.479 \, \text{kg/m}^3$$

Mass Inventory = 1.878*2.479 = 4.7 kg

Bottoms Temperature = 372K

Liquid Densities

$$\rho_{MEK} = 712 \, \text{kg/m}^3$$

$$\rho_{2-But} = 724\,\text{kg/m}^3$$

$$\rho_B = (0.009*712) + (0.991*724) = 724\,\text{kg/m}^3$$

Bottoms product liquid inventory = 0.813*724 = 588.6 kg

Vapour Inventory

$$\rho_{MEK} = 2.351\,\text{kg/m}^3$$

$$\rho_{2-But} = 2.417\,\text{kg/m}^3$$

$$\rho_{DB(Vapour)} = 2.416\,\text{kg/m}^3$$

Mass Inventory = 3.510*2.416 = 8.5 kg

Liquid Inventory

	MEK, kg	2-Butanol, kg	Total, kg
Distillate	98.3	1.0	99.3
Bottoms Product	5.3	583.3	588.6
Total, kg	103.6	584.3	687.9

So the liquid inventory is 492.5 kg of a solution with composition 86.6% 2-Butanol, 13.4% MEK

Gas Inventory

	MEK, kg	2-Butanol, kg	Total, kg
Distillate	4.7	Negligible	4.7
Bottoms Product	0.1	8.4	8.5
Total, kg	4.8	8.4	13.2

Vapour inventory of 8.7 kg of a 33.3% MEK, 66.7% 2-Butanol.

Condenser and Reboiler

Condenser

Distillate Flow from column, D = 18.733 kmol/k

Vapour rate in top of column, V = D(R+1) = 18.733*2.17 = 40.651 kmol/h

Liquid Flow in Column = V-D = 21.918 kmol/h

Latent Heat of Vaporisation

$$H_{V(MEK)} = 31.54*10^3 \text{ kJ/kmol}$$

$$H_{V(2-But)} = 43.44*10^3 \text{ kJ/kmol}$$

Latent Heat of Vaporisation of Distillate = $(0.99*31.54+0.01*43.44)*10^3$

= 31.66 kJ/kmol

$$Q = L*H_V = 21.918*31.66*10^3 = 693.9*10^3 \text{ kJ/h} = 192.8 \text{ kJ/s}$$

Condensing Medium is Water at 24°C, leaving at 40°C

$$\Delta T = \frac{(80-24)-(80-40)}{\ln\left(80-24\middle/80-40\right)} = 47.6\,°C$$

U = 500 W/m²°C

$$A = \frac{192.8*10^3}{500*47.6} = 8.10 \text{ m}^2$$

Start by assuming a standard tube of 5/8 inch outside diameter, 12 ft long (approximately 15.875mm diameter, 3.66 m long).

Heat Transfer Surface = $\pi*15.875*10^{-3}*3.66 = 0.183$ m²

Number of Tubes = 8.10/0.183 = 45

Tube inside diameter = 10mm, cross-sectional area for flow of water = $3.534*10^{-3}$ m²

Mass flow rate of water = 192.8/4.2*16 = 2.869 kg/s

Velocity of water = 2.869/3.534 = 0.81 ms⁻¹.

This value is sufficiently high, so the design is sound.

Shell Diameter

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{1/n_1} = 15.875\left(\frac{45}{0.319}\right)^{1/2.142} = 160 \text{ mm}$$

Shell clearance = 50 mm D_s = 160+50 = 210mm.

Reboiler

Assuming that the feed enters as a saturated vapour, in the bottom section of the column:

$L = 21.918$ kmol/h

$B = 1.761$ kmol/h

So the vaporiser must vaporise 20.157 kmol/h

At the bottoms temperature, 99°C

$$\Delta H_{v(MEK)} = 30.60*10^3 \text{ kJ/kmol}$$

$$\Delta H_{V(2-But)} = 42.23*10^3 \text{ kJ/kmol}$$

Latent Heat of Vaporisation of Bottoms product,

$$\Delta H_v = (0.01*30.6)+(0.99*42.23) = 42.11 \text{ kJ/kg}$$

$$Q = V*H_V = 20.157*42.11*10^3 = 848.8*10^3 = 235.7 \text{ kJ/s}$$

$U = 900$ W/m²s [48]

Heating medium is steam at 140°C, $\Delta T_{lm} = 41$°C

$$A = \frac{253.7*10^3}{900*41} = 6.88 \text{ m}^2$$

Start by assuming a standard tube of 5/8 inch outside diameter, 12 ft long (approximately 15.875mm

diameter, 3.66 m long).

Heat Transfer Surface = $\pi*15.875*10^{-3}*3.66 = 0.183$ m²

Number of Tubes, $N = 6.88/0.183 = 38$

$$D_b = d_o\left(\frac{N_t}{K_1}\right)^{1/n_1} = 15.875\left(\frac{38}{0.319}\right)^{1/2.142} = 148 \text{ mm}$$

Shell clearance = 50mm

Shell diameter, $D_s = 198$m

Appendix D – Manufacture of Acetic Anhydride

The case study is for the design of a plant to manufacture 20000 tonnes per year of acetic anhydride.

The product is to be of 95% w/w purity.

Acetic anhydride is produced from the reaction of acetic acid and ketene:

$$CH_2CO + CH_3COOH \rightarrow (CH_3CO)_2O$$

Ketene   Acetic Acid   Acetic Anhydride

The there are two main feedstocks into the process. Acetone, used to create the ketene in the reactor

vessel, and acetic acid. The acetic acid is used to cool the reactor products in a quench column. The

gases are then cooled. As they condense the acetic acid and ketene react in a tubular condenser

forming acetic anhydride.

The ketene is produced on site from the thermal cracking of acetone at 650°C to 800°C:

$$(CH_3)_2CO \rightarrow CH_4 + CH_2CO$$
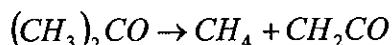
Acetone   Methane   Ketene

Other side reactions are present in this reaction, which are discussed in section 4.2.1. Researchers have

found that the economic conversion for this reaction is 25%. In order to minimise the decomposition

of ketene the gases must be rapidly cooled. This is done by quenching the gases through the injection

of a mixture of acetic acid and acetic anhydride. This is then passed to packed quench tower for further

cooling, and also to ensure that there is sufficient acetic acid in the gas stream for reaction with the

ketene.

The vapours are passed to a condenser, where the reaction of acetic acid with ketene takes place. As

the vapours condense they react with each other forming acetic anhydride. The design of this vessel is

for 90% conversion of the ketene present. The condensed liquor comprising acetone, acetic acid and

anhydride is passed to the acetone recovery column, where the acetone is separated by distillation and

recycled back to the reactor. The bottoms product from this column containing a mixture of acetic acid

and acetic anhydride is passed to a further distillation column where the acetic anhydride is removed as

product.

Fig. 9 – Flowchart for acetic anhydride production

————————▶   Acetic Acid recycle

AD.1   Reactor

Requirements: 20000 tonnes/year acetic anhydride

Assuming continuous production, 8000h/year

$$\text{Anhydride Production rate} = \frac{20000*1000}{8000} = 2500\,\text{kg/h}$$

Plus 8% to account for spillages = 2500*1.08 = 2700 kg/h

So the hourly production rate of anhydride is 2700 kg/h

From Daroux [5] the economic conversion for the reaction of acetone is 25%, and from Jeffreys [20]

the yield of ketene at this conversion is 70%. Therefore, assuming full conversion of the ketene in the

reaction with the acetic acid the required flowrate of acetone is:

$$\frac{2700*58}{102*0.25*0.7} = 8773\,\text{kg/h}$$

The main reaction is the thermal decomposition of acetone to methane and ketene:
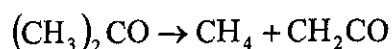
$$(CH_3)_2 CO \rightarrow CH_4 + CH_2CO$$

However, two unwanted side reactions also take place. The first is the decomposition of ketene to

ethane and carbon monoxide:

$$2CH_2CO \rightarrow C_2H_4 + 2CO$$

And the second is the dehydrogenation of acetone:

$$(CH_3)_2 CO \rightarrow 3H_2 + CO + 2C$$
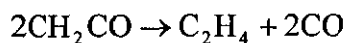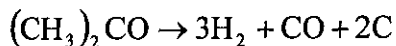
Exit gas flowrates:

Acetone: (1-0.25)*8773 = 6580 kg/h

Ketene: $\dfrac{0.25 * 0.7 * 8773 * 42}{58} = 1112\,kg/h$

From Jeffreys [20] the number of moles of gas (non-ketene) produced per mole of reaction is 0.362 at

25% conversion, and the composition of the gas is:

Methane	67.7%
Unsaturates (ethane)	8.1%
Carbon Monoxide	19.1%
Carbon Dioxide	0.9%
Hydrogen	4.2%

So the flowrate of these gases is:

Methane: $\dfrac{8773}{58} * 16 * 0.362 * 0.677 = 592\,kg/h$

Unsaturates: $\dfrac{8773}{58} * 39 * 0.362 * 0.081 = 179\,kg/h$

Carbon Monoxide: $\dfrac{8773}{58} * 28 * 0.362 * 0.191 = 292\,kg/h$

Carbon Dioxide: $\dfrac{8773}{58} * 44 * 0.362 * 0.009 = 21\,kg/h$

Hydrogen: $\dfrac{8773}{58} * 2 * 0.362 * 0.042 = 4$

Mass Balance

	In		Out	
	Kg/h	Kmol/h	Kg/h	Kmol/h
Acetone	8773	151.3	6580	113.4
Ketene			1112	26.5
Methane			592	137.0
Ethene			172	4.4
Carbon Monoxide			292	10.4
Carbon Dioxide			21	0.5
Hydrogen			4	2
Total	8773	151.3	8773	194.2

The volume of tube required for the reaction can be estimated by assuming the reactor is modelled by plug flow behaviour. Since the reaction is first order, the expression for reactor volume is given by:

$$k \frac{C_{A0} V}{F_{A0}} = -(1 + \varepsilon) \ln(1 - X_A) - \varepsilon_A X_A$$

$$\varepsilon = \frac{194.2 - 151.3}{151.3} = 0.284$$

And if the reactor operates at 5 bar and 650°C, then:

$$C_{A0} = \frac{P_{A0}}{RT} = \frac{5 * 1.01 * 10^5}{8.314 * 922} = 71.7 \, \text{mol/m}^3 = 71.7 * 10^{-3} \, \text{kmol/m}^3$$

$$F_{A0} = 151.3 \, \text{kmol/h} = 0.042 \, \text{kmol/s}$$

$$X_A = 0.25$$

$$k = 34.34 - \frac{68000}{RT}$$

Where $R = 1.987$ cal/molK

If $T_{Av} = (1073 + 923)/2 = 998K$

So $k = 1.05$

Substituting of these values gives:

$$k\frac{C_{A0}V}{F_{A0}} = 0.298$$

$$V = \frac{0.298 * 0.042}{1.05 * 71.7 * 10^{-3}} = 0.166\ m^3$$

Reactor Inventory

Assuming the first half of the reactor is acetone at 650°C and 5 bar, then

$\rho_{Acetone} = 3.817\ kg/m^3$

Inventory = (0.166/2)*3.817 = 0.317 kg

The second half of the reactor has an inventory of the same composition of the reactor products:

$\rho_{Products} = 2.443\ kg/m^3$

Inventory = (0.166/2)*2.443 = 0.203 kg

The reaction takes place in a furnace. The reaction section will only be a minor part of the furnace. The heat transfer in the furnace will require a much larger volume in order to preheat and vaporise the acetone, provide heat of cracking and provide superheat. The design of a furnace is a complex method requiring knowledge of flame temperature, heat transfer coefficients, skin temperature and other thermodynamic properties. Attempts to develop short-cut methods for calculating furnace inventory failed to give results of sufficient accuracy. The above method is given as an example of reactor design. It is not representative of the inventory in the furnace. Therefore the actual inventories will not be calculated as there is no basis of comparison.

AD.2 Quench Units

Assuming the vapours leave the furnace at 850°C, and must be cooled to 540°C in order to prevent the decomposition of ketene. The design must therefore add enough acetic acid and acetic anhydride to cool the gases down to that point. The assumption will also be that the acid and anhydride are added as liquids at ambient temperature (25°C)

Boiling point of Acetic Acid = 112°C

Boiling point of Acetic Anhydride = 140°C

Heat Capacity of Quenching Materials:

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Average liquid heat capacities (from 25°C to boiling point):

$$c_{p(Acid)} = 2.265 \, kJ/kg°C$$

$$c_{p(Anhydride)} = 2.142 \, kJ/kg°C$$

Latent Heat of Vaporisation:

$$H_{V(Acid)} = 397.6 \, kJ/kg$$

$$H_{V(Anhydride)} = 394.7 \, kJ/kg$$

Average Heat Capacities of Gases (from boiling point to 540°C):

$$c_{p(Acid)} = 1.770 \, kJ/kg°C$$

$$c_{p(Anhydride)} = 1.730 \, kJ/kg°C$$

Therefore the heat increase of the quenching materials is:

Acid: ((118-25)*2.265) + 397.6 + ((540-118)*1.770) = 1355.2 kJ/kg

Anhydride: ((140-25)*2.142) + 394.7 + ((540-140)*1.730) = 1333.0 kJ/kg

Assuming equal flow of acid and anhydride, and that the flow of each material is x kg/h then the heat required,

Q = 1355.2x + 1333.0x = 2688.2x kJ/h

Heat Capacity of Reactor Gas

The heat capacity of the reactor gas from 850°C to 540°C is calculated in Appendix C to be 2.740 kJ/kg

$$Q = mC\Delta T = 8773 * 2.740 * 310 = 7.452 * 10^6 \, kJ/h$$

So $x = \dfrac{7.452 * 10^6}{2688.2} = 2772$ kg/h

So the total liquid quench is 5544 kg/h of a mixture containing 50% acetic acid, and 50% acetic anhydride.

Mass Balance

	Gas In, kg/h	Liquid In, kg/h	Gas Out, kg/h
Acetone	6580		6580
Ketene	1112		1112
Methane	592		592
Ethene	172		172
Carbon Monoxide	292		292
Carbon Dioxide	21		21
Hydrogen	4		4
Acetic Acid		2772	2772
Acetic Anhydride		2772	2772
Total	8773	5544	14317

AD.3   Quench Column

The cooled gas stream from the first quench then passes to a packed column where it will be further cooled by direct contact with a liquid stream containing 50% acid and 50% anhydride. The gas leaving the quench column is to be at a temperature of 150°C, and the acetic acid content of the gas stream should be equimolar with the ketene present in the gas.

Ketene present in gas = 1112 kg/h

With a molecular weight of 42, there is therefore 26.48 kmol/h of ketene.

So the flowrate of acetic acid in the exit gas must be 26.48 kmol/h. The molecular weight of acetic acid is 60, so the flow of acetic acid out of the column must be 1590 kg/h. So the 'humidity' of the acid in the gas is 1590/8773 = 0.181 kg acetic acid/kg gas.

Column Design:

Average temperature = (540+150)/2 = 345°C (618K)

Volumetric Flowrate = 194.2*22.4*618/273 = 9847 m^3/h

Assuming the use of 3-inch packed stoneware rings, the economic gas flowrate = 3450 m^3/m^{2}h [40].

$$\text{Correction factor for the gas} = \left(\frac{\text{Density of air at rtp}}{\text{Actual density of gas}} \right)^{0.33}$$

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Density of gas $= \dfrac{45.2 * 1.01 * 10^5}{8.314 * 618} = 0.889 \, \text{kg/m}^3$

Density of air at rtp = 1.15 kg/m^3

Economic Gas Flowrate $= 3450 * \left(\dfrac{1.15}{0.889} \right)^{0.33} = 3756 \, \text{m}^3/\text{m}^2\text{h}$

The cross-sectional area for flow is therefore A = 9487/3756 = 2.526 m^2

So the diameter, d = 1.79m, say 1.80m.

The actual gas flowrate in the column, G = 3728 m^3/m^{2}h

Column Height

Determination of column height is a complicated procedure requiring iterative calculations. It

necessitates the solution of 4 equations over each section of the column, taking into to the mass transfer

of acetic acid and acetic anhydride into the gas phase, and the effect of this on the heat transfer between

the gas and liquid phases. As estimation of the exit temperature of the liquid flow must be made, and

these equations must then be solved by iterative procedure to determine the mass and heat flows in

each specific part of the column. The procedure must be repeated for every section of the column to

calculate the depth of packed bed required to obtain 0.18 kg acetic acid/kg dry gas, and also to

calculate the depth of packed bed required to cool the gas to 150°C. Once this is done the whole

procedure must be repeated for a selection of exit liquor temperatures until the engineer knows which

combination of exit liquor temperature and packed bed height will give an exit gas temperature of

150°C and 0.18 kg acid/ kg gas.

As may be expected this is a lengthy, complicated procedure. Whilst the equations themselves are not

mathematically complicated the number of calculations that must be performed is so large that it could

conceivably take an engineer a day or more to size this item of equipment.

It is hypothesised that the size of the vessel could be estimated by neglecting mass transfer

characteristics, using only a simplification of the heat transfer that occurs in the column. The flow of

gas out of the column could be estimated by calculating the quantity of acetic anhydride at equilibrium

with the 0.18 kg acid/kg gas, from the vapour pressures at the exit temperature.

The equations required for heat transfer in the column are:

$LCdT_l = WsT_g$

$$WsdT_g = Ua(T_g - T_l)dh$$

Liquid Flowrate, L

Average heat capacity of dry gas = 2.137 kJ/kg°C

Heat to be removed from gas = 8773*2.137*(540-150) = $7.312*10^6$ kJ/h

Average heat capacity of liquid = 2.190 kJ/kg°C

Liquid mass flow rate = $7.312*10^6$/2.190*75 = 44518 kg/h

Cross-sectional area, A = $\frac{\pi}{4}*1.8^2$ = 2.545 m^2

Liquid flowrate, L = 44518/2.545 = 17494 kg/m^{2}h

Heat capacity of liquid, C = 2.190 kJ/kg°C

U = Assume 50 W/m^{2o}C

Dry gas rate. W = 3728 kg/m^{2}h

Interfacial area, a = 65.5 m^2

$$LCdT_l = UA(T_g - T_l)dh$$

T_g = 540°C

T_l = 100°C

dT_1 = 100°C – 25°C = 75°C

$$17494 * 2.190 * 75 = 50 * 65.5 * 440 * dh$$
$$dh = 1.99$$

So the height of the packed column is 2.0m

The final acetic acid content of the final gas is 0.18kg per kg dry gas.

Assuming that the ratio of anhydride to acid is equal to the ratio of anhydride to acid at equilibrium

with the exit liquid:

At 100°C, vapour pressure of acid = 56268 Nm^{-2}

Vapour pressure of anhydride = 27075 Nm^{-2}

Vapour pressure of mixture = (56268+27075)/2 = 41672 Nm^{-2}

Inert pressure = $1.01*10^5$ – 41672 = 59328 Nm^{-2}

$$H = \frac{P_a(MW_a)}{P_b(MW_b)}$$

H_{acid} = 0.629

$H_{anhydride} = 0.515$

Therefore the final gas anhydride content = $H_{anhydride} = \dfrac{0.181*0.515}{0.629} = 0.148 \, kg/kg$

Acetic Acid content = 1590 kg/h

Acetic Anhydride Content = 0.148*8773 = 1298 kg/h

Mass Balance

	Gas In kg/h	Liquid In, kg/h	Gas Out, kg/h	Liquid Out, kg/h
Acetone	6580		6580	
Ketene	1112		1112	
Methane	592		592	
Ethene	172		172	
Carbon Monoxide	292		292	
Carbon Dioxide	21		21	
Hydrogen	4		4	
Acetic Acid	2772	22259	1590	23441
Acetic Anhydride	2772	22259	1298	23733
Total	14317	44518	11661	47174

Inventory

Column height 2.0m, 1.80m diameter.

Voidage fraction = 0.72

Liquid Hold-up

$$H_{OW} = 0.143 \left(\frac{L'}{d} \right)^{0.6}$$

$L' = 4.859 \, kg/m^2s$

$d = 75mm$

$$H_{OW} = 0.143 \left(\frac{L'}{d} \right)^{0.6} = 0.028$$

Total Liquid Inventory $= \frac{\pi}{4}d^2 ZH_{OW} = \frac{\pi}{4}*1.8^2*2*0.028 = 0.143\,m^3$

Since the composition of the liquid flow does not change greatly, it will be assumed to be constant at 50% acetic acid, 50% acetic anhydride.

$\rho = 1058\,kg/m^3$

Inventory $= 1058*0.143 = 151.3\,kg$

Gas Inventory $= \frac{\pi}{4}d^2 Z(\varepsilon - H_{OW} + 0.15) = \frac{\pi}{4}*1.8^2*2*0.842 = 4.285\,m^3$

First section, $\rho = 0.675\,kg/m^3$

First section inventory $= 2.443*4.285/2 = 5.2\,kg$

Second section, $\rho = 1.435\,kg/m^3$

Second section inventory $= 3.1\,kg$

Gas Inventory

	Bottom section, kg	Top section, kg	Total, kg
Acetone	2.4	1.7	4.1
Ketene	0.4	0.3	0.7
Methane	0.2	0.2	0.4
Ethene	0.1	0.1	0.2
Carbon Monoxide	0.1	0.1	0.2
Carbon Dioxide	Negligible	Negligible	Negligible
Hydrogen	Negligible	Negligible	Negligible
Acetic Acid	1.0	0.4	1.4
Acetic Anhydride	1.0	0.3	1.3
Total	5.2	3.1	**8.3**

AD.4   Condenser

Gas Flow In:

	Kg/h	Wt. fraction	Kmol/h	Mol fraction
Acetone	6580	0.564	113.4	0.486
Acetic Acid	1590	0.136	26.5	0.114
Acetic Anhydride	1298	0.111	12.7	0.054
Ketene	1112	0.095	26.5	0.114
Methane	592	0.051	37.0	0.159
Ethene	172	0.015	4.4	0.019
Carbon Monoxide	292	0.025	10.4	0.045
Carbon Dioxide	21	0.002	0.5	0.002
Hydrogen	4	Negligible	2	0.009
Total	11661	1.00	233.4	1.00

The assumption will be that there will be no condensation of gases apart from acetone, acetic acid and acetic anhydride. No unreacted ketene will condense.

Vapour pressure of condensable gases at 150°C:

Acetone: $11.491 * 10^5 \text{ Nm}^{-2}$

Acetic Acid: $2.482 * 10^5 \text{ Nm}^{-2}$

Acetic Anhydride: $1.362 * 10^5 \text{ Nm}^{-2}$

The number of moles condensed $= \dfrac{P_1 - P_2}{P_1} * \text{No. moles present}$

In order to react 90% of the ketene, 90% (by mol) of the acetic acid must be condensed.

So the vapour pressure of the acetic acid at the gas exit temperature is:

$$\frac{2.482 * 10^5 - P_2}{2.482 * 10^5} = 0.9$$

$$P_2 = 0.248 * 10^5 \text{ Nm}^{-2}$$

This corresponds to a temperature of 77°C (by trial and error, and rounded down)

Vapour pressures at 77°C

Acetone: $1.962*10^5$ Nm^{-2}

Acetic Acid: $0.242*10^5$ Nm^{-2}

Acetic Anhydride: $0.106*10^5$ Nm^{-2}

Amount condensed:

$$\text{Acetone} = \frac{11.491*10^5 - 1.962*10^5}{11.491*10^5} *113.4 = 94.0 \text{ kmol/h} = 5454 \text{ kg/h}$$

$$\text{Acetic Acid} = \frac{2.482*10^5 - 0.242*10^5}{2.482*10^5} *26.5 = 23.9 \text{ kmol/h} = 1435 \text{ kg/h}$$

$$\text{Acetic Anhydride} = \frac{1.362*10^5 - 0.106*10^5}{1.362*10^5} *12.7 = 11.7 \text{ kmol/h} = 1195 \text{ kg/h}$$

Amount of ketene removed from gas stream = amount of ketene which reacts with condensed acetic acid. Assuming the reaction goes to completion, then the amount of ketene that reacts is

$$\frac{1435}{60} *42 = 1005 \text{ kg/h}$$

Gas Out at 77°C

	Kg/h	Wt. fraction	Kmol/h	Mol fraction
Acetone	1126	0.438	19.4	0.243
Acetic Acid	155	0.060	2.6	0.033
Acetic Anhydride	103	0.040	1.0	0.013
Ketene	107	0.042	2.5	0.031
Methane	592	0.230	37.0	0.464
Ethene	172	0.067	4.4	0.055
Carbon Monoxide	292	0.114	10.4	0.130
Carbon Dioxide	21	0.008	0.5	0.006
Hydrogen	4	0.002	2	0.025
Total	2572	1.00	79.8	1.00

1 mol of acetic acid and 1 mol of ketene will react to form 1 mol of acetic anhydride

$$\text{Amount of anhydride formed} = \frac{1435}{60} *102 = 2440 \text{ kg/h Acetic Anhydride}$$

Total anhydride flow = 2440+1195 = 3635 kg/h

Condensate:

	Kg/h	Wt. fraction	Kmol/h	Mol fraction
Acetone	5454	0.600	94.0	0.725
Acetic Anhydride	3635	0.400	35.6	0.275
Total	9089	1.000	129.6	1.000

AD.5   Absorption Column

	Gas Out from condenser, kg/h	Wt. Fraction	Molar flowrate, kmol/h	Mol. Fraction
Acetone	1126	0.438	19.4	0.243
Acetic Acid	155	0.060	2.6	0.032
Acetic Anhydride	103	0.040	1.0	0.013
Ketene	107	0.042	2.5	0.032
Methane	592	0.230	37.0	0.463
Ethene	172	0.066	4.4	0.055
Carbon Monoxide	292	0.114	10.4	0.131
Carbon Dioxide	21	0.008	.5	0.006
Hydrogen	4	0.002	2	0.025
Total	2572	1.000	79.9	1.000

The uncondensed gas from the condenser is sent to an absorption column where it is absorbed in acetic acid in order to gain maximum acetic anhydride production from the available ketene. The other main purpose of the acetic acid column is to recover the unabsorbed acetone for purification and recycle to the reactor.

From the mass balance it can be seen that the amount of acetone present in the gas stream far exceeds that of the ketene (1126 kg/h acetone as opposed to 107 kg/h ketene). This would suggest that the most appropriate course of action would be to design a packed column for recovery of the acetone, and to assume total recovery (and subsequent reaction) of the ketene.

From Ghmeling and Onken [15] for the system acetone-acetic acid:

$A_{12} = -0.4876$

$A_{21} = -0.5102$

$$\ln \gamma_1 = A_{12}\left(\frac{A_{21}x_2}{A_{21}x_2 + A_{12}x_1}\right)^2$$

Where the subscript 1 refers to acetone, and 2 refers to acetic acid.

At the top of the column the feed is pure acetic acid, so $x_1 = 0$ and $x_2 = 1$, so the activity coefficient

$\gamma_1 = 0.614$

The concentration of acetone at the bottom of the column is unknown at this stage, so for a first

assumption it will be set to 0.3%

$$\ln \gamma_1 = -0.4876\left(\frac{-0.5102*0.7}{(-0.5102*0.7)+(-0.4876*0.3)}\right)^2 = -0.246$$

$\gamma_1 = 0.782$

$$y = \frac{\gamma_1 P^o}{P}x$$

Where P^o = Vapour pressure of acetone at liquor exit temperature

P = Total pressure, $= 1.01*10^5$ Nm^{-2}

y = Mol. fraction of acetone in entering gas = 0.243

x = Mol. fraction of acetone in liquor that would be in equilibrium with the gas.

Making the assumption that the liquor exits at 50°C, $P^o = 81343$ Nm^{-2}

$x_e = 0.386$

$$\left(\frac{L}{G}\right)_m = \frac{y_1 - y_2}{x_e - x_2}$$

If the column is designed for 99% w/w recovery of the acetone, then there will be 11.26 kg/h of

acetone in the outlet stream. With total removal of the ketene, and assuming no absorption of the acid

or anhydride in the gas stream the composition of acetone in the outlet gas stream, $y_2 = 0.003$. And

since the acid to the column is fresh feed, $x_2 = 0$.

$$\left(\frac{L}{G}\right)_m = \frac{0.243 - 0.003}{0.386} = 0.622$$

If the actual liquid flowrate is 1.4 times the minimum value, then

$$\left(\frac{L}{G}\right) = 1.4 * 0.622 = 0.871$$

And at this value $x_1 = \dfrac{0.243 - 0.003}{0.871} = 0.276$

Column Height

$$\frac{y_1}{y_2} = \frac{0.243}{0.003} = 81$$

$$m = \frac{\gamma P^o}{P} = \frac{0.782 * 81343}{1.01 * 10^5} = 0.630$$

$$\frac{mG}{L} = 0.63 * \frac{1}{0.871} = 0.72$$

From Fig. 7 $N_{OG} = 11.5$

Assuming the use of 2 inch rings, From REF HTU = 0.8m

Z = 11.5*0.8 = 9.2m

Column Diameter

With 2-inch rings, 3/16 inch thickness from [40] the economic gas rate, G = 2800 m³/m²h

Correction factor

$\rho_{air} = 1.18$ kg/m³

$$\rho_{gas} = \frac{32.34 * 1.01 * 10^5}{8.314 * 323} = 1.22 \, \text{kg/m}^3$$

$$\text{Economic Gas rate} = 2800 * \left(\frac{1.18}{1.22}\right)^{0.33} = 2769 \, \text{m}^3/\text{m}^2\text{h}$$

Gas flowrate = 79.9 kmol/h

$$\text{Molar volume, V} = \frac{8.314 * 323}{1.01 * 10^5} = 26.59 \, \text{m}^3/\text{kmol}$$

Gas rate = 79.9*26.59 = 2125 m³/h

$$\text{Area, A} = \frac{2125}{2769} = 0.767 \, \text{m}^2$$

Diameter, d = 0.99m, say 1.00m

Actual gas rate, $G = \dfrac{4 * 2125}{\pi * 1^2} = 2706\,\text{m}^3/\text{m}^2\text{h}$

Mass Balance

	Kg/h	Wt. fraction	Kmol/h	Mol fraction
Acetone	11	0.008	0.2	0.003
Acetic Acid	155	0.115	2.6	0.045
Acetic Anhydride	103	0.076	1.0	0.017
Methane	592	0.439	37.0	0.637
Ethene	172	0.127	4.4	0.076
Carbon Monoxide	292	0.216	10.4	0.179
Carbon Dioxide	21	0.016	0.5	0.009
Hydrogen	4	0.003	2	0.034
Total	1350	1.000	58.1	1.00

Absorbed Liquor

107 kg/h of ketene, therefore (107/42)*102 = 260 kg/h of acetic anhydride will be formed

L = 0.871*79.8 = 69.5

Liquid Out

	Kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	1115	0.263	19.2	0.276
Acetic Acid	2868	0.676	47.8	0.688
Acetic Anhydride	260	0.061	2.5	0.036
Total	4243	1.00	69.5	1.00

The amount of acetic acid used in the reaction with ketene is (107/42)*60 = 153 kg. Therefore the flowrate of acetic acid into the column is 2868+153 = 3021 kg.

Inventory

Height = 9.2m, diameter = 1.00m

Voidage fraction = 0.79

Liquid Hold-up

$$H_{OW} = 0.143\left(\frac{L'}{d}\right)^{0.6}$$

L' = 4243/0.785*3600 = 1.50 kg/m²s

$$H_{OW} = 0.143\left(\frac{1.5}{50}\right)^{0.6} = 0.017$$

Liquid Inventory $= \frac{\pi}{4}*1^2 *9.2 * 0.017 = 0.123\,m^3$

First half inventory (acetic acid) = 1041.3*0.123/2 = 64.0 kg

Second half inventory = 1133*0.123/2 = 69.7 kg

Liquid Inventory

	First section, kg	Second section, kg	Total, kg
Acetone		18.4	18.4
Acetic Acid	64.0	47.1	111.1
Acetic Anhydride		4.2	4.2
Total, kg	64.0	69.7	133.7

Gas Inventory $= \frac{\pi}{4}*1^2 * 9.2 * 0.79 = 5.708\,m^3$

Gas out, $\rho = 0.806$ kg/m³

Gas out Inventory = 0.806*5.708/2 = 2.3 kg

Gas In, $\rho = 1.119$ kg/m³

Gas In inventory = 1.119*5.708/2 = 3.2 kg

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Gas Inventory

	First section, kg	Second section, kg	**Total, kg**
Acetone	1.4	0.0	1.4
Acetic Acid	0.2	0.3	0.5
Acetic Anhydride	0.1	0.2	0.3
Ketene	0.1	0.0	0.1
Methane	0.8	1.0	1.8
Ethene	0.2	0.3	0.5
Carbon Monoxide	0.4	0.5	0.9
Carbon Dioxide	0.0	0.0	Negligible
Hydrogen	0.0	0.0	Negligible
Total	3.2	2.3	**5.5**

AD.6 Hold-up Tank

The liquid flow from the condenser and the absorber is combined before being passed to two distillation columns. The first distillation column will remove acetone, which will be recycled back to the reactor. The second column is the anhydride recovery column, from which will come the final product. The flows from the condenser and absorber are combined in a hold-up tank.

Flows into Hold-up tank

	From Condenser, kg/h	From Absorber, kg/h	**Total, kg/h**
Acetone	5454	1115	6569
Acetic Acid		2868	2868
Acetic Anhydride	3636	260	3896
Total	9090	4243	13333

AD.7   Acetone Recovery

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	6569	0.493	113.3	0.568
Acetic Acid	2868	0.215	47.8	0.240
Acetic Anhydride	3896	0.292	38.2	0.192
Total	13333	1.00	199.3	1.00

For the purposes of estimation of column size, the acetic acid and acetic anhydride will be considered to be one material. The ratio of acid to anhydride in the feed, distillate and bottoms will be constant.

$x_f = 0.568$

Assuming $x_d = 0.99$, $x_b = 0.01$

Mass balance on acetone $113.3 = 0.99D + 0.01B$

Mass balance on acid/anhydride $86 = 0.01D + 0.99B$

Solving gives:

$D = 113.6$ kmol/h

$B = 85.7$ kmol/h

Distillate Flow

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	6523	0.987	112.5	0.990
Acetic Acid	37	0.005	0.6	0.005
Acetic Anhydride	51	0.008	0.5	0.005
Total	6611	1.00	113.6	1.00

Bottoms Product

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	46	0.007	0.8	0.009
Acetic Acid	2831	0.421	47.2	0.551
Acetic Anhydride	3845	0.572	37.7	0.440
Total	6722	1.00	85.7	1.00

The top of the column is at a temperature of 56.5°C. The bottom temperature will be assumed to be an

average of the boiling points of acetic acid and acetic anhydride, 129°C.

At the top of the column, $P^o_{acetone} = 102066$ Nm^{-2}

$P^o_{acid} = 10168$ Nm^{-2}

$P^o_{anhydride} = 4017$ Nm^{-2}

Vapour pressure of acid/anhydride mixture = 7342 Nm^{-2}

$\alpha_{56.5} = 102066/7342 = 13.90$

At the bottom of the column $P^o_{acetone} = 741631$ Nm^{-2}

$P^o_{acid} = 139933$ Nm^{-2}

$P^o_{anhydride} = 73341$ Nm^{-2}

Vapour pressure of acid/anhydride mixture = 110354 Nm^{-2}

$\alpha_{129} = 741631/110354 = 6.72$

$\alpha_{av} = \sqrt{\alpha_{56.5} * \alpha_{129}} = \sqrt{13.9 * 6.72} = 9.66$

$$R_m = \frac{1}{(\alpha - 1)x_f} = \frac{1}{8.66 * 0.568} = 0.203$$

$R = 1.3R_m = 0.264$

From Fig.1, $N_m = 5$

$$\frac{R}{R+1} = 0.21, \qquad \frac{R_m}{R_m + 1} = 0.17$$

From Fig.2, $\dfrac{N_m}{N} = 0.2$

$N = 25$

Given 70% efficiency, therefore the total number of trays = 36

If one plate is the reboiler/condenser, then

Height = 35*0.5 = 17.5 m

Calculation of Tower Diameter

Density of distillate vapour, $\rho_{D(v)} = \dfrac{58 * 1.01 * 10^5}{8.314 * 329.5} = 2.138$ kg/m^3 = 0.134 lb/ft^3

Density of distillate liquid, $\rho_{D(l)} = 1313$ kg/m^3 = 82.676 lb/ft^3

$$G = 600\left[\rho_v\left(\rho_l - \rho_v\right)\right]^{0.5} = 1995 \text{ lb/ft}^2\text{h}$$

$$d = \left[\frac{D(R+1)}{0.785G}\right]^{0.5} = \left[\left(\frac{6611*2.2*1.264}{0.785*1955}\right)\right]^{0.5} = 3.46 \text{ ft} = 1.05\text{m}$$

Inventory

Feed point location $\log\dfrac{N_r}{N_s} = 0.206\log\left[\left(\dfrac{B}{D}\right)\left(\dfrac{x_{f,hk}}{x_{f,lk}}\right)\left(\dfrac{x_{b,lk}}{x_{d,hk}}\right)^2\right]$

$$\log\frac{N_r}{N_s} = 0.206\log\left[\left(\frac{85.7}{113.6}\right)\left(\frac{0.192}{0.568}\right)\left(\frac{0.09}{0.05}\right)^2\right]$$

$\dfrac{N_r}{N_s} = 0.96$

$N_r + N_s = 35$

$N_s = 18$

$N_r = 17$

Top product liquid inventory $= 0.044*17*\dfrac{\pi}{4}*1..05^2 = 0.647 \text{ m}^3$

Bottom product liquid inventory (including liquid sump, 8% of total column height)

$$= 0.044*\frac{\pi}{4}*1.05^2*(18+35) = 2.019 \text{ m}^3$$

Vapour Inventory = Inventory on top plates + Inventory on Bottom Plates + Inventory in Disengagement Space

$$v_B + v_D + 0.044\frac{\pi}{4}Nd^2 = 0.50\frac{\pi}{4}Nd^2$$

and $\dfrac{v_B}{v_D} = \dfrac{18}{17} = 1.06$

Solving these equations

$v_D = 6.709 \text{ m}^3$

$v_B = 7.111 \text{ m}^3$

Bottom product vapour inventory = 7.111 m^3

Top product vapour inventory = $v_D + 0.044 \frac{\pi}{4} N d^2 = 8.042 \text{ m}^3$

Top Product Liquid Inventory, at 56.5°C

$\rho_D = 1313 \text{ kg/m}^3$

Mass Inventory = 0.647*1313 = 849.5 kg

Top Product Vapour Inventory

$\rho_{Acetone} = 2.138 \text{ kg/m}^3$

$\rho_{Acid} = 2.212 \text{ kg/m}^3$

$\rho_{Anhydride} = 3.761 \text{ kg/m}^3$

$\rho_{D(Vapour)} = (0.987*2.138)+(0.005*2.212) + (0.008*3.761) = 2.151 \text{ kg/m}^3$

Mass Inventory = 8.042*2.151 = 17.3 kg

Bottom Product Liquid Inventory, at 129°C

$\rho_B = 935 \text{ kg/m}^3$

Mass Inventory = 2.019*935 = 1887.8 kg/h

Bottom Product Vapour Inventory

$\rho_{Acetone} = 1.753 \text{ kg/m}^3$

$\rho_{Acid} = 1.813 \text{ kg/m}^3$

$\rho_{Anhydride} = 3.082 \text{ kg/m}^3$

$\rho_{B(Vapour)} = (0.007*1.753) + (0.421*1.813) + (0.572*3.082) = 2.538 \text{ kg/m}^3$

Bottom product vapour inventory = 2.538*7.111= 18.0 kg.

Liquid Inventory

	Top section, kg	Bottom section, kg	**Total, kg**
Acetone	838.5	13.2	851.7
Acetic Acid	4.2	794.8	799.0
Acetic Anhydride	6.8	1079.8	1086.6
Total, kg	849.5	1887.8	2737.3

Gas Inventory

	Top section, kg	Bottom section, kg	Total, kg
Acetone	17.1	0.1	17.2
Acetic Acid	0.1	7.6	7.7
Acetic Anhydride	0.1	10.3	10.4
Total, kg	**17.3**	**18.0**	**35.3**

AD.8   Anhydride Purification

The bottoms product from the acetone recovery column is sent to acetic anhydride purification, where the acetic anhydride will be taken off as bottom product. However, some of this will be recycled back to the quench system, to replace the acid and anhydride lost as vapour from the quench column. From the mass balance on that unit it can be seen that 1298 kg/h anhydride and 1590 kg/h acid must be recycled. The flow of bottoms product from the acetone will therefore be split, recycling 1298 kg/h of anhydride and a portion of the acid. Fresh acid will then be added to this stream to make-up the 1590 kg/h required.

Bottoms Product from Acetone recovery

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	46	0.007	0.8	0.009
Acetic Acid	2831	0.421	47.2	0.551
Acetic Anhydride	3845	0.572	37.7	0.440
Total	**6722**	**1.00**	**85.7**	**1.00**

If this stream is split to obtain 1298 kg/h, then the amount of acetic acid that we be split will be (2831/3845)*1298 = 956 kg/h. Also, 16 kg/h acetone will be recycled back to quench.

	From acetone recovery, kg	To quench, kg	To anhydride purification, kg
Acetone	46	16	30
Acetic Acid	2831	956	1875
Acetic Anhydride	3845	1298	2547
Total	6722	2270	4452

634 kg/h of pure acid must be added to the quench stream as make-up.

Column design

Flow In

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	30	0.007	0.5	0.009
Acetic Acid	1875	0.421	31.3	0.551
Acetic Anhydride	2547	0.572	25.0	0.440
Total	4452	1.00	56.8	1.00

The product is to be of 95% w/w purity. Therefore, the purity of the bottoms product in terms of molar

percentage is $\dfrac{95/102}{(95/102)+(5/60)} = 92\%$

With respect to the acid, therefore $x_f = 0.551$

$x_D = 0.99$

$x_B = 0.08$

Mass balance on acid $31.3 = 0.99D + 0.08B$

Mass balance on anhydride $25.0 = (1-0.99-(0.5/D))D+0.92B$

Solving gives $D = 29.4$ kmol/h, $B = 27.4$ kmol/h

Distillate

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetone	30	0.016	0.5	0.016
Acetic Acid	1755	0.932	29.3	0.951
Acetic Anhydride	99	0.052	1.0	0.033
Total	1884	1.00	30.8	1.00

Bottoms Product

	kg/h	Wt. fraction	Kmol/h	Mol. fraction
Acetic Acid	120	0.047	2.0	0.077
Acetic Anhydride	2448	0.953	24.0	0.923
Total	2568	1.00	26.0	1.000

The top of the column is at a temperature of 118°C, and the bottom temperature is 140°C.

At the top of the column

$P^o_{acid} = 100833$ Nm^{-2}

$P^o_{anhydride} = 51335$ Nm^{-2}

$\alpha_{118} = 1.964$

At the base

$P^o_{acid} = 190456$ Nm^{-2}

$P^o_{anhydride} = 102397$ Nm^{-2}

$\alpha_{140} = 1.860$

$\alpha_{av} = 1.911$

$$R_m = \frac{1}{(\alpha-1)x_f} = \frac{1}{0.911*0.551} = 1.99$$

$R = 1.3R_m = 1.3*1.99 = 2.59$

From Fig.1, $N_m = 9$

$$\frac{R}{R+1} = 0.72, \qquad \frac{R_m}{R_m+1} = 0.67$$

From Fig.2 , $\dfrac{N_m}{N} = 0.48$

N = 18.75

Given 70% efficiency, therefore the total number of trays = 27

Number of plates in the column = 26

With 0.5m plate spacing Z = 26*0.5 = 13m

Column diameter

Density of distillate vapour, $\rho_{D(V)}$ = 1.900 kg/m³ = 0.119 lb/ft³

Density of distillate liquid, $\rho_{D(L)}$ = 943 kg/m³ = 59.032 lb/ft³

$$G = 600\left[\rho_v\left(\rho_l - \rho_v\right)\right]^{0.5} = 600\left[0.119\left(59.032 - 0.119\right)\right]^{0.5} = 1589 \text{ lb/ft}^2\text{h}$$

$$d = \left[\frac{D(R+1)}{0.785G}\right]^{0.5} = \left[\frac{1884*2.2*3.59}{0.785*1589}\right]^{0.5} = 3.45 \text{ ft} = 1.04, \text{ say } 1.05\text{m}$$

Inventory

Feed point location $\log\dfrac{N_r}{N_s} = 0.206\log\left[\left(\dfrac{B}{D}\right)\left(\dfrac{x_{f,hk}}{x_{f,lk}}\right)\left(\dfrac{x_{b,lk}}{x_{d,hk}}\right)^2\right]$

$$\log\frac{N_r}{N_s} = 0.206\log\left[\left(\frac{26.0}{30.8}\right)\left(\frac{0.440}{0.551}\right)\left(\frac{0.077}{0.033}\right)^2\right]$$

$\dfrac{N_r}{N_s} = 1.3$

$N_r + N_s = 26$

$N_s = 11$

$N_r = 15$

Top product liquid inventory = $0.044*15*\dfrac{\pi}{4}*1.05^2 = 0.571\text{m}^3$

Bottom product liquid inventory (including liquid sump, 8% of total column height)

$$= 0.044*\frac{\pi}{4}*1.05^2(11+26) = 1.410\,\text{m}^3$$

Vapour Inventory = Inventory on top plates + Inventory on Bottom Plates + Inventory in

Disengagement Space

$$v_B + v_D + 0.044 \frac{\pi}{4} Nd^2 = 0.50 \frac{\pi}{4} Nd^2$$

and $\dfrac{v_B}{v_D} = \dfrac{11}{15} = 0.733$

Solving these equations

$v_D = 5.924 \, \text{m}^3$

$v_B = 4.342 \, \text{m}^3$

Bottom product vapour inventory = 4.342 m³

Top product vapour inventory = $v_D + 0.044 \dfrac{\pi}{4} Nd^2 = 6.915 \, \text{m}^3$

Top Product Liquid Inventory, at 118°C

$\rho_D = 943 \, \text{kg/m}^3$

Mass Inventory = 0.571*943 = 538.5 kg

Top Product Vapour Inventory

$\rho_{Acetone} = 1.802 \, \text{kg/m}^3$

$\rho_{Acid} = 1.864 \, \text{kg/m}^3$

$\rho_{Anhydride} = 3.169 \, \text{kg/m}^3$

$\rho_{D(Vapour)} = (0.007*1.802) + (0.421*1.864) + (0.572*3.169) = 2.610 \, \text{kg/m}^3$

Mass Inventory = 6.915*2.610 = 18.0 kg

Bottom Product Liquid Inventory, at 140°C

$\rho_B = 923 \, \text{kg/m}^3$

Mass Inventory = 1.41*923 = 1301.4 kg/h

Bottom Product Vapour Inventory

$\rho_{Acid} = 1.765 \, \text{kg/m}^3$

$\rho_{Anhydride} = 3.000 \, \text{kg/m}^3$

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$$\rho_{B(Vapour)} = (0.421*1.765) + (0.597*3.000) = 2.534 \text{ kg/m}^3$$

Bottom product vapour inventory = 4.342*2.534 = 11.0 kg

Liquid Inventory

	Top section, kg	Bottom section, kg	**Total, kg**
Acetone	8.6		8.6
Acetic Acid	501.9	61.2	563.1
Acetic Anhydride	28.0	1240.2	1268.2
Total	538.5	1301.4	**1839.9**

Gas Inventory

	Top section, kg	Bottom section, kg	**Total, kg**
Acetone	0.3		0.3
Acetic Acid	16.8	0.5	17.3
Acetic Anhydride	0.9	10.5	11.4
Total	18.0	11.0	**29.0**