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An Investigation into the Gasification of Coals, Coal Macerals and Chars at High Pressure

by

Stuart Maxwell

A Doctoral Thesis submitted in partial fulfilment of the requirements for the
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Abstract

A suite of coals covering a range of properties was gasified in a pressurised thermogravimetric analyser (p.t.g.a.) at 950°C and 2.5 MPa. The reactivities of the coals to steam were measured to determine any relationships between coal properties and reactivity. Some of the coals were pre-pyrolised to produce chars, and the reactivity of these chars was measured both in steam and CO₂. The results show that no simple relationships exist but trends can be shown whereby reactivity increases with decreasing carbon content, increasing volatile matter and decreasing mean vitrinite reflectance. Coal minerals, notably CaO also increased reactivity to some extent in coals of low carbon content, yet carbon content itself influenced reactivity more than mineral content. The effect of pre- pyrolysis of the coals on reactivity appears to be dependant on coal rank, with higher rank coals (carbon content above 83%) showing an increase in reactivity whereas lower rank coals show a marked decrease.

The reactivity of two chars in various mixtures of H₂O/H₂ and CO₂/CO was measured. The effects of H₂ and CO were to inhibit the gasification reactions in steam and CO₂. H₂ appeared not only to inhibit the rate of reaction but also to prevent full carbon conversion being achieved. This may also be true for CO, though it is less clear from the results.

Maceral concentrates were derived from some of the coals using a density separation technique and the gasification behaviour of these was also studied using the p.t.g.a. at 950°C and 2.5MPa.. Both CO₂ and steam were used as gasifying agents. Some of the maceral concentrates were pre-pyrolised in a fluidised bed reactor (f.b.r.) to produce chars, which were also studied under similar conditions. The success of the maceral separation technique was limited, making interpretation of the results difficult. Vitrinites appeared to be the most reactive fractions

although there were clear differences between vitrinites from different coals. Inertinites were the least reactive fractions, with liptinites being of intermediate reactivity. There were differences between the liptinites and inertinites from different coals, though these were less marked than for the vitrinites.. Pre-pyrolysis of the samples in the f.b.r. decreased the reactivity of the vitrinite significantly in most cases, whilst the reactivity of the other fractions was affected much less. The results obtained in this study suggest that a maceral analysis by itself would be of little use as a predictive tool for gasification reactivity, however, more work would need to be carried out in order to prove this.

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Chapter 1

Introduction

1.1 Background

The future of coal as a fuel for power generation depends, to some degree, on the extent to which power generation techniques can be improved. British Coal's Coal Technology Development Division (CTDD) spent many years developing an advanced power generation system known as the Air Blown Gasification Cycle (ABGC).⁽¹⁾ It was expected that compared with conventional methods of electricity generation from coal, the ABGC would offer improved efficiency and be less environmentally damaging.

An important aspect of the development of such a system is the use of mathematical modelling of the chemical and physical processes involved. Such models may be used to predict gasifier performance and optimal operating conditions and to provide design information for scale up. In order to develop suitable models, fundamental information on the behaviour of coals during gasification must be gathered.

Previous work ⁽²⁾ has already studied the effect of gasification and pyrolysis conditions on a single coal. The purpose of the current study is to compare the gasification behaviour of a range of different coals, having differing compositions and properties, in

order to attempt to relate the gasification performance to these properties. The range of coals chosen for study also have differing maceral compositions and it is hoped that maceral concentrates can be separated out from the coals, so that the influence of the different macerals can be studied. From this work it should be possible to determine whether or not gasification performance can be reliably predicted from maceral analysis.

1.2 Power Generation

1.2.1 Conventional Power Generation

The majority of coal fired power stations operate by the combustion of pulverised fuel (PF). This is usually bituminous coal which is ground to a particle size of approximately 70-80%-75 μ m. The PF is used to fuel large water tube boilers to produce steam which is fed through a steam turbine to generate electricity. PF firing has been widely adopted for a number of reasons. These include the suitability of the coal feeding and firing methods for use with large boilers, the strongly radiating flame produced by the combustion of a cloud of coal particles, and the suitability of the technique for use with caking and swelling coals which could not be burnt on a grate. Subcritical steam conditions (typically 16 MPa steam pressure and 538°C or 566°C steam temperature) are well suited to coal fired power stations in the range of about 300-600 MW output. A diagram of such a power station is given in Figure 1.1. Smaller units use lower pressure. The overall efficiency of subcritical plant is about 38% at best, but this can be improved to about 45% by using supercritical steam conditions (see section 1.2.2.1).

1.2.2 Advanced Power Generation

There is growing worldwide interest in the so called Advanced Power Generation systems by which electricity may be generated more efficiently and with less environmental impact.⁽³⁾ Numerous systems are currently under consideration and at different stages of development. Advanced power generation systems include the following examples.

1.2.2.1 Supercritical Pulverised Fuel Firing

This is the most established of the advanced power generation techniques with several high pressure and high temperature units of relatively small capacity being constructed in the 1950s and 1960s. Supercritical steam conditions have been applied to larger power plants in Europe, Japan and the United States for more than twenty five years. In the early 1980's, following the oil crisis, and the introduction of new environmental legislation, further impetus was gained for the development of these systems. They are now very reliable, typically 2-5% more efficient than standard plants. Typical supercritical steam conditions are 24 MPa steam pressure and 538°C or 566°C steam temperature. Recent improvements in materials and designs allow commercial plants to apply even higher steam temperatures (593°C or 600°C) using ferrite steels to improve efficiency another 2-5%. With the use of ultra supercritical double reheat steam conditions (35 bar and 600°C) and other improvements such as higher feedwater temperature, waste heat recovery devices and improved turbine design, net thermal

efficiencies of 46-47% are possible. In the future, with the development of more sophisticated materials, it is hoped to be able to use steam pressures of 37.5 MPa and temperatures of 700°C.

1.2.2.2 Circulating Fluidised Bed Combustion Plant (CFBC)

Here, coal is burnt in a fluidised bed at atmospheric pressure and about 850°C. The off-gases and entrained solids are separated in a high efficiency cyclone. The solids are returned to the bed whilst the gases are cooled in a waste heat boiler. Heat is also extracted from the combustor. These boiler systems produce superheated steam which drives a conventional condensing steam turbine which generates power. NO_x emissions are inherently low and SO₂ emissions may be reduced by the addition of limestone to the coal. Currently there are 160 units in operation or under construction worldwide with a maximum unit size of 200MWe. The units are particularly suitable for use with low or variable quality fuels. A schematic diagram of a CFBC system is given in Figure 1.2.

1.2.2.3 Pressurised Fluidised Bed Combustion (PFBC)

In PFBC systems coal is burnt in a fluidised bed at about 1.2 MPa and 850°C. Off-gases pass via a cyclone to a gas turbine. Exit gases from the turbine are fed to a waste heat boiler. Heat from the waste heat boiler and the combustor heat exchangers is used to produce steam which is used to drive a steam turbine. Again NO_x emissions are inherently low and SO₂ emissions are controlled by the addition of limestone to the bed.

A schematic diagram of a PFBC system is given in Figure 1.3.

1.2.2.4 Integrated Gasification Combined Cycle (IGCC)

In IGCC systems coal is fed to a gasifier which operates at elevated pressure. Here it reacts with oxygen and steam to produce a raw fuel gas. After cleaning the gas is expanded through a gas turbine to generate electricity. The exhaust gas exits via a waste heat boiler, in which steam is raised to drive a steam turbine. In IGCC systems the coal is completely gasified. The principal combustible components of the gas are carbon monoxide and hydrogen. A number of different IGCC systems are currently being developed. The main difference between the systems is the type of gasifier on which they are based. The three main types are entrained, fixed bed and fluidised bed gasifiers. A typical fluidised bed gasifier is illustrated in Figure 1.4 and a fixed bed gasifier is illustrated in Figure 1.5. A schematic diagram of an IGCC system is given in Figure 1.6

1.2.2.5 Topping Cycles

The former British Coal developed the topping cycle process, in which coal is partially gasified, and the gas, after cleaning is expanded through a gas turbine. The residual char is burnt in a combustor and the heat is used to raise steam which drives a steam turbine. Different types of gasifier and combustor may be used which gives rise to a number of system options.

British Coal favoured the option known as the Air Blown Gasification Cycle (ABGC).

Here coal is gasified in an air blown spouted bed gasifier at pressures up to 2.5 MPa and temperatures up to 1000°C. Limestone or dolomite is added to the bed to reduce H₂S levels in the fuel gas. The gas is firstly cleaned in a cyclone and then cooled and passed through a candle filter to remove residual particulate material, before entering the gas turbine. The exhaust gases from the turbine pass to a waste heat boiler and then to atmosphere.

Between 70 and 80 % of the coal is converted into a low calorific fuel gas. The unconverted coal feed is mainly removed as cyclone fines and particles collected by the hot gas filters. Residual gasifier material consisting of char and partly sulphided calcium oxide is removed from the base of the bed and transferred with the fines to a circulating fluidised bed combustor where they are burnt to generate steam.

Such a system is expected to have greater operating flexibility and overall efficiency than any of the other systems discussed earlier. It will also have high sulphur retention efficiency and low emissions of NO_x and particulates. The Air Blown Gasification Cycle system is illustrated in Figure 1.7.

Figure 1.8 shows the efficiency of the different electricity generation processes discussed above, and compares them with conventional power generation systems. It should be noted that conventional power generation systems are rendered less efficient by the retrofitting of Flue Gas Desulphurisation (FGD) equipment. The reduction in efficiency is typically one percentage point, however the inclusion of FGD gives a fairer basis for

comparison with other more environmentally acceptable systems.

1.3 Basic Gasification Processes

The phenomenon of coal gasification was first noted in the late eighteenth century by the Italian priest and scientist, Felice Fontana. His discoveries were confirmed subsequently by the French scientist Antoine Lavoisier. As a result of the discoveries of Fontana and Lavoisier and subsequent research and development by many other scientists and engineers gasification of coal and other solid fuels has become an established part of a number of industrial processes including,

1. Gas production for use in synthesis and reduction processes, for heating purposes and fuel gas (as used in the combined cycle power plants described above).
2. Activation of carbonaceous materials to produce adsorbents.
3. Regeneration of adsorbents and catalysts by the removal of carbon deposits.

Gas may be produced from coal by two basic means. Firstly by pyrolysis, which involves thermal decomposition of the coal in an inert atmosphere to produce gaseous and liquid products (tar) and a solid residue (char). Pyrolysis occurs whenever coal is heated above about 400°C. The second process is gasification itself in which the coal reacts with a gasifying agent such as H₂O or CO₂ to produce gaseous products. The organic components of the coal may be completely converted to gas by this means,

leaving only a residue of ash. In most industrial applications of gasification these two processes will be occurring simultaneously and in order to gain a fuller understanding of the overall process, it is necessary that the influence of each of the two steps is understood.

The main constituent of a coal char is carbon. Therefore the main reactions involved in char gasification may be written as follows

1. $C + H_2O = H_2 + CO$
2. $CO + H_2O = H_2 + CO_2$
3. $CO + 3H_2 = CH_4 + H_2O$
4. $C + 2H_2 = CH_4$
5. $C + O_2 = CO_2$
6. $2C + O_2 = 2CO$
7. $2CO + O_2 = 2CO_2$
8. $C + CO_2 = 2CO$

Reaction 1 is called the heterogeneous water gas reaction. The products of the reaction participate in two further reactions; the homogeneous water gas or water gas shift reaction (2) and the methanation reaction (3). Methane can also be produced by the direct action of hydrogen on carbon (4). The three combustion reactions (5, 6 and 7) must also be considered. They serve as heat generating processes in connection with the heterogeneous water gas reaction which is endothermic. Reaction (8) is the gasification of carbon by CO_2 to form CO. This is often known as the Boudouard reaction. A more

detailed description of the basic processes and reactions is given in the literature review in Chapter Two.

1.4 Objectives of this Work

The objectives of this work are as follows:-

To obtain data on the reactivities of a number of coals to steam and CO₂ at 2.5 Mpa. The coals will be obtained from various countries and will have a range of differing properties. The coals will be fully analysed in order to gain as much knowledge of their composition and properties as possible. By studying the properties in conjunction with the reactivity data it is hoped to be able to show which of the properties influences coal reactivity at high pressure, and which, if any, might be used in order to predict gasification behaviour.

Some of the coals will be selected for separation into their component macerals, and the gasification behaviour of the individual macerals will be studied. From this work it is hoped to show whether or not predictions of gasification behaviour from maceral compositions is viable.

Chars derived from these coals and maceral concentrates will also be studied in order to determine the effect of pre-pyrolysis on reactivity. The inhibiting effect H₂ and CO on reactivity will also be examined

This work will involve using a Pressurised Thermogravimetric Analyser which can measure the reactivity of coals and coal chars under the range of operating conditions (eg temperature, pressure and reactant gas composition) which would be appropriate to the gasifier.

Chapter Two of this thesis contains a review of some of the most important literature published to date on the subject of gasification. Chapter Three gives details of the experimental programme and the equipment used to carry out that programme. Chapter Four gives the results obtained from the experimental programme together with discussion and explanation of those results.

A typical 500MW pulverised coal fired power generation unit

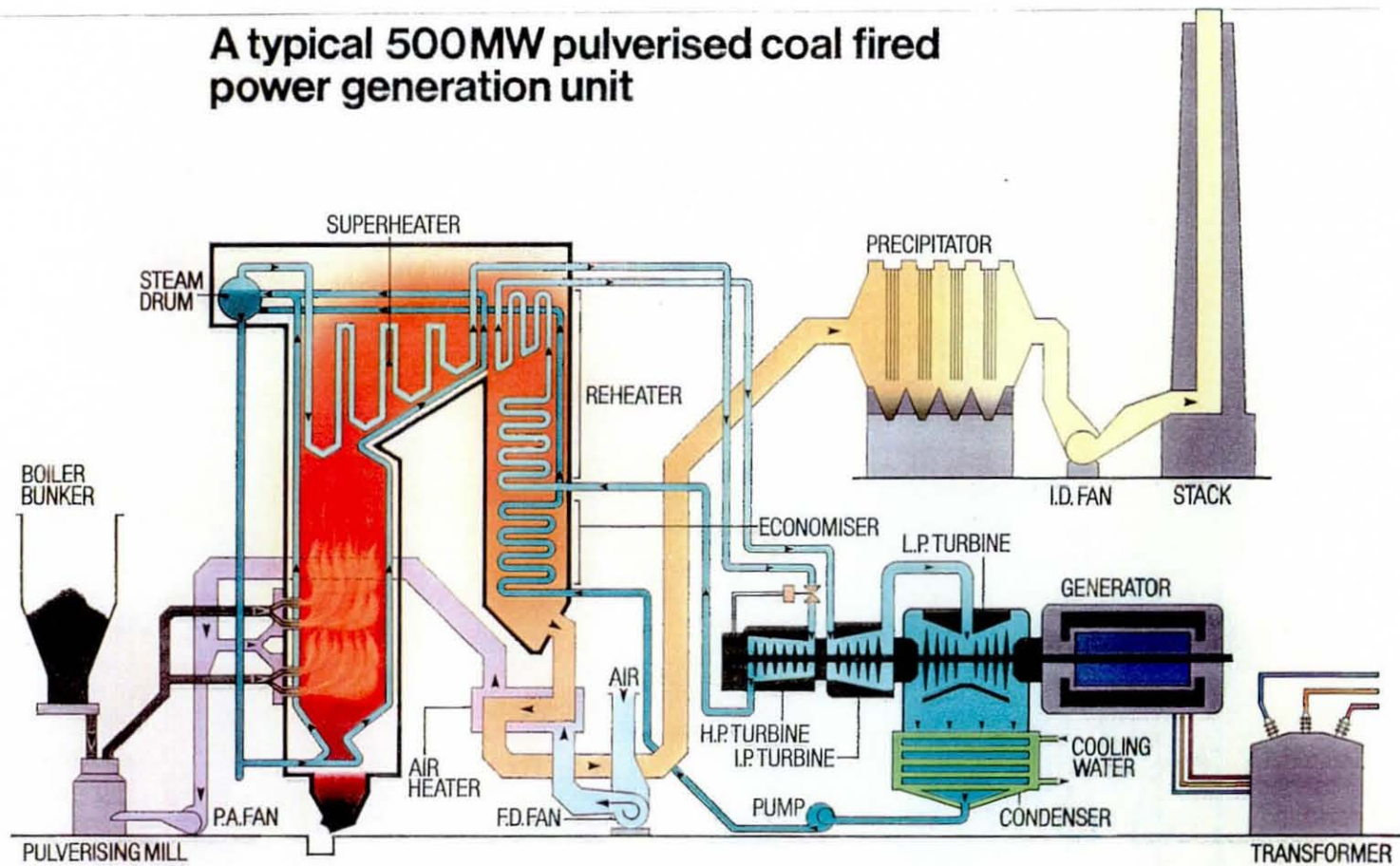


Figure 1.1

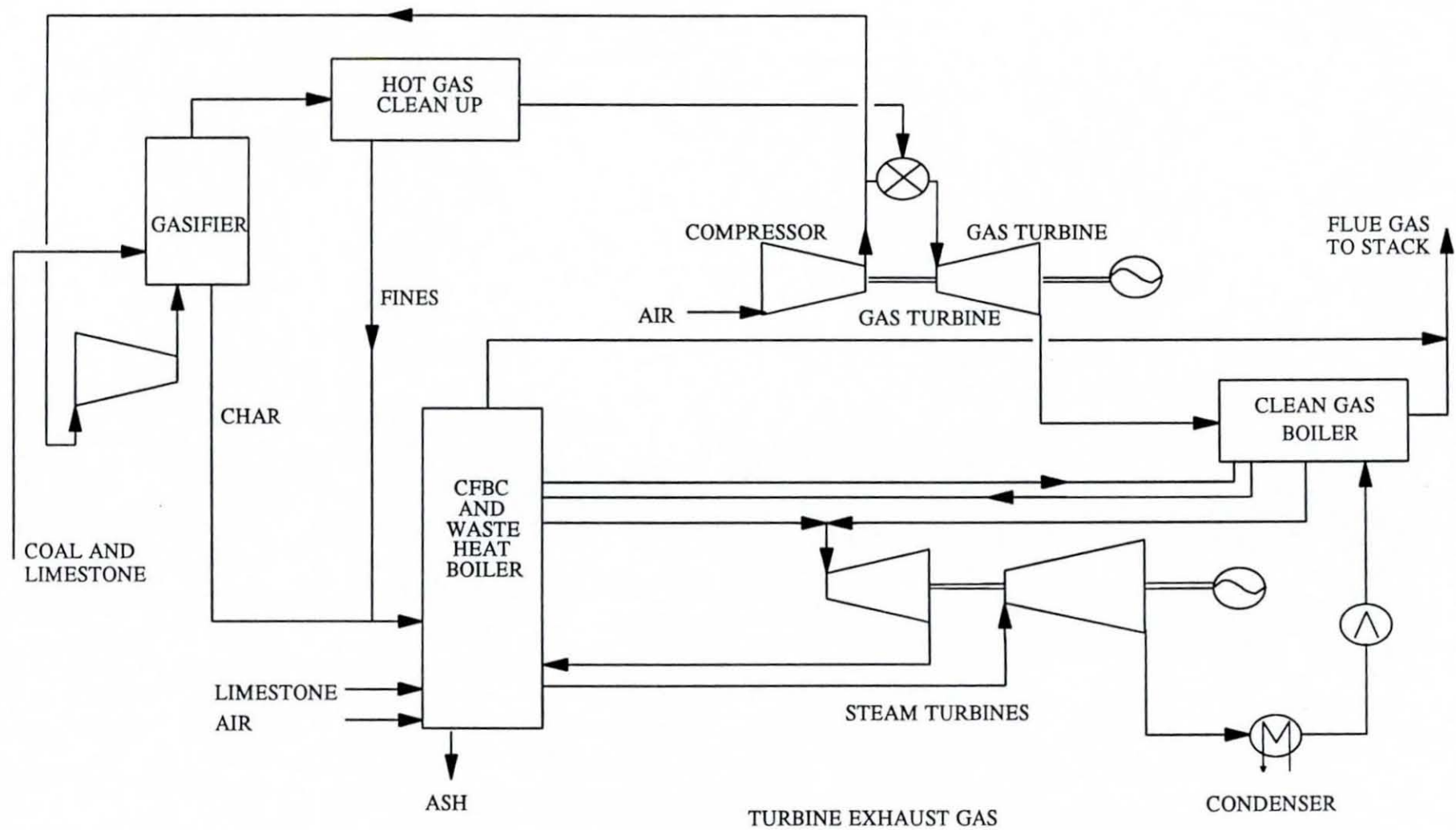


Figure 1.2 CFBC Power Generation System

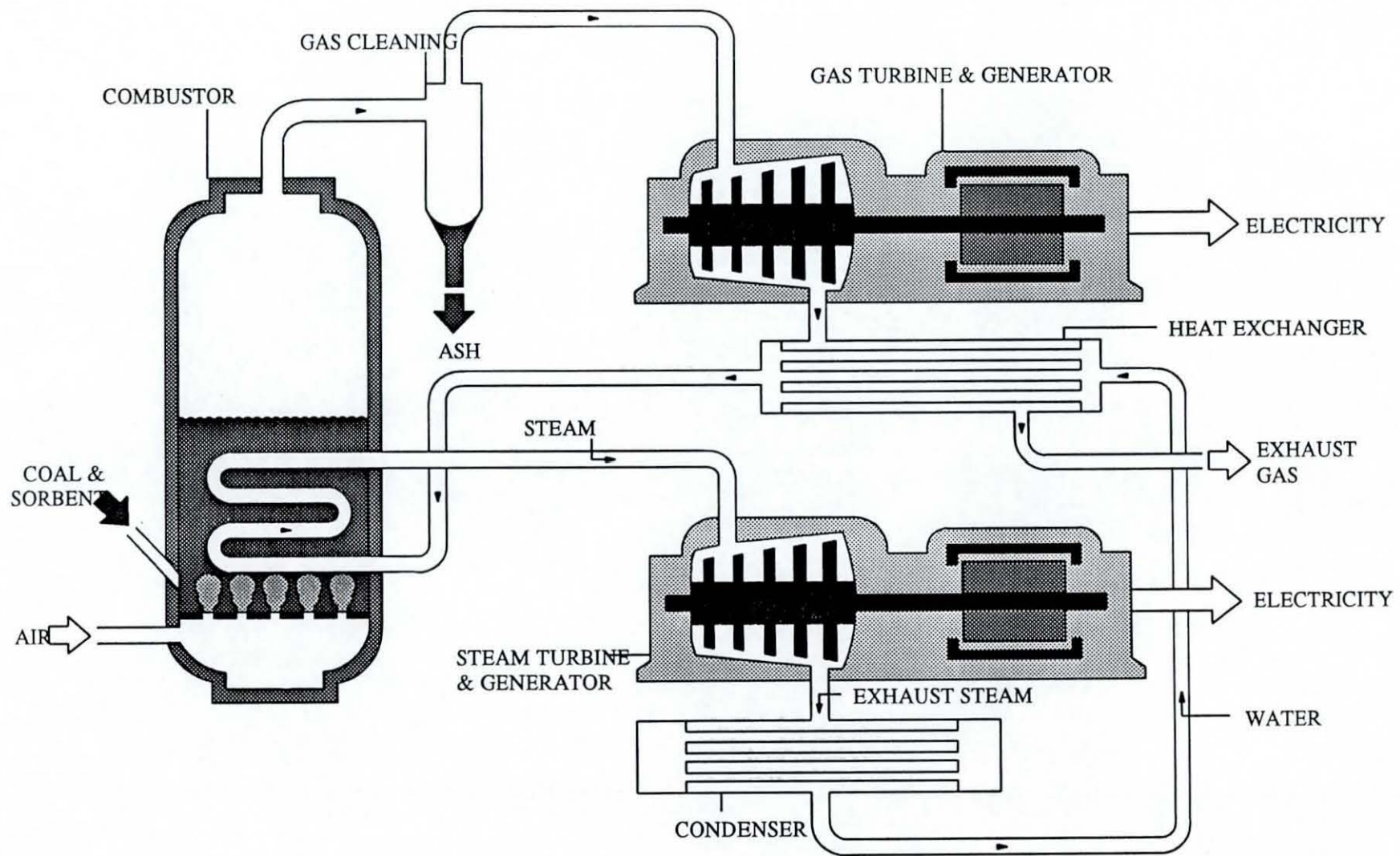


Figure 1.3 PFBC Power Generation System

FB GASIFIER

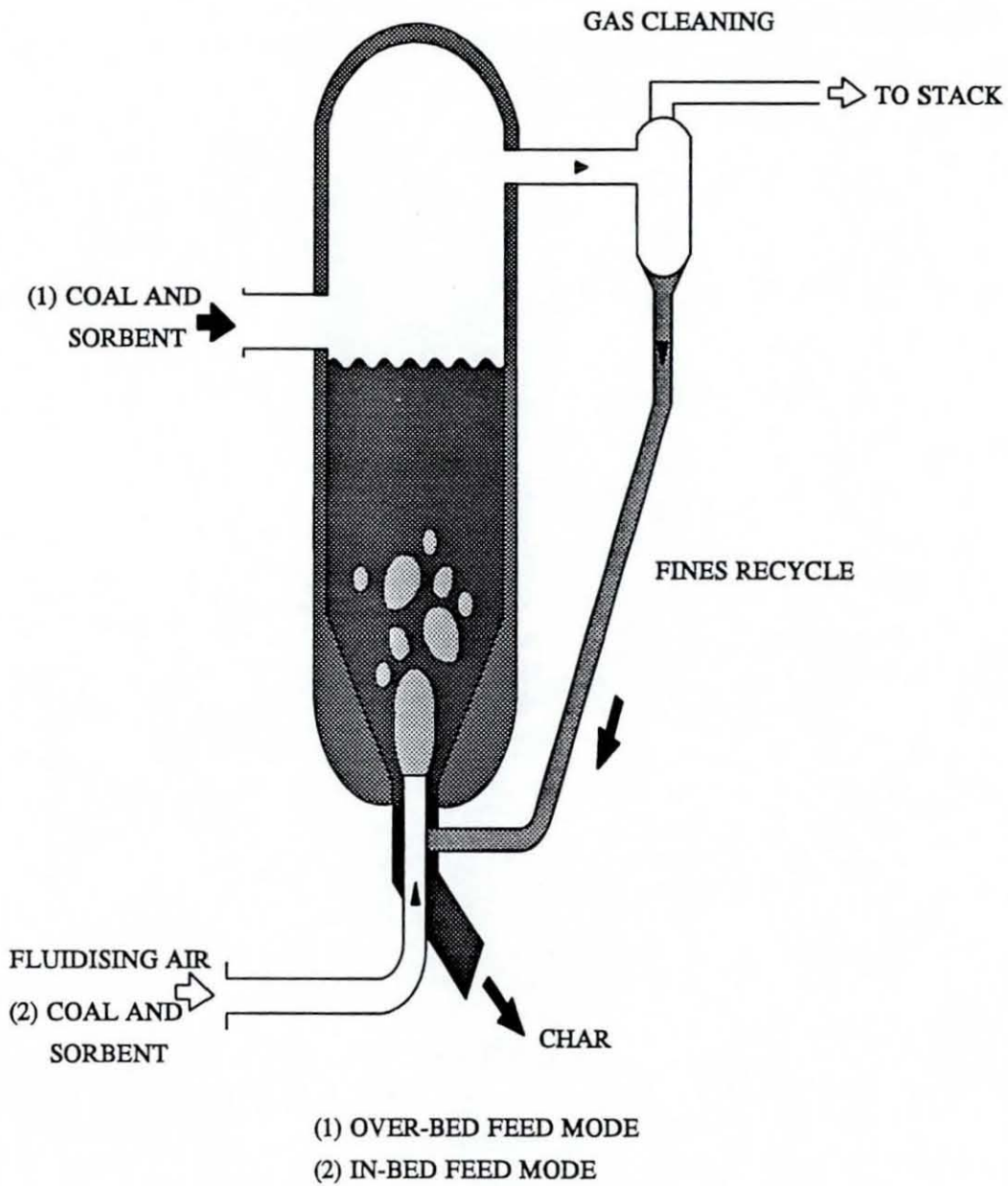


Figure 1.4 Fluidised Bed Gasifier

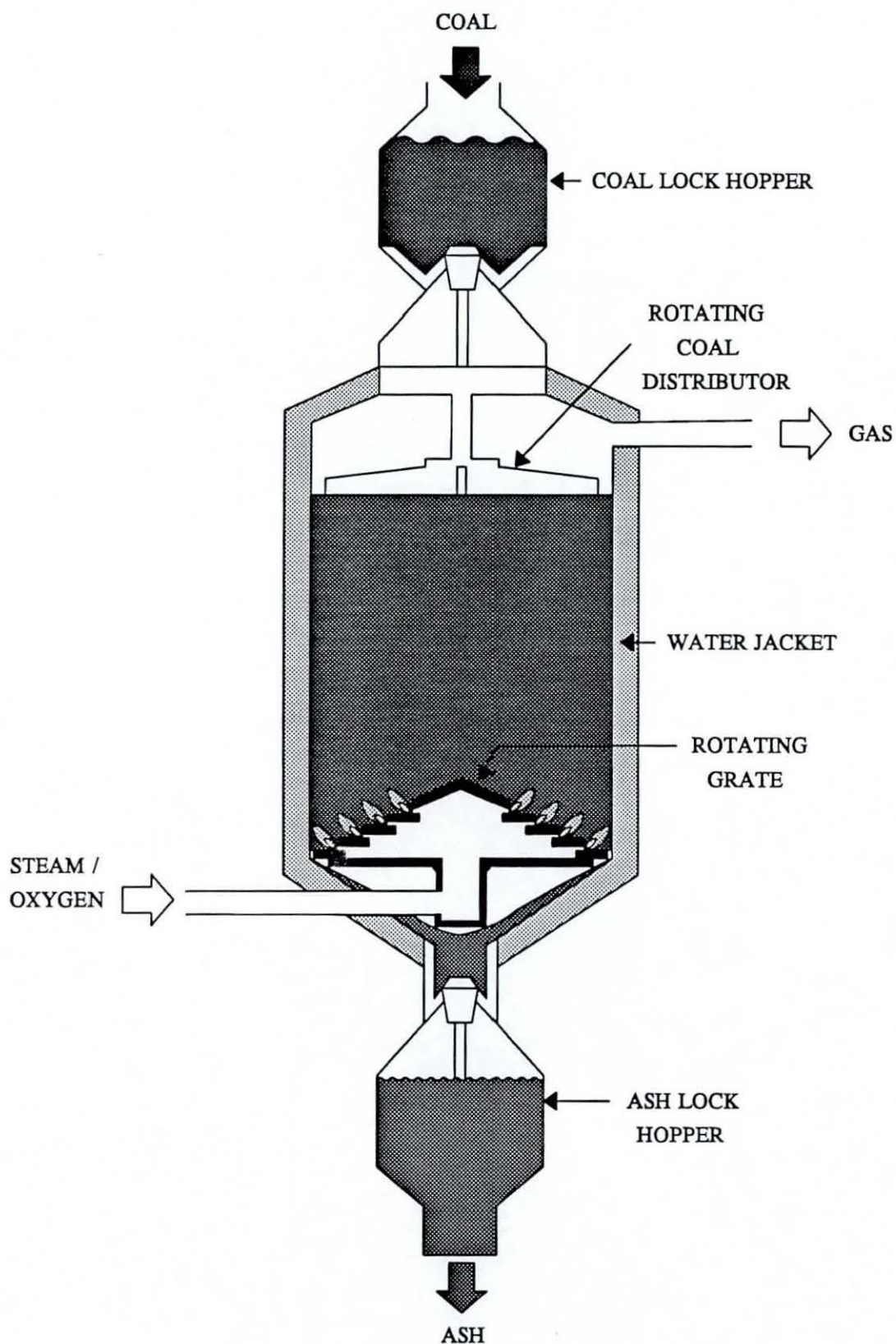


Figure 1.5 Fixed Bed Gasifier

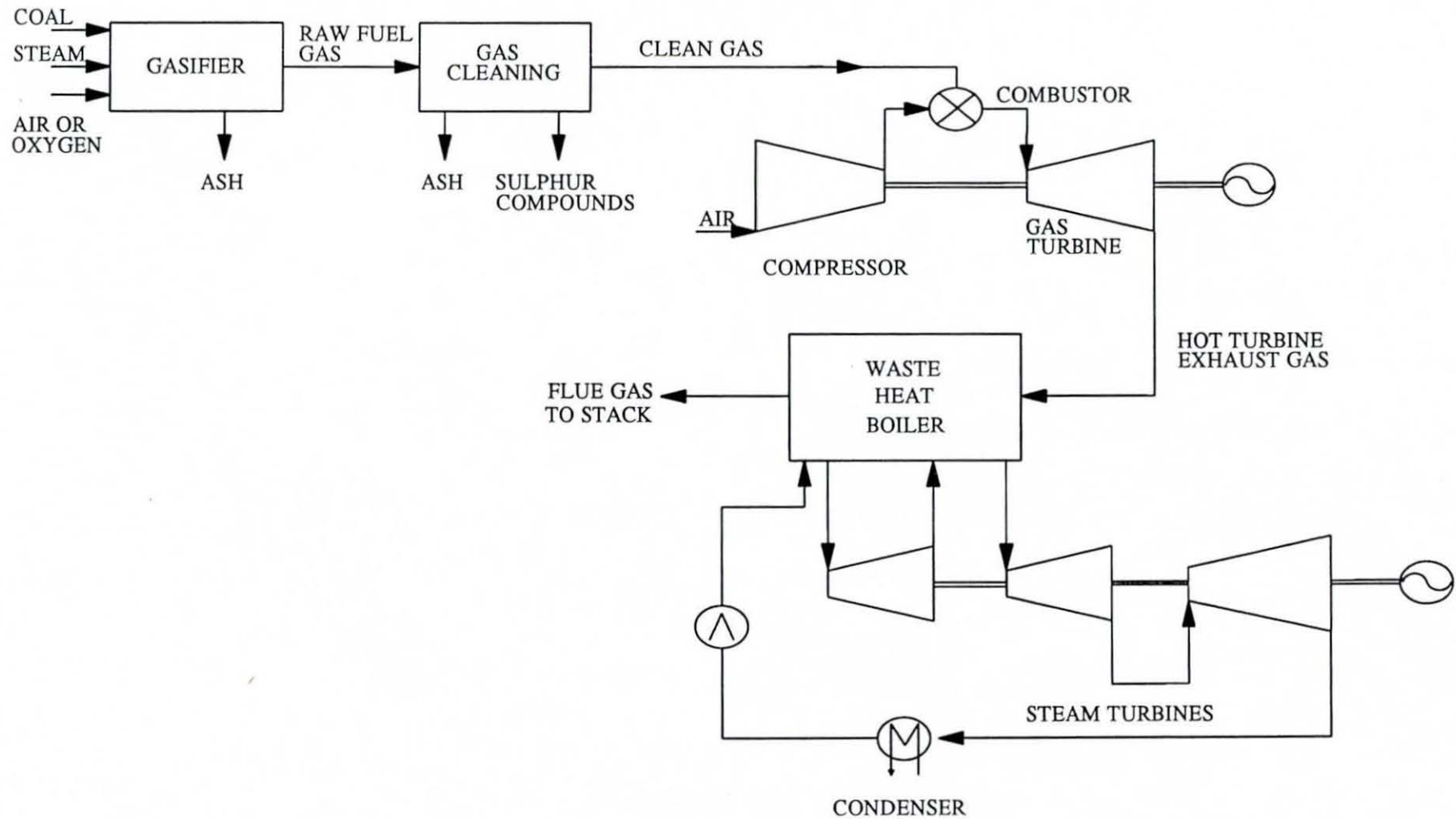


Figure 1.6 IGCC Power Generation System

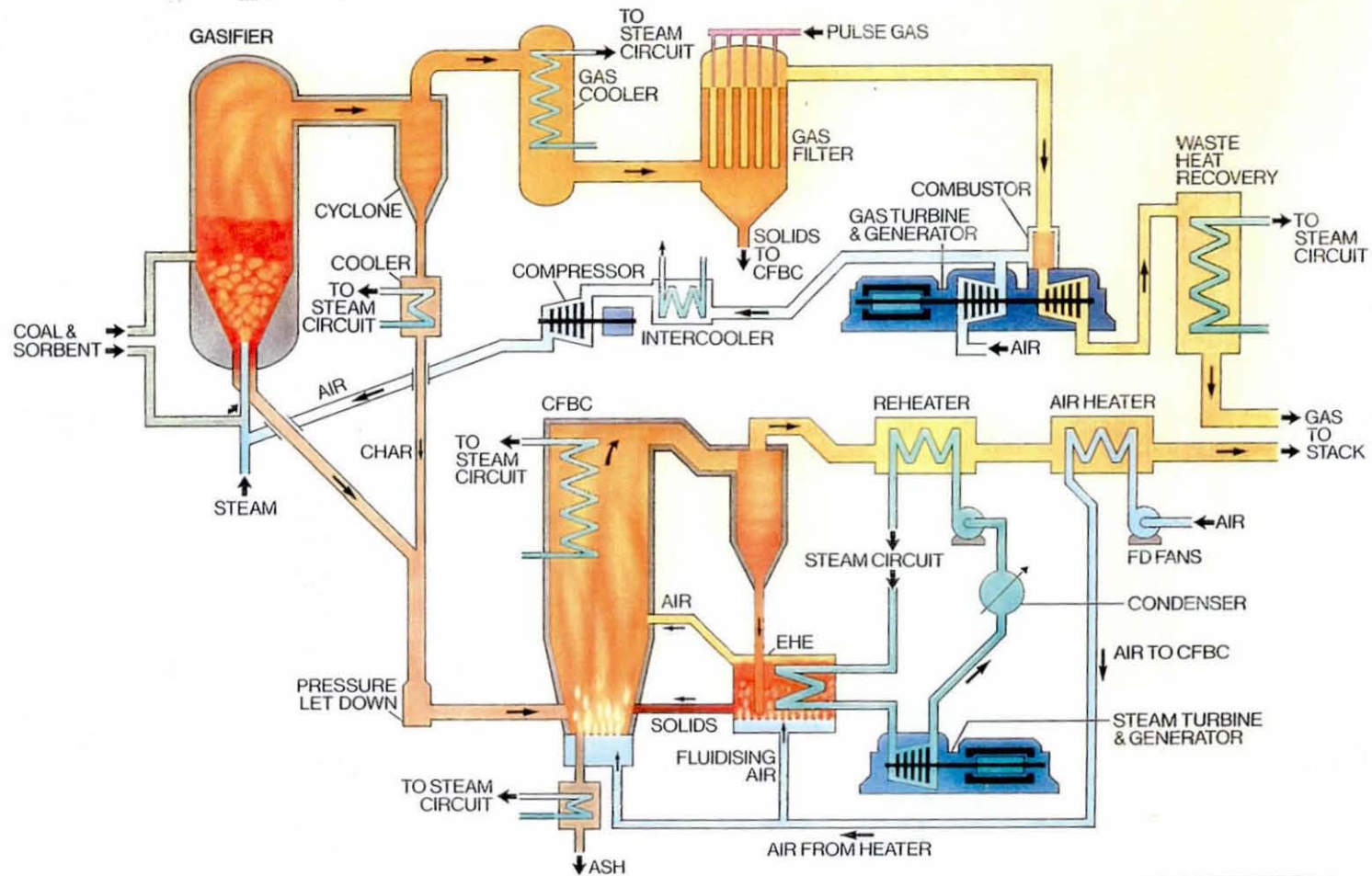
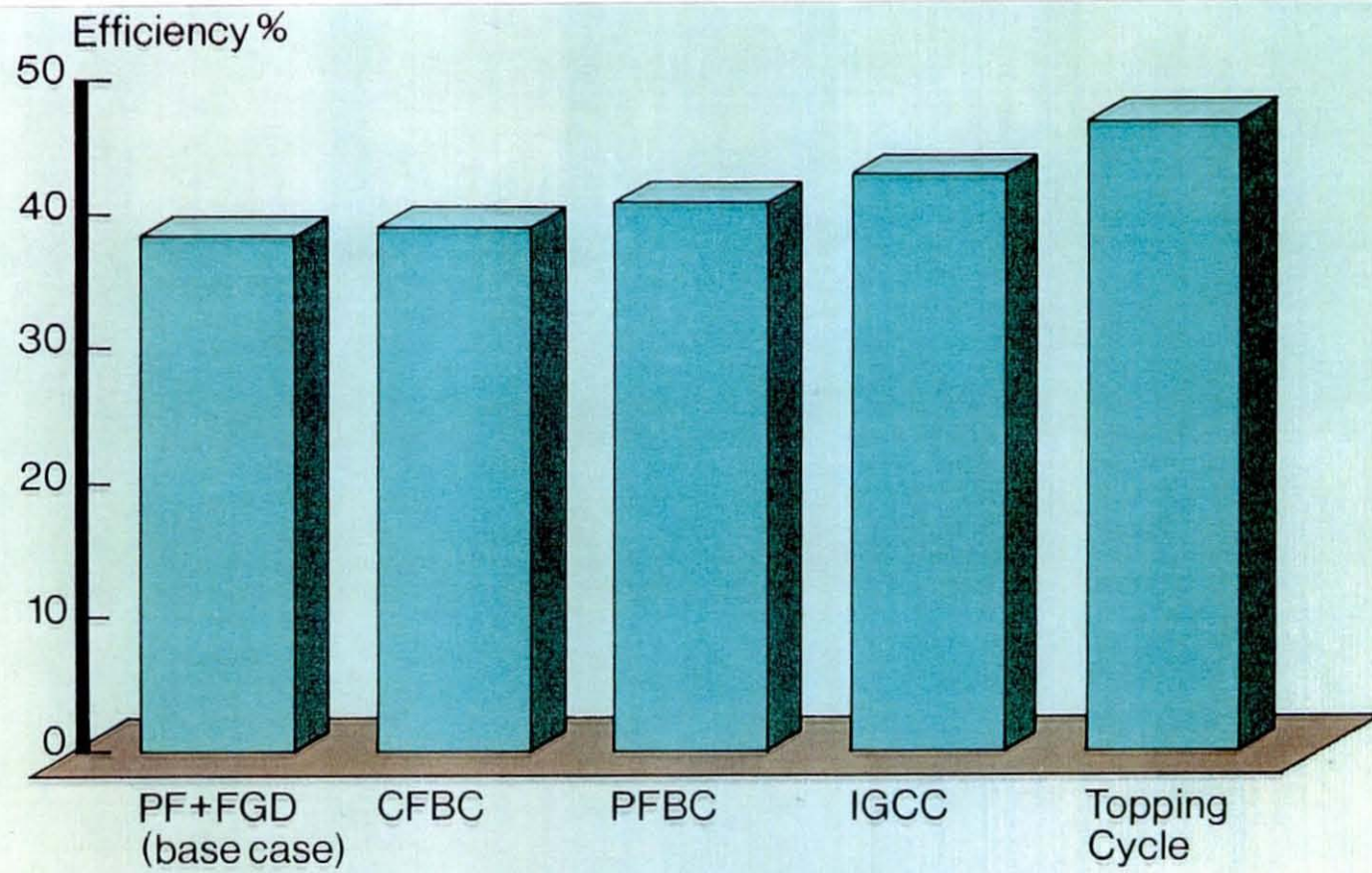


Figure 1.7 The Air Blown Gasification Cycle



Efficiency of coal based power generation systems

Figure 1.8

Chapter 2

Literature Review

2.1 Introduction

In the two hundred years since the process of gasification was first observed a wealth of literature has been produced on the subject. It is however only in the latter half of this century that the requirement for gasifiers of much higher performance has caused concerted efforts to be made to achieve a fuller understanding of the basic principles involved. The purpose of this chapter is to review some of the more important work that has been published concerning these basic principles. The concept of active sites is dealt with initially, followed by a discussion of work on gasification at atmospheric and sub-atmospheric pressures. Work on gasification at high pressures is discussed in section 2.6. In section 2.7, work on catalysed gasification is reviewed. Section 2.8 is concerned with the development of macroscopic models and section 2.9 relates to commercial gasifiers. Firstly, however, the classification of coal is reviewed and the nature of coal macerals is briefly discussed.

2.2 The British Coal Coal Classification Scheme

This scheme classifies coals according to their volatile matter, determined on a dry

mineral matter free basis, and their caking properties according to the Gray-King low temperature carbonisation assay.

Coals are divided into groups numbered in hundreds from 100 to 900 and the groups are subdivided into classes. For coals with volatile matter contents up to 32% volatile matter is the primary basis of classification. Such coals fall into groups 100-300 with the lowest volatile coals (anthracites) in group 100. For coals of above 32% volatile matter, Gray-King coke type is the primary basis of classification with group 400 being the most strongly caking and group 900 being non caking. The groups are divided into two classes. Those with 32.1 to 36.0% of volatile matter will be in groups 401 to 901 depending on coke type. Those with over 36% of volatile matter will be in groups 402 to 902 depending on coke type. Full details of this system of classification are readily available in the literature⁽⁴⁾

2.3 Coal Macerals

Coal is an organic rock. The term maceral was introduced by MC Stopes in 1935 to designate the microscopic constituents of the coal, by analogy with the minerals in inorganic rock. Macerals are the remains of plants and degraded plant materials. The properties of the maceral and hence of the coal depend of the nature of the plant material (ie the type of plant and the part of the plant) and how this material has been naturally modified according to the microenvironmental conditions under which coalification occurred.

Macerals are divided into three groups, namely vitrinite, liptinite and inertinite. The

term vitrinite covers a wide range of different materials. It is the most abundant material in typical coals, forming the matrix in which other materials are embedded. Vitrinites are derived from woody materials, eg. stems and roots of trees and vascular tissues of leaves which have been heat treated to various degrees. Sometimes remnant cell structures are visible within the vitrinite. Such material is usually called tellinite. The other maceral in the vitrinite group, collinite, is without visible botanical structure. Vitrinites generally appear dark grey to yellowish white, depending on concentration and rank, the reflectance of the vitrinite being a sensitive indicator of the rank of the coal. Higher rank coals have higher reflectances and lower volatile matters. As reflectance increases, then gasification reactivity tends to decrease. Also, an overlap of the reflectance values of liptinite and vitrinite indicates a high reactivity of all the coal. A high rank coal such as an anthracite would be virtually free of liptinite, and the vitrinite would have a high reflectance of 2 to 4. This indicates low reactivity. The vitrinite from lignites is quite dissimilar chemically to that from bituminous coal. At any given rank level, vitrinites contain more oxygen than other macerals.

The macerals in the liptinite group are sporinite, cutinite, resinite and alginite. Liptinites tend to have higher volatile matter and hydrogen contents than vitrinites particularly at lower ranks. At higher ranks, as hydrogen and volatile matter content decrease, they can become difficult to distinguish from vitrinites. They are derived geologically from resinous material, spores and cuticles and are usually the least abundant. They generally appear grey to brownish, depending on rank, are highly fluorescent to ultra violet light and are believed to be the most reactive of all the

macerals.

Inertinite is the collective term for the macerals micrinite, semifusinite, fusinite and sclerotinite. Inertinite is derived from similar materials to vitrinite, but this material has been thermally or biologically oxidised prior to coalification which gives rise to high carbon contents. Because of the high carbon content, the composition of inertinites varies little with rank. They vary in colour from light grey to white or even yellow. The reactivity of inertinites during combustion and gasification can vary particularly across the Southern Hemisphere where some high inertinite coals are quite reactive. Southern Hemisphere coals are generally thought to be higher in inertinite content than those from the Northern Hemisphere, and this largely holds true for the coals selected for this study. Further information on coal macerals may be found in 'Coal,' by DW van Krevelen, and 'A Textbook of Coal Petrography' by E Stach. Table 3.5 shows the petrographic analyses of the coals used in this study.

2.4 The Concept of Active Sites

The concept of active sites will be referred to a number of times throughout this review. It therefore seems appropriate to give some explanation here as to the nature and significance of these sites.

It is generally recognised that only a poor correlation exists between char reactivity and total surface area (TSA). A better correlation exists between char reactivity and active surface area (ASA). The idea of active surface area was first introduced into

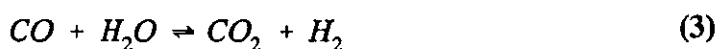
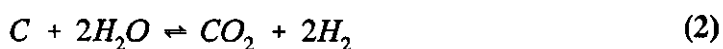
gasification literature by Laine et al ⁽⁵⁾ in 1963. The active surface area is comprised of specific regions on the carbon surface which are known as active sites.^(6, 7) Here gasification reactions proceed via the formation of carbon-oxygen complexes. The desorption of carbon monoxide and carbon dioxide from these sites is an important step in most kinetic schemes for coal char gasification.

It is thought that active sites arise because of particular structural features of the coal char such as defects in carbon layer planes, edge carbon atoms, the presence of heteroatoms (O,S,N) and mineral matter.

It is convenient to distinguish between a free active site which is usually denoted C_f and an occupied one which is usually denoted $C(O)$. The ASA of carbons is most commonly determined by low temperature chemisorption, usually using oxygen as the adsorbate. It is known however that only a fraction of the total active surface area participates in gasification reactions. This fraction is known as the reactive surface area (RSA). Measurement of RSA is a rather difficult experimental task, but has been carried out successfully for example by Lizzio et al⁽⁸⁾ using a gas switching technique, also called a transient kinetics technique. In this technique, chars are partially gasified and during the course of the reaction the reactive gas is substituted with nitrogen. The RSA can be calculated from the rate of decay of CO formation.

2.5 Gasification at Atmospheric and Sub-Atmospheric Pressures

In 1946 Gadsby et al ⁽⁹⁾ studied the reactions of the steam-carbon system over a range of pressures from 10-760mm Hg. Chars produced from both coals and coconut shells were used. The basic reactions of the steam-carbon system were given as



The complexity of studying the kinetics and mechanism of this system derives at least in part from the fact that there are two possible primary reactions, (1 and 2) the products of which may enter into secondary reactions. In Gadsby's work a series of conditions was chosen so that for a given set of conditions each of the above reactions would predominate and the interference from the other possible reactions would be minimised.

It was shown that the C-H₂O reaction was strongly retarded by hydrogen and the C-CO₂ reaction was strongly retarded by carbon monoxide.

An equation was given to represent the rates of both of these reactions.

$$r_5 = \frac{k_A p_1}{1 + k_B p_2 + k_C p_1} \quad (5)$$

where p_1 and p_2 are respectively the pressures of steam and hydrogen for the C-H₂O reaction and of carbon dioxide and carbon monoxide for the C-CO₂ reaction.

It should be noted that the equation

$$r_6 = \frac{k_A P_{\text{reactant}}}{1 + k_B P_{\text{product}} + k_C P_{\text{reactant}}} \quad (6)$$

is the general form of the Langmuir rate equation.

Possible reaction mechanisms were discussed using RO to represent the reactant (steam or carbon dioxide) and R to represent the retarding product (hydrogen or carbon monoxide); in each case R is the molecule obtained by removing an oxygen atom from the reacting molecule. Molecules chemisorbed on the carbon surface are represented by symbols enclosed in brackets.



The conditions for a steady state on a surface of equivalent and independent sites, each of which can be occupied by one molecule of reactant or retarding product are

$$k_7 p_1 (1 - \theta_1 - \theta_2) = (k_{-7} + k_9) \theta_1 \quad (10)$$

$$k_8 p_2 (1 - \theta_1 - \theta_2) = k_{-8} \theta_2 \quad (11)$$

Where θ_1 and θ_2 are the fractions of the surface occupied by reactant and retardant respectively. The rate of reaction is given by

$$rate = \frac{\frac{k_7 k_9 p_1}{k_{-7} + k_9}}{1 + \frac{k_8 p_2}{k_{-8}} + \frac{k_7 p_1}{k_{-7} + k_9}} \quad (12)$$

This mechanism can account for the fact that the reaction of RO with carbon is retarded by R. If the adsorption of the reactant requires its dissociation so that (RO) represents an atom of oxygen and retarding product on neighbouring sites, then the reaction of RO must take place on sites which can also adsorb R.

This is compared with the mechanism suggested by Frank-Kamenetzky and Semechkova,⁽¹⁰⁾ for the C-CO₂ reaction.



Here, the reactant reacts with the surface to give an atom of oxygen which remains adsorbed while the rest of the molecule passes into the gas phase. There are two possible explanations for the retardation effect. Either the retarding product is adsorbed onto active sites, or it reacts with adsorbed oxygen molecules according to the reverse component of reaction 13. Whichever of these mechanisms predominates, a rate expression of the desired form is obtained. The conditions for a steady state at the surface are

$$k_{13}p_1(1-\theta_1-\theta_2) = (k_{14} + k_{-13}p_2)\theta_1 \quad (15)$$

$$k_8p_2(1-\theta_1-\theta_2) = k_{-8}\theta_2 \quad (16)$$

where θ_1 and θ_2 are now the fractions of the surface occupied by oxygen atoms and retarding product respectively. If the retardation is largely due to the adsorption of

the retarding product and k_2 can be neglected, then the rate of reaction is given by

$$rate = \frac{k_{13} P_1}{1 + \frac{k_8 P_2}{k_{-8}} + \frac{k_{13} P_1}{k_{14}}} \quad (17)$$

If the retardation is largely due to the reaction with adsorbed oxygen atoms (reaction - 13) and the adsorption of the retarding product (reaction 8) can be neglected, then the rate of reaction is given by

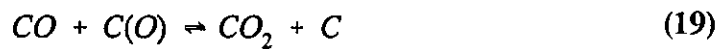
$$rate = \frac{k_{13} P_1}{1 + \frac{k_{-13} P_2}{k_{14}} + \frac{k_{13} P_1}{k_{14}}} \quad (18)$$

Experimental evidence indicates that carbon dioxide is not adsorbed by carbon at high temperatures but reacts with the surface according to equation 13. This implies that the mechanism of Frank-Kamenetzky and Semechkova, or of equations 18 or 19 is appropriate for C-CO₂ gasification. For the C-H₂O reaction Gadsby concludes that the mechanism described by equations 7 to 9 is more probable.

In an extension to the study of Gadsby et al, further work into the detailed mechanism of the C-H₂O reaction was carried out by Long and Sykes in 1948⁽¹¹⁾. It was suggested that if retardation is caused by the product occupying active sites on the carbon surface, then the rate of the slowest step in the mechanism would have to be

controlled by the attack of the reactant molecules upon the active sites, which form about 2% of the total surface. A close correlation was observed between the fraction of active sites occupied by hydrogen and the retardation of the reaction. Although adsorbed oxygen reacts slowly to form gaseous carbon monoxide, this has no retarding effect upon the C-H₂O reaction, thus indicating that different types of active site are involved in the C-H₂O and C-CO₂ reactions.

Ergun⁽¹²⁾ disagreed with the view of Long and Sykes, suggesting that the slowest step in the steam gasification process is the transfer of carbon from the solid to the gas phase and proposed that the retardation is due to a dynamic oxidation/reduction equilibrium between solid and gas phases as indicated below



and



In order to choose the most appropriate hypothesis, the rate determining step (RDS) of the reaction must be identified. If the RDS involves the desorption of the carbon/oxygen complex into the gas phase, then the mechanism described by Ergun is the most appropriate. If however the RDS involves the attack of reactants upon active sites, then the mechanisms described by Gadsby et al are more appropriate.

The mechanism of the carbon-carbon dioxide reaction was further studied by Gadsby et al ⁽⁹⁾. The important steps in the reaction are given as



Retardation by carbon monoxide is due to its adsorption onto the active sites which in this case represent about 0.5% of the carbon surface. Assuming the active sites to be equivalent, independent and each capable of adsorbing one oxygen atom or one carbon monoxide molecule, the rate of reaction in the steady state is given by

$$rate = \frac{i_1 p_{CO_2}}{1 + \frac{i_2 p_{CO}}{j_2} + \frac{i_1 p_{CO_2}}{j_3}} \quad (24)$$

which is of the same form as equation 5, where $i_1 = k_A$, $j_3 = k_A/k_C$ and $i_2/j_2 = k_B$

These constants are evaluated by Gadsby et al. ⁽¹³⁾

2.6 Gasification at Elevated Pressure

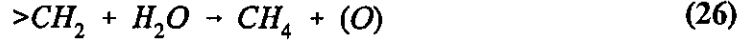
In comparison with the volume of work carried out into gasification at atmospheric pressure or below, the amount of work carried out on gasification at high pressure is small. This is due in part to the extra difficulties associated with obtaining data at pressure. However, in order to optimise the performance of commercial gasifiers, it is important to study gasification reactions at pressures at which they operate or are likely to operate.

Blackwood and McGrory⁽¹⁴⁾ studied the reaction of carbon and steam over a temperature range from 750 to 830 °C and a pressure range of 1 to 50 atm. They found that methane was always present in the product gases. It was noted that the appropriate Langmuir equation ie.

$$Rate = \frac{k_A P_{H_2O}}{1 + k_B P_{H_2} + k_C P_{H_2O}} \quad (25)$$

could only fit the data satisfactorily at higher temperatures; the results at lower temperatures could not be fitted to equation 25. It was also noted, particularly at lower temperatures and higher steam partial pressures, that the retarding effect of hydrogen was not as great as would be predicted by equation 25. A new rate equation was developed based on the assumption that methane formation was removing hydrogen from the carbon surface thus leaving more active sites available for reaction. However this was still unsatisfactory. A new reaction was considered in which

methane is produced by the reaction between steam and hydrogen adsorbed onto the carbon surface.



where $>CH_2$ represents the adsorbed hydrogen on the surface of the carbon.

A new rate equation was developed on this basis

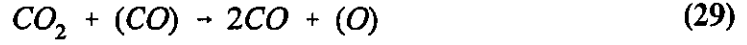
$$rate = \frac{k_A p_{H_2O} + k_D p_{H_2} p_{H_2O} + k_E p_{H_2O}^2}{1 + k_B p_{H_2} + k_C p_{H_2O} + k_F p_{H_2} p_{H_2O} + k_G p_{H_2O}^2} \quad (27)$$

Using suitably chosen values for the constants, this expression was found to fit the experimental data quite well. Since the constants k_F and k_G are very small they may be neglected so that the expression becomes

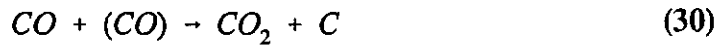
$$rate = \frac{k_A p_{H_2O} + k_D p_{H_2} p_{H_2O} + k_E p_{H_2O}^2}{1 + k_B p_{H_2} + k_C p_{H_2O}} \quad (28)$$

In 1959, Blackwood and Ingeme⁽¹⁵⁾ studied the C-CO₂ reaction at pressures up to 40 atmospheres and in the temperature range 790-870°C. The rate of formation of carbon monoxide was found to be much greater than that predicted from the mechanism proposed by Gadsby⁽¹³⁾ for atmospheric or sub-atmospheric pressures.

Blackwood explained this increase by modifying Gadsby's mechanism with some additional steps in which a carbon dioxide molecule interacts with an adsorbed carbon monoxide molecule to produce adsorbed oxygen, thus:



Although at high carbon dioxide partial pressures production of carbon monoxide is favoured, when the temperature is decreased and the carbon dioxide pressure is increased, the equilibrium composition is more in favour of carbon dioxide. It was therefore necessary to consider a reverse mechanism by which carbon monoxide could be converted to carbon dioxide. the additional step suggested is represented by



The rate equation derived by incorporating these additional steps was as follows.

$$rate = \frac{k_1 p_{CO_2} + k_4 p_{CO} p_{CO_2} + k_5 p_{CO_2}^2 - k_8 p_{CO}^2}{1 + k_2 p_{CO} + K_3 p_{CO_2} + k_6 p_{CO} p_{CO_2} + k_7 p_{CO_2}} \quad (31)$$

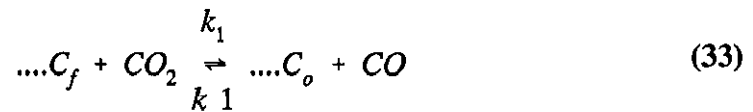
The experimental results presented in this paper showed that some of the terms in this equation were small enough to be ignored and thus the equation could be simplified to

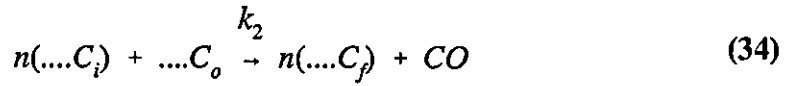
$$rate = \frac{k_1 p_{CO_2} + k_5 p_{CO_2}^2}{1 + k_2 p_{CO} + k_3 p_{CO_2}} \quad (32)$$

Blackwood was able to obtain values of the rate constants which gave predicted rates in good agreement with the experimental values.

In an interesting piece of theoretical work by Shaw⁽¹⁶⁾ in 1976 the work of Blackwood was reconciled with that of Ergun and others to produce a complex rate equation for the general case of gasification in any mixture of carbon dioxide, carbon monoxide, steam and hydrogen, at any temperature and pressure within the range of the original data.

Shaw began with Ergun's reaction scheme.



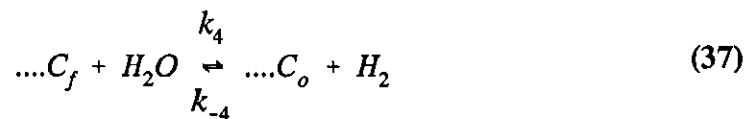


The meaning of this reaction scheme is as follows. Equation 33 represents the reversible attack by a carbon dioxide molecule from the gas on a free active site written $....C_f$. The free site is oxygenated and carbon monoxide is released. In equation 34 the oxygenated carbon atom $....C_o$ is discharged from the surface exposing formerly inactive sites $....C_i$ which may become active as a result. Equation 35 represents the decay of the free active sites to inactive ones.

Shaw gives the Langmuir Hinshelwood type equation developed from this reaction scheme in a slightly different form.

$$R_1 = \frac{a(p_{CO_2})}{(1 + b(p_{CO}) + c(p_{CO_2}))} \quad (36)$$

using a, b and c as his constants. By introducing another step into the reaction scheme;



another rate equation of the same form may be obtained to take account of the C-H₂O reaction.

$$R_2 = \frac{d(p_{H_2O})}{(1 + e(p_{H_2}) + f(p_{H_2O}))} \quad (38)$$

The rate equations of Blackwood and McGrory⁽¹⁴⁾ and Blackwood and Ingeme⁽¹⁵⁾ for the

C-H₂O and C-CO₂ reactions at pressure are then presented in the same form.

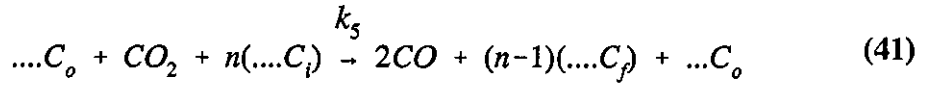
$$R_3 = \frac{(g(p_{CO_2}) + h(p_{CO_2})^2)}{(1 + i(p_{CO}) + j(p_{CO_2}))} \quad (39)$$

and

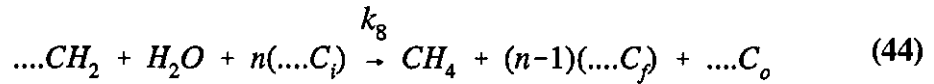
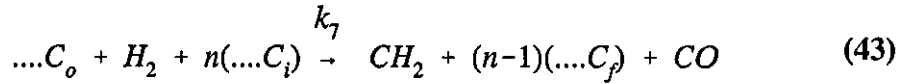
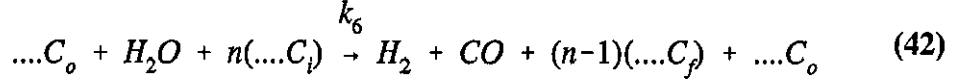
$$R_4 = \frac{(k(p_{H_2O}) + l(p_{H_2})(p_{H_2O}) + m(p_{H_2O})^2)}{(1 + n(p_{H_2}) + o(p_{H_2O}))} \quad (40)$$

Shaw explains these rate equations by adding new steps to the reaction sequences already presented. For the carbon-carbon dioxide reaction only one further step needs to be added to steps 33, 34 and 35.

For the general case of gasification in steam and carbon dioxide three further steps



have to be included as does equation 37. The three new steps are;



The meaning of these additional steps is this: In step 41 a molecule of carbon dioxide approaches an oxygenated carbon atom on the surface of the carbon. The oxygenated carbon atom leaves the surface as a carbon monoxide molecule. Its departure exposes some formerly inactive sites $....C_i$ which are then rendered active. One of these new active sites $....C_i$ is oxygenated by the incoming carbon dioxide, reducing this to the second molecule of carbon monoxide. Therefore one oxygenated carbon atom is discharged but a new one is formed on a neighbouring site. Step 42 is analogous to

the preceding step but here the reactant is H_2O . In step 43 a hydrogen molecule is seen as attacking an oxygenated carbon atom which is discharged as carbon monoxide. This exposes formerly inactive sites rendering them active as a result and one is hydrogenated. This is seen as a chemical reaction rather than just physical adsorption. In step 44 the methylene group formed in step 43 is removed as methane by the attack of a steam molecule. This leads to the formation of an active site which is then oxygenated. From these steps Shaw developed a rate equation for isothermal gasification in steam and carbon dioxide acting together.

$$R_s = \frac{a'(p_{CO_2}) + b'(p_{H_2O}) + c'(p_{CO_2})^2 + d'(p_{CO_2})(p_{H_2O}) + e'(p_{H_2O})^2 + f'(p_{CO_2})(p_{H_2}) + g'(p_{H_2O})(p_{H_2})}{h'(p_{CO_2}) + i'(p_{H_2O}) + j'(p_{CO}) + k'(p_{H_2}) + 1} \quad (45)$$

In recent years some of the most important work on the theory of gasification kinetics has been undertaken by van Heek and Mühlen.^(17, 18, 19) Their work is of particular relevance to the present studies since it forms the basis of the interpretation of the data produced. Their approach was also incorporated into the HHK model described in chapter one. Van Heek introduces the use of different parameters to measure reactivity. They are defined as follows.

- r' is the rate related to initial mass, m_0 and is calculated by equation (46)

If r' is constant when plotted against fractional conversion, X , also known as burn off, then the reaction is zero order with respect to X . This is the general case for catalysed gasification.

$$r' = \frac{dX}{dt} \quad (46)$$

where

$$X = 1 - \frac{m(t)}{m_0} \quad (47)$$

Here m_0 is the initial mass and $m(t)$ is the remaining mass at time t . These quantities are calculated on a dry ash free basis.

- r'' is the rate related to the mass of carbon present in the reactor at time, t . If the experimental r'' calculated according to equation (48) is plotted against "burn-off" is constant, then the reaction is first order with respect to $(1-X)$:-

$$r'' = \frac{dX}{dt} (1-X)^{-1} \quad (48)$$

- r_s is again related to mass of carbon present at time, t . If the experimental r_s equation (49) is plotted against "burn-off", and it is constant then the reaction is $\frac{2}{3}$ order with respect to $(1-X)$. This is due to the progress of the reaction at spherical surfaces.

$$r_s = \frac{dX}{dt} (1-X)^{-2/3} \quad (49)$$

Thus the order of the reaction and hence the appropriate rate parameter can be determined by plotting each rate parameter against conversion and looking for the line which is most nearly horizontal.

Clearly for a given programme of experimental work a judgement needs to be made on which of these parameters is the most appropriate. In this work r_g has been used. This choice is discussed more fully in chapter 4. For any study of reactivities, the reactivity at $t=0$ is of particular importance since it is at $t=0$ that most information is known about the reacting sample. For example if a char is prepared to a specific particle size it is difficult if not impossible to determine how this particle size changes as the reaction progresses. The same is true of any information obtained on pore sizes and structures or surface areas etc. Analysis of the equations for the three rate parameters shows that at $t=0$ all three are numerically equal. Therefore although it is r_g which is of primary interest in this study, the quantity r_0 meaning reactivity at $t=0$ is often referred to , since it is clearly unnecessary to specify which rate parameter has been used.

Some authors observed that the overall gasification rate depended on the degree of carbon conversion, and suggested that this was due to an increase in the average activation energy caused by the inhomogeneity of the char. Because of the difficulty in determining a single activation energy they proposed an exponential factor which is a function of temperature, pressure and the composition of the gasifying agent.

$$r_s = r_s(X=0) \exp\left(\frac{-bX^2}{RT}\right) \quad (50)$$

$$b = f(p_{H_2O}, p_{H_2}, p_{CO_2}, p_{CO}, T) \quad (51)$$

Van Heek and Mühlen derived the following equation

$$r_s = \exp\left(\frac{-bX^2}{RT}\right) \frac{r_1 p_{CO_2} + r_8 p_{CO_2} + r_9 p_{H_2O} + r_{11} p_{H_2O}^2 + r_{12} p_{H_2O} p_{H_2} + r_4 p}{1 + r_2 p_{CO_2} + r_3 p_{CO} + r_{10} p_{H_2O} + r_5 p_{H_2}}$$

In practice the value of 'b' has to be determined experimentally from reaction rate curves as do the values of the other rate constants. Sowa,⁽²⁰⁾ developing the work of Mühlen and van Heek, quoted a 'b' value for a German coal which was given by

$$b = (1245 - T) / 1.56 \quad (53)$$

Van Heek and Muhlen have also studied the influence of gasification conditions upon the rate of gasification of some coals and chars. Figure 2.1 shows the effect of temperature and pressure on gasification rate r_s in steam. It can be seen that gasification rate increases with increasing temperature. It also increases with increasing pressure at pressures below about 15 bar. Increasing the pressure above this value has little effect though the exact value of the saturation pressure increases with increasing temperature.

Laurendeau⁽²¹⁾ summarises some of the kinetic data found by other workers. He gives values for activation energies determined from a number of different studies. These were measured under a variety of conditions for both steam and CO₂ gasification. These values are given in Tables 2.1 and 2.2 below.

Table 2.1: Literature Values of Activation Energies for Steam Gasification

Investigation	Sample	Temperature (K)	Pressure (atm)	Activation Energy (kcal/mol)
Zielke and Gorin ⁽²²⁾	Disco char	1090-1200	1-30	40-75
Blakely and Overholser ⁽²³⁾	Graphite	1050-1200	1	~50
Stewart and Diehl ⁽²⁴⁾	Chars	1175-1275	1	34-40
Van Heek et al ⁽²⁵⁾	Chars	875-1375	1-70	36-50
Fuchs and Yavorsky ⁽²⁶⁾	Chars	1025-1175	18-70	~50
Kayembe and Pulsifer ⁽²⁷⁾	Bituminous Char	875-1125	1	61
Kaftanov and Fedoseev ⁽²⁸⁾	Graphite	1175-1475	-	70
Linares et al ⁽²⁹⁾	Lignite Char	1025-1205	(8.5 - 23) x10 ⁻³	42

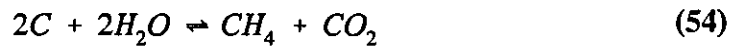
Table 2.2: Literature Values of Activation Energies for CO₂ Gasification

Investigation	Sample	Temperature (K)	Pressure (atm)	Activation Energy (kcal/mol)
Gadsby et al ⁽¹³⁾	Coconut char	975-1075	1	59
Blakely and Overholser ⁽³⁰⁾	Graphite	1050-1300	1	55-60
Blake et al ⁽³¹⁾	Coke	1125-1175	1	57
Turkdogan and Vinters ⁽³²⁾	Graphite, coconut char	975-1475	10 ⁻³ -10	68
Lewis ⁽³³⁾	Carbon	-	-	58-66
Tyler and Smith ⁽³⁴⁾	Petroleum coke	1020-1180	1	51-57
Fuchs and Yavorsky ⁽²⁶⁾	Chars	1025-1175	18-35	55
Dutta et al ⁽³⁵⁾	Chars	1115-1365	1	59

2.7 Catalysis in Gasification

The influence on gasification rates of external factors such as temperature, pressure, particle size, and pyrolysis history was the subject of an earlier project.⁽²⁾ The purpose of the current study is to consider the influence of coal properties on gasification rates. Such properties will include those related to the rank of the coal and its content of catalytic minerals.

There has been considerable interest, in recent years, in the use of catalysts to improve the overall efficiency of gasification processes. For practical purposes this normally entails enhancing methane production by the promotion of reactions such as



A review of earlier work on catalysis is given by Johnson⁽³⁶⁾ who lists six general conclusions from it. These are:

- 1 Relative catalytic effects decrease with increasing gasification temperature.
- 2 In the gasification process catalysts are generally more effective with gases containing steam than with hydrogen alone.

- 3 There is usually an intermediate optimum catalyst concentration, beyond which either negligible or negative effects result.
- 4 The relative effects of different catalysts can differ at different reaction conditions.
- 5 The specific methods and conditions used for catalyst impregnation can significantly affect subsequent gasification reactivity.
- 6 Catalyst impregnation is more effective than physical mixing with the carbon.

Catalysts surveyed include metals, metal oxides, metal halides, alkali carbonates, and iron carbonyls with particular emphasis on K_2CO_3 , Na_2CO_3 , KCl , $NaCl$, CaO and transition metals. It is of course perfectly possible for some of the above to be found as naturally occurring constituents of the coal ash. This gives added importance to the understanding of the effects of such constituents.

By using 5% $KHCO_3$ Gardner et al ⁽³⁷⁾ achieved a twofold improvement in gasification rates in hydrogen at 500psi (35 bar) and 950°C, whereas in steam a threefold increase was observed.

At the Institute of Gas Technology, lignites were studied.⁽³⁸⁾ These were firstly treated with hydrochloric acid to remove inherent calcium or sodium which are known to be present in them and thought to have a catalytic effect. Following the acid

treatment controlled amounts of calcium or sodium were added to the lignites. These combine with carbonyl groups in the coal as follows:



When using a steam/hydrogen mixture with a 3% sodium addition, a twentyfold increase in gasification rates was observed at 760°C and 500psi, compared to the acid treated lignite.

Addition of sodium and calcium to bituminous coals offered no benefit and this is thought to be due to their lack of carbonyl groups.

Walker et al ^(39, 40) studied the gasification of chars of demineralised coals loaded with calcium and magnesium, and demonstrated that the reactivity of lignite chars is controlled mainly by the catalytic effect of calcium associated with carboxyl groups, however, Miura et al ⁽⁴¹⁾ state that which ranks of coal have reactivity which is affected by mineral matter is 'a question still to be answered.'

A US bureau of Mines study⁽⁴²⁾ evaluated the effects of about 40 catalysts on the yields obtained by the gasification of a high volatile bituminous coal with steam at 850°C and 300psi (21 bar). The best overall reactivities were obtained with K₂CO₃ and KCl. With these materials a carbon conversion of about 80% was achieved during a four hour test period compared to a reference carbon conversion of about

50% using no catalyst.

Of particular interest here is the catalytic effect of inherent, rather than added minerals. Van Heek ⁽¹⁷⁾ reported on the catalytic effect of minerals in gasification reactivities. He found some correlation between the reactivities of lignites and their content of alkaline earth metals. If these are removed by demineralisation, the samples become much less reactive, and their reactivities compare with those of chars derived from hard coals. In the case of hard coals, minerals were found to have a much smaller effect on reactivity and in some cases (especially with high ash coals) they were thought to have an inhibiting effect on reactivity. Kristiansen ⁽⁴³⁾ states that in many low rank coals, a large proportion of the inherent sodium, magnesium and calcium occurs as cations associated with the carboxylate functional groups. Because of this association, these ions are easily exchanged, in other words, are available for catalysis. Potassium is also known to catalyse coal gasification, but inherent levels are typically too low to be significant. Other workers, eg Clemens ⁽⁴⁴⁾ whilst investigating the effect of calcium showed that its effect was to some extent temperature dependant. They produced chars from acid washed New Zealand lignite and subbituminous coal containing less than 10% of their original calcium content. They also produced char from samples which had had their calcium levels partially restored by ion exchange. At 1073K the acid washed chars took about three times longer to reach 20% carbon consumption than those which had had 25% or more of their original calcium content restored. Further calcium additions had little more effect on reactivity. These findings were repeated at 1173K but the effect was much smaller, and at 1273K the effect had all but disappeared. The reason for this

presumably is that at higher temperatures, mass transport effects are controlling overall reaction rates, whereas at lower temperatures, chemical reaction is controlling overall reaction rates.

Catalysed gasification however is still not without its problems and there is still a need for additional research in this area. Such research would include for example, development of new catalysts, detailed kinetic studies to determine optimal operating conditions, investigation of the detailed mechanism of interaction between the catalyst and the coal, and improving methods of catalyst recovery. Without reasonable recovery rates, catalysed gasification, though successful, may still not be economically viable.

2.8 Development of an Appropriate Macroscopic Model

It is often useful to have a simple, idealised, conceptual picture representing the progress of a reaction. A number of different types of these have been developed.

In the progressive conversion model, reactant gas is visualised as entering and reacting with the particle at all times and at different rates in different locations throughout the particle. Hence the solid is converted continuously and progressively throughout the particle.

In the shrinking core model, the reaction is visualised as occurring initially only at the outer surface of the particle. The reaction zone moves into the particle and may leave

behind a layer of ash. This process is represented in Fig 2.2.

Investigation of partially reacted solid particles often shows an unreacted core of solid material surrounded by a layer of ash. In fact, evidence from a wide variety of different reactions (for example, many combustion reactions) suggests that the shrinking core model reasonably represents reality in many situations.

Having chosen the appropriate model kinetic equations can be developed for it. The shrinking core model was first developed by Yagi and Kunii⁽⁴⁶⁾. They described the following five successive stages in a reaction.

- Step 1. Diffusion of gaseous reactant through the gas film surrounding the particle, to the surface of the solid.
- Step 2. Penetration and diffusion of gaseous reactant through the blanket of ash to the surface of the unreacted solid core.
- Step 3. Reaction of gaseous reactant with solid at this reaction surface.
- Step 4. Diffusion of gaseous products back through the ash to the exterior surface of the particle
- Step 5. Diffusion of gaseous products back through the gas film, into the main body of gas.

For certain reactions, some of the above steps may be inappropriate, eg there may be no gaseous products. The shrinking core model describes char gasification in terms of the rate of carbon conversion, given by the expression,

$$dX / dt = K (1-X)^{2/3} \exp (-\alpha X^2) \quad (57)$$

Where:

K = overall rate constant

t = time

X = carbon conversion fraction

The term $(1-X)^{2/3}$ is proportional to the effective surface area undergoing gasification, and the term $\exp(-\alpha X^2)$ represents the relative reactivity of the effective surface area, which decreases with increasing conversion

Clearly a model which envisages reactions occurring only at the surface of a solid is only likely to be applicable where the solid is non-porous or at least where the rate of pore diffusion is small enough to be negligible in comparison to the rate of chemical reaction. Since coal chars are very porous the simple shrinking core model is unlikely to be the most useful, and more sophisticated models can be considered.

One extension of the basic shrinking core model is the grain model of Szekely, Evans and Sohn.⁽⁴⁷⁾ This envisages a particle comprising small non-porous grains. Gas may therefore diffuse throughout the particle to the surface of the grains whereupon it reacts via a shrinking core mechanism. This particular model assumes that the size of the grains remains constant throughout the reaction. Other models eg Georgakis et al⁽⁴⁸⁾ assume that the grains can change in size during the reaction. Some systems,

including some gasification reactions, exhibit a maximum in the reaction rate. This is normally attributed to an increase in the reacting surface area during the early stages of the reaction. The 'overlapping grain model' of Lindner and Simonsson⁽⁴⁹⁾ can predict the maximum surface area and the maximum reaction rate during the course of the reaction.

Another category of model, the so called capillary models, assume that the particle contains a network of pores. The simplest of these models, proposed by Petersen⁽⁵⁰⁾ assumes that the solid consists of uniform cylindrical pores of constant radius. Petersen expressed surface area as a function of pore radius and derived a relationship between porosity and surface area. This model does not take into account pore growth and combinations. A more sophisticated example of a capillary model is the Random Pore Model of Bhatia and Perlmutter.⁽⁵¹⁾ Here the reaction is assumed to take place within a network of randomly intersecting pores within the particle. These become enlarged as the reaction proceeds and may eventually merge. The rate of gasification is assumed to be controlled only by the rate of chemical reaction on the pore surface and resistance to pore diffusion is assumed to be negligible.

The ratio of measured reaction rate to intrinsic (chemical) reaction rate is called the effectiveness factor, ϵ . The effectiveness factor therefore gives an indication of the magnitude of the resistance to pore diffusion. If the effectiveness factor is unity, then there is no resistance to pore diffusion and the measured reaction rate is equal to the chemical reaction rate. During previous work at CTDD⁽⁵²⁾ char samples derived from Kiveton Park coal were gasified isothermally at temperatures of 900, 950 and 1000°C.

The calculated effectiveness factors were found to lie close to unity, decreasing only slightly at the highest temperature. This suggested that under the conditions used, even at temperatures as high as 1000°C, the reaction rate is under chemical rate control.

2.9 Commercial Gasifiers

Although coal gasification technology has advanced significantly in recent years, it still generally lags behind CFBC and PFBC in terms of its prospects for commercialisation⁽⁵³⁾. There are, however a number of gasification plants worldwide, which are at, or nearing the commercial stage. These include the Dakota Gasification Corporation's Lurgi plant in Beulah, North Dakota and a two stage entrained flow slagging gasifier at the Plaquemine plant in Baton Rouge, Louisiana. In Europe the Shell based Buggenum plant is gradually moving towards full commercial operation and an IGCC facility is under construction at Puertollano in Spain.

Gasification processes can be separated by reactor type. There are three generic types of reactor namely, fixed bed, fluidised bed, and entrained bed⁽⁵⁴⁾.

2.9.1 Fixed Bed Gasifiers

In this type of reactor, an example of which is shown in Figure 1.5, the reactive gases enter the bed either in concurrent or countercurrent flow. In the case of countercurrent flow large particles of coal move slowly down through the bed whilst the reacting gases move up through the bed. The coal entering at the top is heated and dried while the product gas is cooled prior to leaving the reactor. The coal is further heated as it descends through the carbonisation zone. Here the hot gas causes devolatilisation of the coal. Below this zone is the gasification zone where the coal is gasified by reaction with steam and carbon dioxide. The highest temperatures occur in the combustion zone at the bottom of the gasification zone, where the remaining char reacts with oxygen. The major differences between various fixed bed gasifiers are due to the ash condition at the exit (dry bottom or slagging).

2.9.2 Fluidised Bed Gasifiers

The fluidised bed gasifier uses finely divided coal which is suspended in a rising stream of steam and oxygen or other gas (Figure 1.4). The fluidising action causes thorough mixing of the coal and close contact with the gases. The reactors operate at near to isothermal conditions with temperatures typically in the range 800-1000°C, depending on coal type.

Fluidised beds can handle higher coal feed rates than fixed beds because of their mixing capability. In comparison with fixed beds, fluidised beds in general have:

1. More solids carried over with the product gases.

2. Less tar and soot production.
- 3 More unreacted carbon in the ash.

Again, differences between fluidised bed gasifiers are due to ash conditions (dry or agglomerated).

Dry ash conventional fluidised beds operate most successfully on low-rank coals. Operating with agglomerated ash increases the ability of the fluidised bed to gasify high-rank coals efficiently.

2.9.3 Entrained bed gasifiers

In an entrained bed gasifier the coal particles are carried, or entrained, by the reacting gases. Therefore the coal particles used are very much smaller than those used in the other types of gasifier. Residence times are short and operating temperatures are high, (well above ash slagging temperatures).

Differences between entrained bed gasifiers are due to different types of coal feed mechanism, special design features to contain the very hot reaction mixture, and configurations used to facilitate efficient recovery of the large amount of sensible heat in the raw gas.

Nomenclature

r	reaction rate (general)
r'	reaction rate for zero order reaction
r''	reaction rate for first order reaction
r_s	reaction rate for 2/3 order reaction
k	rate constant
i	rate constant
j	rate constant
p	partial pressure
P	total pressure
X	carbon conversion or burn-off
m	mass
b	a function of temperature and partial pressure, $b = f(p_{H_2O}, p_{H_2}, p_{CO_2}, p_{CO}, T)$
T	Temperature
R	The universal gas constant

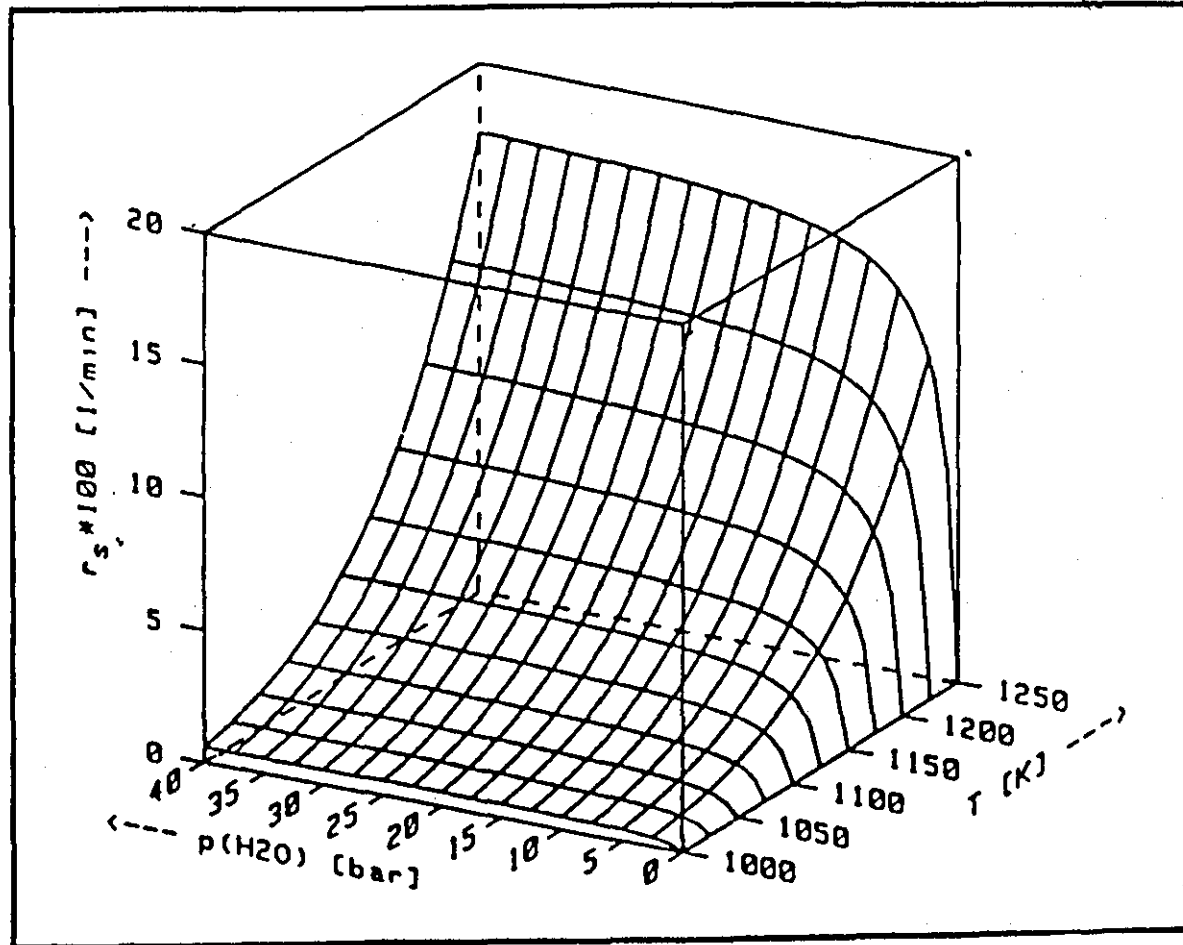


Figure 2.1: The Effect of Pressure and Temperature on Steam Gasification (From van Heek⁽¹⁷⁾)

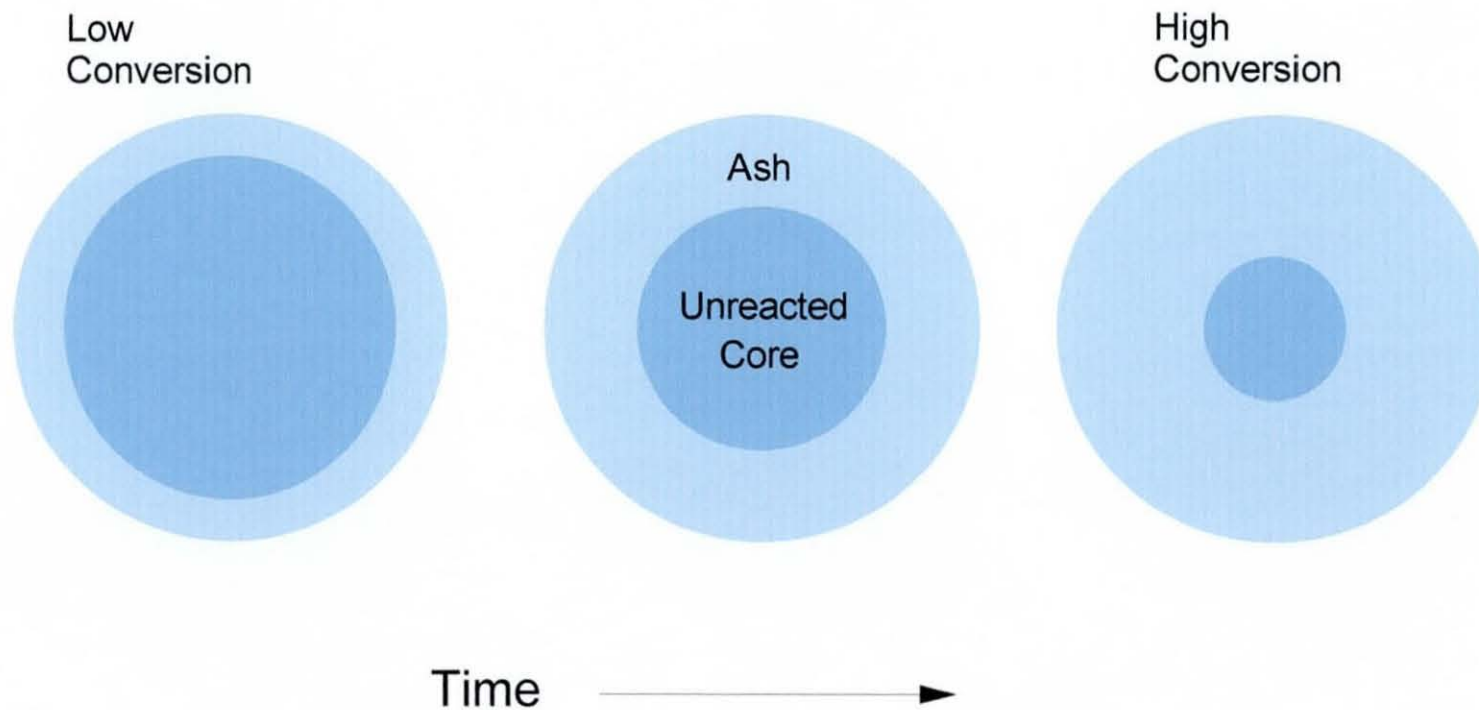


Figure 2.2 Illustration Of The Basic Shrinking Core Model

Chapter 3

Experimental Work

3.1 Introduction

This chapter discusses the experimental programme, which was divided into a number of sections. Firstly the selection of coals which is described in section 3.2. Seventeen coals were selected. Of these five were selected to be separated into their component macerals. This selection process is described in section 3.2.1, and the maceral separation technique is described in section 3.3. Chars were produced from the coals in a Fluidised Bed Reactor which is described in section 3.4. The 17 coals and the chars derived from them were gasified in the Pressurised Thermogravimetric Analyser (p.t.g.a.) at 950°C and 2.5MPa. Under these conditions, the reactivity of the coals was measured to steam and to CO₂. This work is described in section 3.5, and the techniques used for char analysis are discussed in section 3.6.

3.2 Selection of Coals

Whereas the gasification behaviour of Daw Mill coal has studied extensively under a wide range of conditions,⁽²⁾ one of the aims of this project was to compare the gasification behaviour of a number of coals of different type. These coals were obtained from sources around the world in order to compare their gasification behaviour under a set of standard

conditions.

The choice of coals was determined by a number of general as well as specific considerations. In order to assess the effect of a number of fuel properties on reactivity, it was desirable to try to achieve the widest possible range of variation in a relatively small number of coals. Furthermore, coals from the UK were selected from UK mines which are likely to be producing coal within five years from the inception of the project. Also, internationally traded coals were selected that could be burned in advanced power generation systems in the future within the EEC. Three southern hemisphere coals, two from Australia and one from South Africa were also chosen, along with two US coals which have been widely investigated in coal utilisation. The coals selected are listed below with a brief note explaining the reason for the inclusion of each. The properties of all of the coals are given in tables 3.1 to 3.5

The Coals chosen were as follows:-

1 Daw Mill Coal (washed) UK

Daw Mill is a likely long life mine serving the industrial as well as the power generating market in the UK. Daw Mill power station smalls coal, which is part washed, has been tested under a range of conditions in CTDD gasifiers. It has an ash content typically of 13.5%. It was therefore decided to study a washed product from Daw Mill with an ash content of 5.4%. This will enable comparison with the power station grade, which has been studied previously.

2 El Cerrejon Coal (Columbia)

This coal is widely exported from Columbia and is thought to have a low reactivity. It is therefore being included as an example of a readily available widely used imported coal.

3 Drayton Coal (Australia)

This is the design coal for the Shell entrained flow gasifier at Buggenum. Petrographic analysis shows that it has a higher inertinite content than the northern hemisphere coals in the programme. It also has a fairly low sulphur content. There the influence of high inertinite content and low sulphur content on reactivity can be assessed.

4 Rietspruit Coal (South Africa)

This is a potential fuel for a possible clean coal power plant in Northern Ireland, and it is also used in the Shell gasifier at Buggenum. Its analysis shows a high inertinite content although some historical data show a lower value.

5 Rheinbraun Lignite (Germany)

As a low rank coal this is likely to perform differently to bituminous coals. It also has a high moisture content.

6 Gardanne Coal (France)

This is a sub-bituminous coal. Its reactivity may also be affected by its high ash content.

7 Illinois No 6 Coal (USA)

This is a widely tested bituminous coal which is used as a standard by the US Department of Energy. It has a very high vitrinite content and a low ash deformation temperature.

It also has a high sulphur content.

8 Teruel Mequinenza (Spain)

A high sulphur lignite which has been reported to be very reactive. It is included to increase the range of coal properties being considered.

9 Taff Merthyr (UK)

A low volatile steam coal expected to have very low reactivity.

10 Hunter Valley (Australia)

This has been used in gasification hot gas filter trials in a previous DTI sponsored contract. It is included as another example of a southern hemisphere coal.

11 Janowice

An internationally traded coal from Poland

12 Longannet

This is a non-caking coal which might be compared to Maltby coal which is strongly caking.

13 Silverwood

Occupies the middle of the range of many of the properties under consideration.

14 Maltby

A strongly caking coal.

15 Harworth

Chosen for its high sulphur and swelling properties

16 Littleton

A high chlorine coal

17 Thoresby

A high chlorine coal

3.2.1 Selection of Coals for Maceral Separation

The separation of coals into macerals is a time consuming and expensive process. It was therefore impractical to attempt to separate all the coals into their component macerals. Also, because of the composition of the coals it would probably be unnecessary. Therefore, having considered the results of the petrographic analysis given in Table 3.5 six of the coals were initially selected for maceral separation. These were:

1 Longannet

This was chosen for its low mean vitrinite reflectance (MVR) value and high inertinite concentration.

2 Silverwood

This was chosen for its high MVR value and high liptinite concentration.

3 Rheinbraun

This has a very low MVR and a high liptinite concentration

4 Drayton

This has a wide spread of the different macerals

5 Rietspruit

This has a very high inertinite concentration

6 Daw Mill

This was used because it is now regarded as a 'standard' coal having been extensively studied and used in previous laboratory and pilot scale testing. It has a relatively low vitrinite content and a high liptinite content.

However was the German lignite, Rheinbraun, proved impossible to separate. Therefore maceral concentrates were finally produced only from the remaining five coals.

3.3 Experimental Method for Separation of Macerals

The maceral concentrates used in this study were separated under the supervision of Dr M. Cloke at Nottingham University. The bulk of each of the samples was intended for use in another project being undertaken at CTDD,⁽⁵⁵⁾ so that only the residue was available for this work.

Separation was achieved by density using an aqueous solution of sodium metatungstate. This was obtained from Sometu-Metawo of Germany under the generic name of sodium polytungstate (SPT). The density of the solution can be varied over a wide range by varying the dilution using distilled or de-ionised water. SPT solutions have the advantages of having a low viscosity, low toxicity and a wide range of densities. However SPT is expensive.

All separations were carried out under gravity using 500 or 1000 cc closed separating funnels. In order to minimise entrainment were retreated at least once. The method used is similar to one described previously by Birtek ⁽⁵⁶⁾. In general good separations were achieved. Following separation the samples were washed twice with hot, de-ionised water to remove traces of SPT. The SPT was recovered and re-used.

The coals were prepared for petrographic analysis using the method of Cloke et al ⁽⁵⁷⁾. The method involves mixing the samples with Simplex Rapid, which is a powdered

dental resin. The resin and coal were mixed in the proportions 2:5 by weight, and the grains wetted with a small amount of methylmethacrylate. The mixture is pressed at 150°C and 300 KPa pressure for 15-20 minutes, followed by three minutes cooling time, in a Presi Mecapress C, to produce a 30mm block. The blocks are then polished for about three minutes using a Struers Pedemat Rotapol polisher. This method produces good quality blocks relatively quickly. The microscope used was a Leitz Ortholux II POL-BK, which was fitted with a UV light source for fluorescence. All samples were analysed by manual point counting of 500 points.

Prior to separation the coal samples were mounted and a petrographic analysis carried out as described above. This enabled a qualitative assessment to be made regarding the degree of liberation of the individual macerals and hence the likely success of the density separation. Initial densities for the separating solution were chosen on this basis and subsequent densities were chosen so as to enable the highest degree of maceral concentration commensurate with a reasonable sample size to be obtained. In order to make comparisons between the results of this study and those from previous studies carried out at CTDD a 1mm particle size was chosen for this work. However one difficulty in using a 1mm particle size is that different macerals are associated within each particle. Crushing the particles down to micron size would liberate the macerals, but would also be likely to affect the gasification reactivities of the coals

The maceral compositions of the separated coal fractions are shown in Tables 3.7a and 3.7b. Separations are by no means complete, but are very good given the particle size

used. From each coal, three fractions were selected for further study, namely the fraction with the highest concentration of each of the macerals. These fractions are listed in Table 3.8. For each of the coals, it is the vitrinite concentrate which has the greatest purity. Purity ranges between 78% for Daw Mill and 97% for Longannet. Liptinite separation is less good, and is more variable, with the Daw Mill liptinite concentrate containing 48% liptinite, and the Longannet liptinite concentrate containing only 4% liptinite. This sample was also used as the inertinite sample since it had not only a higher liptinite content than any of the other Longannet fraction but also a higher inertinite content at 38%. For the other inertinite concentrates, Rietspruit contained the most inertinite with 58% and Silverwood contained the least at 37%.

3.4 The Fluidised Bed Reactor

In order to prepare samples of char for reactivity measurements a laboratory scale fluidised bed reactor was used (figure 3.1). The apparatus consists of an electrically heated silica reactor vessel with a conical base. Near to the base of the vessel is a sintered disc (zero grade, 3mm thickness) which acts as a distributor for the fluidising medium, which for these experiments was nitrogen. At the top of the vessel is a lid with openings for the injection and removal of coal samples and through which thermocouples can be positioned. The reactor vessel contains 200g of sand, the particle size of which is varied according to the desired particle size of the char so that the two could be conveniently separated by sieving. For example, a char of 1mm particle size (nominal) was prepared using a sand bed with a particle size of $<500\mu\text{m}$. The sand bed was

fluidised with nitrogen using a flow rate of 12.5 litres/minute. The bed temperature was measured using a thermocouple inserted through the reactor top. The vessel was insulated with refractory cement.

The coal injection system consists of a long tube inserted through the top of the reactor and down into the bed. At the top of the tube is a pneumatically operated actuator valve. Below this is the exit line which is connected by a system of valves to a vacuum line. A cyclone is fitted to the exit line in order to separate the particles removed from the bed. These particles are collected in a water cooled catchpot at the base of the cyclone.

Chars were prepared by placing a 5g coal sample in the top of the coal injection tube with the actuator valve closed and a small pressure (2.5psi) of nitrogen applied to it. When the desired bed conditions had been attained the actuator was opened and the coal was blown into the bed by the nitrogen pressure. The actuator was then closed. After the correct residence time had elapsed the valve to the vacuum system was opened and the sample was removed by suction. Thus the pyrolysis time of the char samples may be accurately controlled. The char product was separated from bed material using an appropriately sized sieve. For this test programme a coal particle size of 1.0mm was used. The coals were pyrolysed at 950°C for 5 minutes.

3.4.1 Operational Difficulties with the Fluidised Bed Reactor

Fluidised bed reactors of the kind described above have been in use at CTDD for a

number of years and have proved to be reliable. The reliability does to some extent depend on the exact application to which the apparatus is being put. Problems experienced with the reactor during this work are detailed below.

The reactor vessels stand up surprisingly well to their daily regime of being repeatedly heated, cooled, blasted with hot sand, disassembled from the rest of the apparatus and cleaned, then reassembled. However clearly such a regime gives them a finite lifetime. Previous experience has suggested that silica reactor vessels of this type tend to last for about 6 months under these conditions. Also cracks developing in the refractory cement around the vessel can prevent it from reaching its desired operating temperature. Obviously the fluidising nitrogen also has a significant cooling effect on the reactor so good insulation is essential.

Often when the samples were removed via the vacuum system the cyclone did not remove all the particulate material, resulting in a small amount collecting in the vacuum lines. Over the course of a number of runs, enough material would collect in the vacuum lines to block them completely, so regular cleaning of the vacuum lines was necessary.

Previous experience has shown that the sample injection system, though operated successfully using Daw Mill coal, does not work well with high swelling coals. The dilation of the swelling coals can often be sufficient to block the sample injection tube completely.

3.5 Thermogravimetric Analysis

A convenient method for following the course and rate of many reactions (usually gas/solid reactions) is to measure weight changes in the reactant solid. Such reactions normally occur at high temperatures and the technique is known as thermogravimetry. A simple thermogravimetric analyser would consist of a furnace through which reactant gases may be passed, and a sensitive balance capable of measuring the weight of a sample placed in the furnace. The output of the balance and the furnace temperature might be recorded by a chart recorder, or computer.

Such a device would only be suitable for studying reactions at atmospheric pressure. Since the gasifier used in the ABGC is designed to operate at elevated pressure a Pressurised Thermogravimetric Analyser was used for this study.

3.5.1 The Pressurised Thermogravimetric Analyser (p.t.g.a.)

The p.t.g.a. used for this work was designed, built and supplied by DMT (formerly Bergbau Forschung) in Germany⁽⁵⁸⁾ A schematic diagram of the apparatus is shown in Figure 3.2. A photograph of the equipment shortly after its arrival at CTDD is shown in figure 3.3, however a different type of steam generator to that illustrated was fitted before this work programme commenced.

The p.t.g.a. consists of a stainless steel reactor tube of approximately 290mm in length

with an internal diameter of 16.7mm. The tube is heated by an externally wound electrical heating element. The maximum operating temperature is 1100°C, and the temperature is controlled by a type K (NiCr/Ni) duplex thermocouple placed under the element with its tip in the hottest part. Duplex thermocouples are essentially two separate thermocouples in the same housing. They are useful whenever a temperature reading from a given location is required to be sent to two different instruments simultaneously, (for example a controller and a recorder). The type K thermocouple is chosen as is it the most appropriate for the temperature range being measured and gives reasonable accuracy throughout the range. Between 50 and 400°C the type K thermocouple is accurate to within $\pm 3^\circ\text{C}$. Between 400 and 1300°C it is accurate to $\pm 0.75\%$.

The reactor is located within a refractory lined pressure vessel. For the purposes of this investigation the samples to be analysed were placed in a sample holder in the form of an incoloy wire basket. The sample is admitted to the reactor via the sample lock, where it is suspended from the balance by a chain. The sample lock is a separate water-cooled pressure vessel which is located above the reactor vessel. Here the sample may be retained until the desired reaction conditions of pressure, temperature and reactant gas concentration are established in the reactor tube. At this point the sample may be lowered into the reactor using an electric winch. The unit may either be operated isothermally or non-isothermally using a pre-set temperature program. The sample temperature is measured by another type K duplex thermocouple inserted up through the centre of the reaction tube, from the base. The tip of this thermocouple is positioned so that it is 5mm below the sample when the sample holder is lowered into position. This

gives accurate measurements of sample temperature since there is a constant temperature zone of about 20mm length at the centre of the reactor tube (see chapter 2). The weight of the sample is measured by a Sartorius balance, model number M25-DP, which reads to ± 0.01 mg. Weight changes and sample temperatures are logged automatically using dedicated software running on a Hewlett-Packard Vectra PC.

The reactor is supplied by three gas lines. Through one of the lines helium is passed continuously as a purge, in order to keep the reactant gases and gaseous products away from the balance. The other two lines are used to feed in reactant gases. For the purpose of this work the reactant gases used were CO, CO₂ and H₂, but for other experiments other gases might be used. For example with minor modifications the p.t.g.a. has been used to test the sulphur retention efficiency of various sorbents such as limestone and dolomite, by passing SO₂ and H₂S over them. Mass flow controllers are incorporated into each gas line in order to measure and/or control the flow of gas. Although the mass flow controllers are calibrated for specific gases, they can be used with any gases by making use of the appropriate correction factor. These enable gas mixtures of precisely known proportions to be used. Typical gas flow rates are 1-1.5 litres/min for the helium purge and 2 litres/min for the reactant gas or gas mixture.

Steam may be generated for use as a reactant by a separate steam generating system. This consists of an HPLC pump which injects water at a constant rate into a small volume boiler where it is vaporised. It then passes along an externally heated line into the base of the reactor.

The pressure in the rig is controlled by either or both of two pressure regulating valves. The maximum operating pressure of the rig is 10.0 MPa. The exit lines from the reactor incorporate a filter for removing particulates, and a temperature controlled tar trap for collecting pyrolysis products. Finally, the exhaust gases pass through a condenser to condense the steam. The condensate is collected and weighed. This may serve as a useful check for the measurement of the steam flow rate.

3.5.1.1 Operating Description

Essentially the experimental procedure is similar for all tests and may be summarised as follows:-

Approximately 70mg of sample is weighed into the sample basket, which is then introduced into the water cooled sample lock. The reactor temperature is adjusted gradually, to reach the desired reaction temperature. All experiments in this programme were carried out isothermally. The pressure in the rig is then raised to the desired value using helium. The reactant gas is then introduced into the system. After allowing several minutes in order for the reactant gas to enter the reactor and for the helium to be displaced the sample is lowered into the reactor. The path of the reactant gas through the reactor is shown in Figure 3.4 which shows more detail of the internal construction of the reactor vessel. The time taken for the helium to be displaced by reactant gas may be calculated as follows.

The volume of helium which needs to be displaced before the reaction can occur may be calculated from the internal volume of the reactor. This is given by the total internal volume of the reactor vessel, minus the volume of the refractory lining material, minus the external volume of heated reactor tube, plus the volume of the reactor tube up to the point where the sample is located during the experiment. This point is typically 180mm from the bottom of the tube. This gives a volume of 9.64×10^{-2} litres, which can be taken as 0.1litres. Assuming a reactant gas flow rate of two litres per minute the time take for one volume change assuming complete displacement would be approximately 3 seconds. This of course only applies at room temperature and pressure and a suitable correction would need to be made according to the actual temperature and pressure of any particular test. For example for a test at 25 bar and 950°C the effective volume of helium to be displaced would be

$$V_{He} = 0.1 \times \frac{25}{1} \times \frac{288}{1223} = 0.589 \approx 0.6 \text{ litres}$$

This is calculated as 0.589 litres which may be taken as 0.6 litres. This means that the time taken for the helium to be displaced would be 18 seconds. Thus having switched to the reactant gas, a wait of 5 minutes before introducing the sample would give 16.6 volume changes.

Having introduced the sample, the temperature is then readjusted manually to maintain the desired value. The weight loss data together with temperature and pressure readings

are collected on the computer and subsequently evaluated using the software specifically written for this purpose.

DMT, the manufacturers and suppliers of the p.t.g.a., undertook many tests to ensure the reproducibility of its results. Some of these test results are shown in Appendix 1, and they show that the reproducibility is indeed very good. Further tests were carried as part of this present study. The reproducibility is less good than that achieved by DMT, but nevertheless it is quite reasonable. An example of a comparison between two identical tests on Daw Mill coal at 0.8 Mpa and 850°C is given in Appendix 1a. r_s at $t=0$ is about 6.25 in one test and 6.5 in the other which is a difference of four percent. Under the low temperature and pressure conditions used, where reactivities are low making small errors more significant, this is adequate. The difference is exacerbated at higher conversion reaching a maximum at about 88% conversion. It is recognised that errors are increased at higher conversions and this is discussed earlier. As r_s at 75% is the value of most interest, differences between test results at higher conversions than this will have little impact.

3.5.1.2 Operational Difficulties with the p.t.g.a.

The p.t.g.a. had been in use at CTDD for some years prior to this programme of work being undertaken. It had, however, not been used for some months immediately before this programme was started. A previous test programme had involved testing the

efficiency of various sorbents by passing H_2S over them in the p.t.g.a.. It is thought that most of the problems experienced early on in this test programme were due to a combination of these factors.

The first problem to be experienced was a failure of the heating element. It is thought that this is due to the element being corroded by H_2S . Replacement of the heating element is a major operation involving extensive dismantling of the rig. During this operation it was found that many of the heating tapes which are used to prevent steam from condensing inside the entrance and exit lines from the rig had become brittle and these too needed to be replaced. Subsequently a number of heating elements failed and it proved impossible to determine the cause for this. However because of the delays and expense which these failures caused a slight modification was made to the equipment. This was the installation of a high temperature cut-out device to protect the heating element. This device has an adjustable set point which may be set to a temperature just above the maximum temperature required for a particular test. Thus if for any reason this temperature is exceeded the power supply to the heating element is interrupted to prevent the element from burning out.

Further protection was given to the heating element by reducing the nominal output voltage of its supply transformer from the recommended 150V to 130V. This was done because the transformer was designed for a 220V input voltage rather than the 240V which was actually used. Even with this reduced setting the heating element was still capable of heating the reactor tube to the maximum desired operating temperature.

Another problem which was discovered early on in the test programme was that, for reasons which are not clear, the chain on which the sample is lowered into the reactor was about 15mm too short. This meant that the sample was not located in the centre of the constant temperature zone and was about 20mm away from the sample temperature thermocouple rather than 5mm as it should be. This meant that some tests were carried out at a somewhat lower temperature than had been intended. Having installed a new chain of the correct length a number of the tests were repeated. By comparison of the reactivity values obtained with the new and old chains, a temperature correction for the tests carried out with the old chain was calculated.

A problem occurred with the data logging system which meant that sample weight changes were not being recorded properly. This was eventually traced to the software and a new version of the software was acquired from DMT which rectified the problem.

The other area which gave cause for concern during the test programme was that a number of valves failed to perform adequately. Early in the test programme the pressure regulating valves were found to be sticking and had to be completely overhauled. Also the isolating valves on the steam generator still allowed steam to pass even when they were apparently closed. This allowed steam to flow back into the gas mass flow controllers where it condensed causing considerable damage. Although the isolating valves were replaced the new valves quickly failed in a similar fashion and the newly repaired mass flow controllers were again damaged. No satisfactory solution was found to this problem but it was avoided to a large extent by arranging the work programme so

that as many CO₂ gasification tests as possible were carried out first and steam gasification tests were carried out subsequently.

3.6 Char Analysis

It is appropriate to mention briefly the technique used for proximate analysis of the chars. Proximate analysis is normally carried out according to British Standard BS1016⁽⁵⁹⁾. This requires a minimum sample weight of about 3g. Because of the difficulty of obtaining large quantities of char from the small fluidised bed reactor it was decided to employ a different method for proximate analysis for the purposes of this work.

The method chosen was the so called 'micro-proximate' analysis method which is performed in an atmospheric thermogravimetric analyser such as that described in section 3.2. It has been shown that results obtained by this method give good agreement with those obtained by the British Standard method⁽⁵⁹⁾⁽⁶⁰⁾. The experimental procedure is as follows:-

The tests were carried out using a Stanton Redcroft STA 780 Thermal Analyser. A sample of approximately 15-20mg, usually crushed to -212μ , is heated from ambient to 815°C at 15°C min⁻¹ in an atmosphere of nitrogen (flow rate 50ml min⁻¹). This temperature is clearly lower than the 900°C used conventionally for proximate analysis, however it has been shown to give good agreement with results obtained by conventional means. The first weight loss observed occurs at about 100°C which

corresponds to the moisture content of the sample. When the sample reaches 815°C it is then maintained at these conditions until the weight is constant. The additional weight loss represents the volatile matter of the sample. The atmosphere is then changed to air using the same flow rate. The test is complete when there is no further weight loss. The residual weight gives the ash content of the sample. The results of the micro proximate analysis for all the char samples used in this work programme are given in table 3.6

Table 3.1. Proximate Analysis of Coals

Coal	Country of Origin	Moisture (%)	Ash (% ad)	Volatile Matter (% ad)	Fixed Carbon (% ad)	Volatile Matter (daf)
Longannet	UK	8.4	14.1	27.6	49.9	35.6
Daw Mill	UK	6.4	5.4	37.2	51.0	42.1
Thoresby	UK	5.6	4.9	34.2	55.3	38.7
Silverwood	UK	1.8	7.8	33.8	56.6	37.3
Maltby	UK	1.8	4.5	36.4	57.3	38.8
Harworth	UK	2.8	10.4	32.0	54.8	36.8
El Cerrejon	Colombia	6.4	9.2	33.2	51.2	39.3
Hunter Valley	Australia	4.8	9.4	31.7	54.1	36.9
Hambach Rhenish	Germany	18.0	3.5	41.0	37.5	53.0
Janowice	Poland	3.5	5.6	34.9	56.0	38.3
Illinois No.6	USA	12.7	8.8	34.1	44.4	43.4
Gardanne	France	8.0	19.0	40.4	32.6	55.3
Rietspruit	S. Africa	3.7	12.4	30.5	53.4	36.3
Drayton	Australia	5.3	9.0	33.4	52.3	38.9
Teruel Mequinenza	Spain	17.0	20.8	37.7	24.5	60.6
Taff Merthyr	UK	11.1	6.5	13.1	79.3	14.1
Littleton	UK	6.1	3.3	33.7	56.9	37.1

ad - as determined

daf - dry ash free

Table 3.2 Ultimate Analysis of Coals

	Carbon (dmmf)	Hydrogen (dmmf)	Oxygen (dmmf)	Nitrogen (dmmf)	Total Sulphur (db)	Organic Sulphur as S (db)	Chlorine (db)	Carbon dioxide (db)	Mineral matter (db)
Longannet	82.9	5.0	10.0	1.6	0.4	0.3	0.12	0.1	13.0
Daw Mill	81.3	4.8	11.5	1.3	1.5	1.1	0.21	0.4	5.8
Thoresby	84.3	4.6	7.9	1.8	2.0	1.1	0.67	0.1	6.5
Silverwood	85.6	5.2	6.3	1.8	1.5	0.9	0.16	0.1	14.6
Maltby	85.6	4.9	6.9	1.6	1.5	0.9	0.0000	0.4	15.7
Harworth	86.6	4.9	5.2	1.9	2.7	1.2	0.21	0.2	25.4
El Cerrejon	82.2	4.8	10.4	1.7	1.1	0.8	0.02	0.2	10.9
Hunter Valley	83.4	4.9	9.1	1.8	0.6	-	0.04	0.2	10.9
Hambach Rhenish	67.5	4.4	27.2	<0.1	0.7	-	0.02	0.3	4.6
Janowice	83.0	4.9	9.7	1.6	0.5	-	0.04	0.6	6.7
Illinois No.6	76.5	3.4	17.1	1.2	4.2	1.5	0.06	0.1	13.0
Gardanne	80.4	4.1	11.8	1.4	5.3	1.6	0.02	6.0	29.6
Rietspruit	83.6	4.7	9.2	1.7	0.5	-	0.02	0.2	14.2
Drayton	82.6	4.4	10.5	1.6	0.3	-	0.03	0.1	10.3
Teruel Mequinenza	76.1	5.4	13.8	1.1		3.5	0.01	1.2	34.0
Taff Merthyr	91.5	4.1	2.0	1.5	0.6	<0.1	0.01	0.3	7.4
Littleton	83.3	5.1	8.7	1.7	0.9	0.8	0.79	0.4	4.3

dmmf - dry mineral matter free

db - dry basis

Table 3.3 Ash Fusion Temperature, Caking and CV

Coal	Ash Fusion Range (°C)			Caking Properties		Calorific Value kJ/kg (daf)
	Deformation Temp	Hemisphere	Flow	Gray -King Coke	Swelling	
Longannet	>1500	>1500	>1500	C	2.5	32940
Daw Mill	1240	1270	1320	C	1.0	32820
Thoresby	1060	1090	1220	G5	5.5	34680
Silverwood	1390	1440	>1500	G5	7	35240
Maltby	1170	1360	>1500	F	4.5	34520
Harworth	1170	1380	1450	G	5.5	34380
El Cerrejon	1140	1240	1360	B	0.5	33220
Hunter Valley	1280	1480	>1580	C	1	33720
Hambach Rhenish	1310	1350	1350	A	0.0000	26060
Janowice	1180	1250	1360	C	1	33220
Illinois No.6	1060	1090	1210	A	0.0000	30500
Gardanne	1180	1360	1370	A	0.0000	29300
Rietspruit	>1500	>1500	>1500	D	2	34140
Drayton	1300	1500	>1500	C	1	33960
Teruel Mequinenza	1140	1160	1230	A	0.0000	28820
Taff Merthyr	1330	1350	>1500	B	1	36500
Littleton	1090	1120	1160	D	1	34100

Table 3.4 Ash Analysis of Coals

Coal	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	SO ₃	TiO ₂	Mn ₂ O ₄	P ₂ O ₅
Longannet	0.2	0.4	1.8	0.6	1.6	40.3	51.1	0.6	1.5	<0.1	1.3
Daw Mill	1.5	0.5	12.0	2.5	11.2	23.9	36.8	12.9	1.1	0.4	<0.3
Thoresby	5.9	1.4	3.3	0.7	26.3	23.8	34.3	3.1	0.9	<0.2	<0.2
Silverwood	0.4	3.4	1.0	1.3	10.0	26.2	55.1	0.9	0.9	<0.1	0.4
Maltby	0.8	3.6	2.5	1.5	11.6	25.7	50.1	2.4	1.0	<0.1	0.4
Harworth	0.8	3.8	0.9	1.2	13.5	25.8	50.2	0.7	0.9	<0.1	0.3
El Cerejon	1.4	2.2	3.5	2.1	9.1	19.9	57.6	4.2	0.8	<0.1	0.2
Hunter Valley	0.2	1.6	0.8	0.7	7.4	22.3	63.9	0.5	0.8	<0.1	0.7
Harnbach Rhenish	0.7	<0.5	35.8	16.3	18.6	1.5	1.3	20.0	<0.1	0.3	<0.5
Janowice	1.2	2.1	4.6	2.8	12.7	28.6	39.3	3.8	0.8	0.1	2.2
Illinois No.6	1.4	2.0	4.3	1.0	20.3	17.3	50.0	4.9	0.9	0.1	<0.1
Gardanne	0.2	0.2	37.4	1.7	7.1	6.3	14.1	31.8	0.2	0.1	1.0
Rietspruit	0.3	1.0	1.4	0.6	4.5	30.2	61.2	0.8	1.4	<0.1	0.6
Drayton	0.4	0.7	1.5	0.8	6.9	25.1	63.9	1.2	1.3	<0.1	0.2
Teruel mequinenza	0.7	0.2	13.8	2.2	6.3	11.2	43.0	18.1	0.7	<0.1	0.3
Taff Merthyr	2.9	0.4	3.9	1.0	3.7	39.5	39.2	2.6	0.6	<0.1	5.2
Littleton	4.4	1.5	9.5	3.0	13.3	21.7	32.4	10.7	0.8	0.2	0.7

Table 3.5 Petrographic Analysis of Coals

Coal	Maceral (% mmf)			Mean random vitrinite reflectance (%)	Vitrinite standard deviation
	Vitrinite	Liptinite	Inertinite		
Longannet	55.9	16.2	28.0	0.56	0.10
Daw Mill	67.4	16.7	20.9	0.60	0.12
Thoresby	79.7	4.9	15.4	0.71	0.08
Silverwood	71.4	13.7	15.0	0.88	0.08
Maltby	57.9	19.2	22.8	0.85	0.14
Harworth	87.1	6.0	6.9	0.87	0.08
El Cerrejon	83.7	2.3	14.0	0.72	0.48
Hunter Valley	75.0	3.9	21.1	0.67	0.07
Hambach Rhenish	91.4	7.8	0.8	0.28	0.05
Janowice	73.0	9.3	17.7	0.76	0.09
Pittsburgh No.8	90.8	2.5	6.7	0.61	0.05
Illinois No.6	92.0	2.4	5.6	0.40	0.05
Gardanne	82.2	6.8	11.0	0.48	0.10
Rietspruit	63.1	3.8	33.1	0.73	0.15
Drayton	74.8	4.4	20.7	0.65	0.08
Teruel Mequinenza	78.6	10.2	2.4	0.29	0.08
Taff Merthyr	85.9	0	14.1	1.90	0.30
Littleton	73	9	18	0.72	0.21

mmf - mineral matter free

Table 3.6: Microproximate Analysis of Chars

	Ash	Moisture	Volatile Matter
Daw Mill	28.6	5.2	nd
Janowice	23.8	0.1	0.9
El Cerrejon	26.7	0.1	2.2
Illinois No 6	19.3	3.4	3.6
Thoresby	51.4	0.0	0.6
Rietspruit	18.7	0.6	2.0
Gardanne	45.2	1.4	nd
Pittsburgh	69.1	0.0	nd
Drayton	43.7	0.2	nd
Rheinbraun	nd	nd	nd

Table 3.7a Macerals Separated at Various Densities

	Wt (g)	Vitrinite	Liptinite	Inertinite	Mineral	Pyrite
		(% by volume)				
Daw Mill						
Original	200	66	11	20	1	1
sg <1.26	2	45.2	48.2	6.6	0.00	0
1.28	4	60.5	29.5	10.0	0	0.2
1.30	38	77.6	13.0	9.4	0	0
1.35	113	69	11.2	19.8	0	0
1.40	21	32.1	19.9	48	0	0.4
>1.40	15	36.1	11.0	52.9	15	3.0
Rietspruit						
Original	93	59	4	31	6	0
sg <1.28	45	88.4	2.8	8.8	0.4	0
1.30	13	85.4	3.2	11.3	1.2	0
1.33	25	68.3	6.8	25.0	2.2	0
1.37	30	60.6	7.1	32.3	4.0	0
1.40	16	45.3	5.9	48.9	4.6	0
>1.45	19	34.7	3.2	62.1	7.2	0
Silverwood						
Original	203	65	12	14	8	0.8
sg <1.26	31	75.4	15.4	9.2	0	0.2
1.28	55	80.6	9.4	10.0	0	0
1.30	35	73.9	6.5	19.6	0	0.2
1.35	33	60.6	14.3	25.1	2	0.2
1.40	12	46.8	14.4	38.8	4	0.8
>1.40	37	53.4	11.1	35.6	57	1.8

Table 3.7b Macerals Separated at Various Densities

	Wt (g)	Vitrinite	Liptinite	Inertinite	Mineral Matter	Pyrite
		(% by volume)				
Drayton						
Original	132	71	4	20	5	0.2
sg <1.26	9	84	9	7	0.2	0.4
>1.26	32	86	4	9	1.0	0.2
<1.28	25	84	8	7	0.8	0.2
1.30	20	82	3	14	0.6	0
1.33	14	73	3	20	3.6	0.2
1.37	14	57	7	30	5.6	0.2
1.40	8	51	5	37	6.6	0.2
1.45	10	37	5	53	5.4	0
Longannet						
Original	200	54	16	27	3.4	0
sg <1.30	2	97	1	1	0.6	0
<1.33	11	96	2	1	0.8	0
1.35	9	93	3	3	1.4	0
1.37	20	88	4	7	0.8	0
1.40	26	74	9	15	1.4	0
1.45	50	51	19	25	5.0	0
>1.45	82	28	24	38	9.8	0.4

< - lighter than

> - heavier than

Table 3.8 The Composition of the Selected Maceral Concentrates

		Actual Maceral Concentration		
Sample Name		Vitrinite (% by volume)	Liptinite(% by volume)	Inertinite (% by volume)
Daw Mill	Vitrinite	78	13	9
	Liptinite	45	48	7
	Inertinite	32	20	48
Rietspruit	Vitrinite	88	3	9
	Liptinite	58	7	32
	Inertinite	32	3	58
Silverwood	Vitrinite	81	9	10
	Liptinite	75	15	9
	Inertinite	44	4	37
Drayton	Vitrinite	86	4	9
	Liptinite	84	9	7
	Inertinite	37	5	53
Longannet	Vitrinite	97	1	1
	Liptinite	28	4	38
	Inertinite	28	4	38

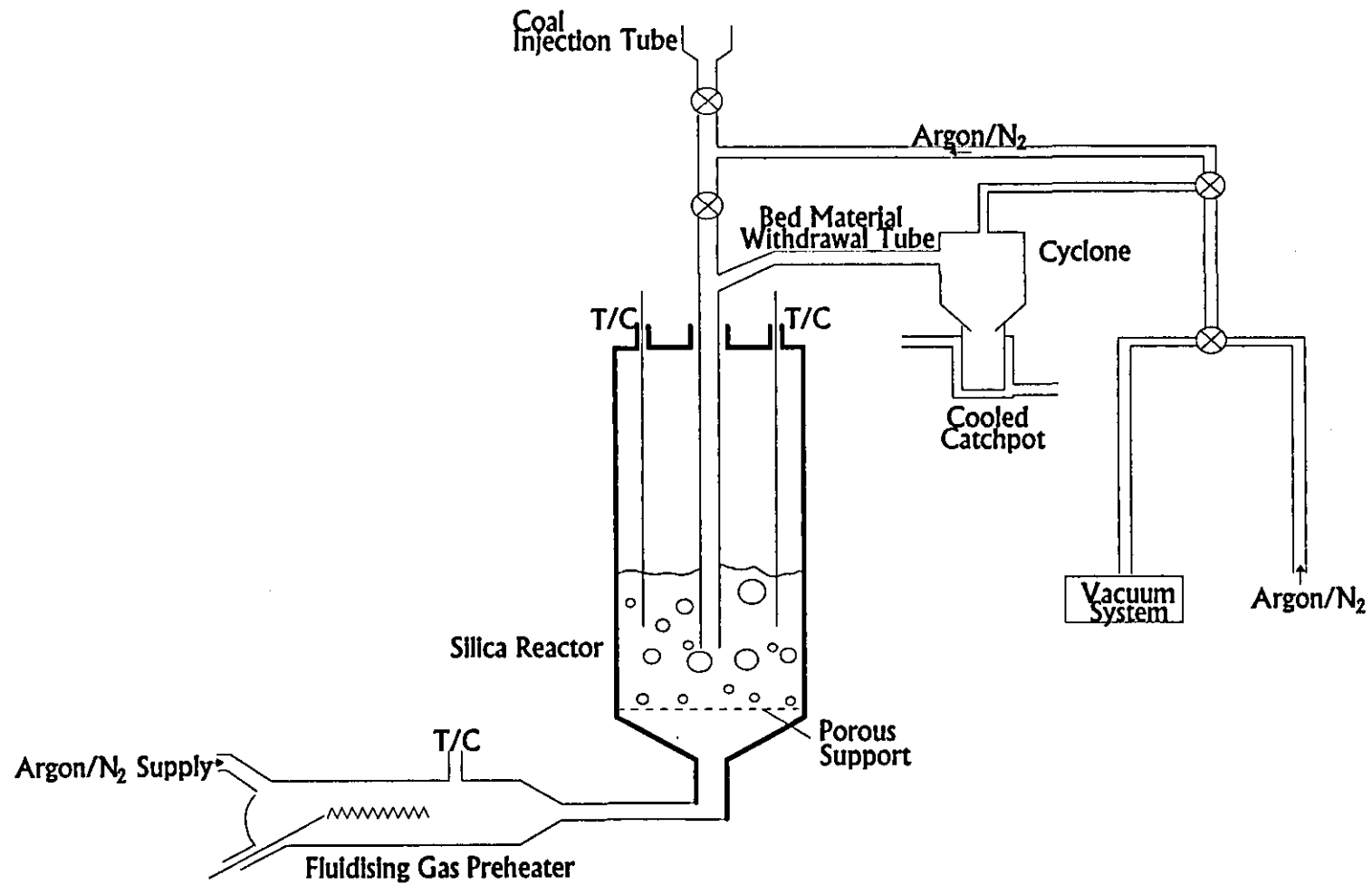


Figure 3.1 Fluidised Bed Reactor

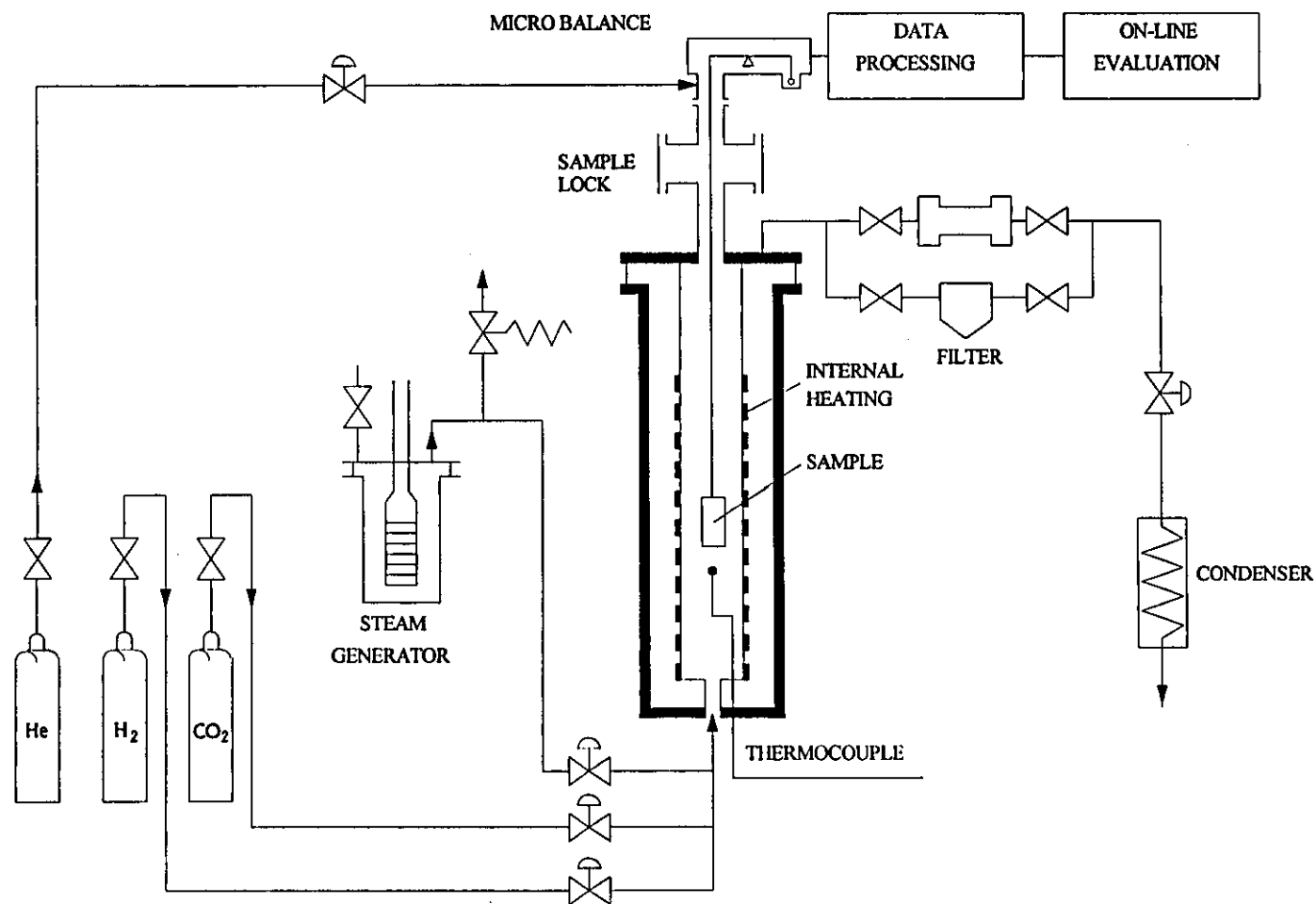


Figure 3.2 Schematic Diagram of the Pressurised Thermogravimetric Analyser

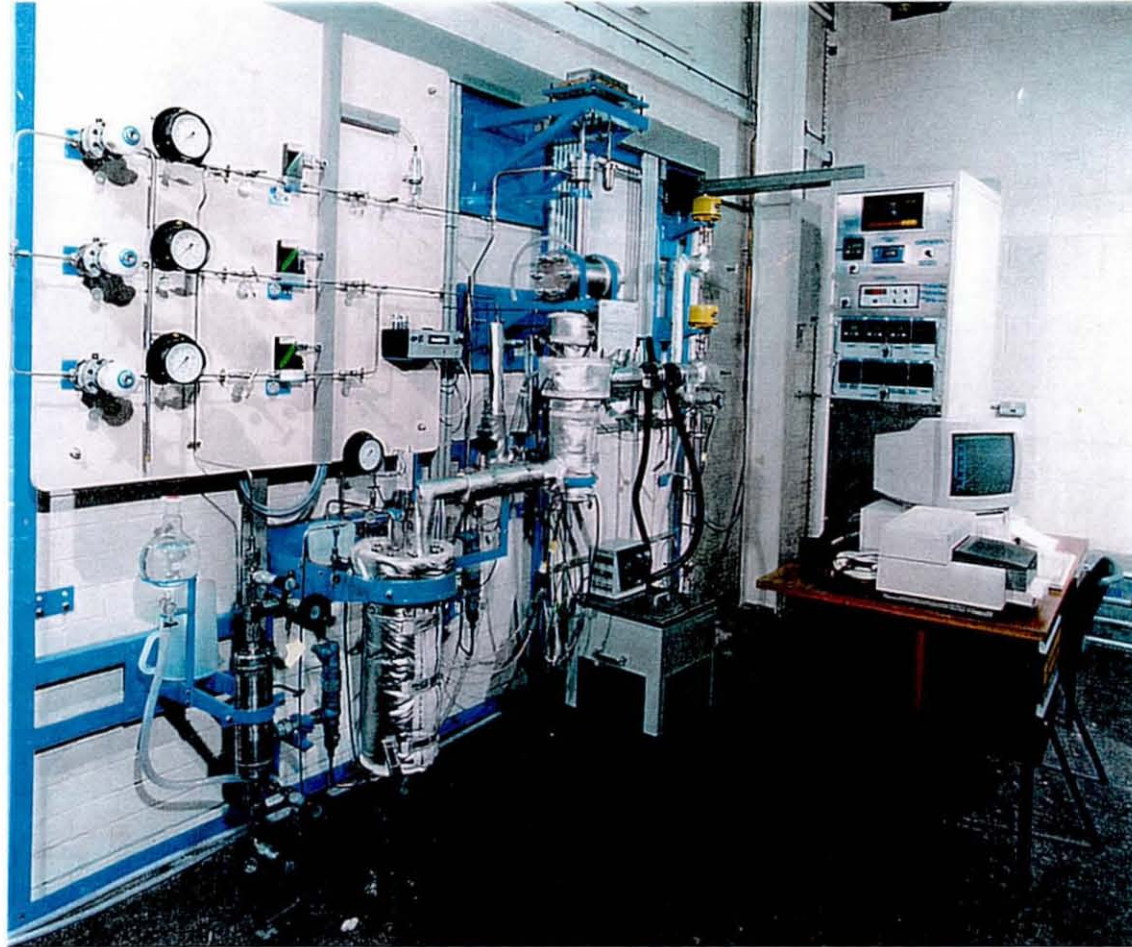


Figure 3.3 The Pressurised Thermogravimetric Analyser

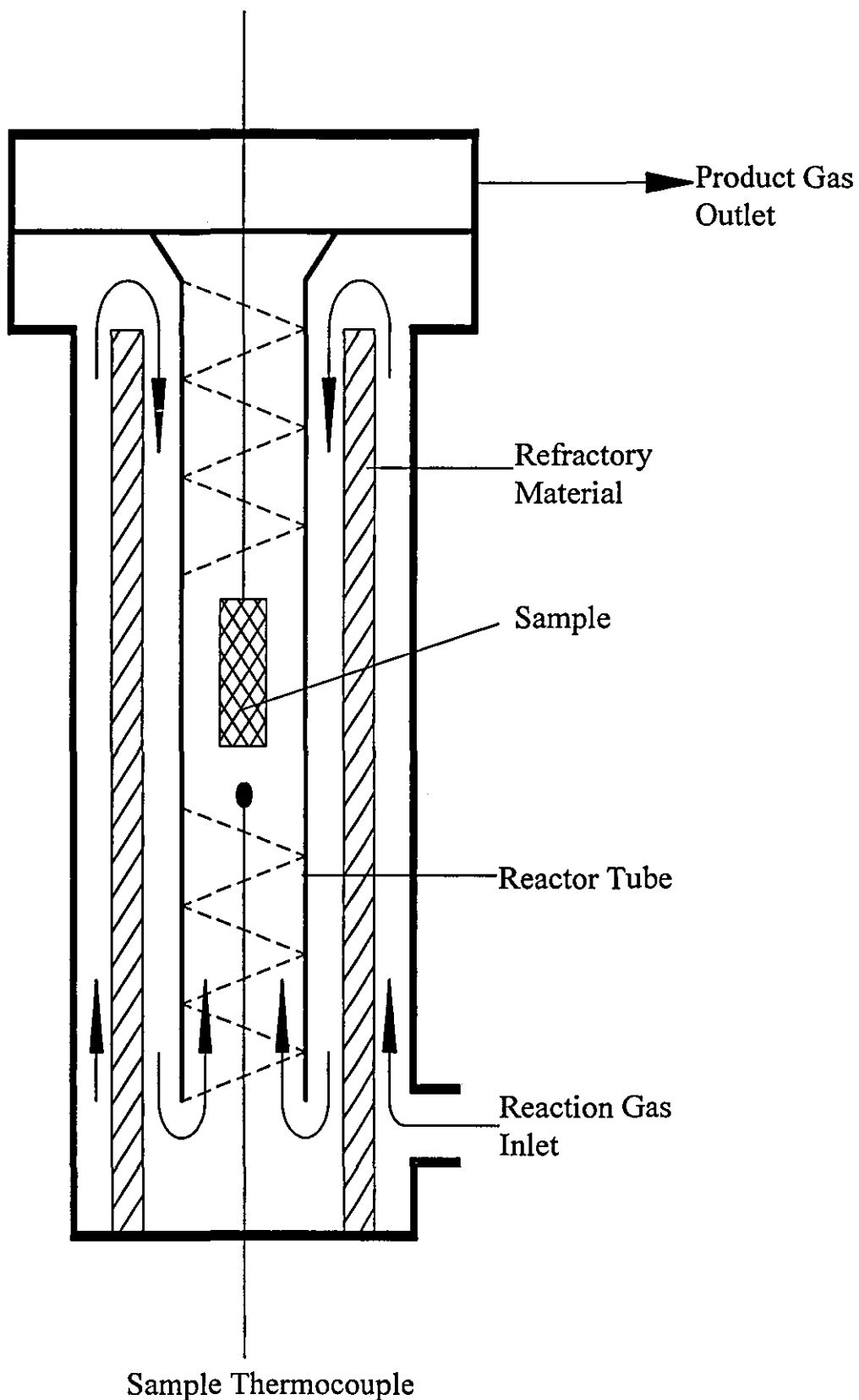


Figure 3.4 Diagram of Gas Flow Through The PTGA Reactor

Chapter 4

Results and Discussion

4.1 Introduction

Samples of various coals, coal chars and coal maceral concentrates have been gasified in the p.t.g.a. described in Chapter Three. Figure 4.1 shows a typical weight loss trace from the p.t.g.a.. The information is presented in a slightly different way in Figure 4.2, as conversion against time. The rates of reaction may be defined as the change in the mass of carbon (expressed by the degree of gasification X or "burn-off") as a function of time.

There are three definitions given by Van Heek and Mühlen⁽¹⁷⁾ for reaction rates and a judgement is needed on which definition should be used to express the rate from the experimentally determined weight losses. The definitions of reaction rate are given in Chapter 2. These are designated as r' , r'' and r_s . For a given programme of work a choice of the most appropriate rate parameter must be made.

Figure 4.3 shows r' , r'' and r_s for a particular test plotted against conversion. This test was chosen as being typical of the other tests to illustrate the difference between the rate parameters. At $X=0$ the value of all three rate measurements is 20%/min. At $X=0.5$ r'' has increased to 30%/min, r_s has increased to 24%/min and r' has decreased to 17%/min. At $X=0.7$ r'' has increased further to 33%/min, r_s has fallen back slightly

to 22%/min and r' has decreased further to 12%/min. Clearly the graph of r_s versus conversion gives a plot which is more nearly horizontal, when compared to the other rate parameters. Therefore, for this work, the gasification is best described by a reaction order of $\frac{2}{3}$. Thus r_s has been used as the basis of comparison between experiments. The choice of the most appropriate parameter for rate measurement is also discussed in chapter 2. It must be noted that at $X = 0$, all three parameters are numerically equal, whilst at $X > 0$ it is always the case that $r' < r_s < r''$. For example at $X = 0.5$, $(1-X)^{-1} = 2$, and $(1-X)^{-\frac{2}{3}} = 1.59$. Therefore, $r'' = 2.00r'$ and $r_s = 1.59r'$. Similarly at $X = 0.99$, $(1-X)^{-1} = 100$, and $(1-X)^{-\frac{2}{3}} = 21.54$. Thus it should be expected that r'' tends to infinity as X tends to 1. r_s should also tend to infinity as X tends to 1, but less quickly than r'' . This is not always observed in practice, possibly because dX/dt tends to 0 more rapidly than does $(1-X)$, and also because at high conversions the remaining sample weights are so small that there could be significant scope for errors.

A $\frac{2}{3}$ reaction order is typical of reactions at spherical surfaces so the fact that r_s is the most appropriate rate parameter implies that this is a good approximation here.

4.2 Relative Reactivities of Coals

Gasification tests on a range of coals were carried out using the p.t.g.a., in order to determine whether any of the coal properties analysed correlated with gasification reactivity and to try to obtain a better understanding of how these properties influence coal reactivity at elevated pressures. Gasification reactivities were determined for

seventeen coals at the following conditions:

Temperature	950°
Coal size	1 to 2 mm
Gasifying agent	Steam
Pressure	2.5 MPa
Approximate sample weight	70 mg

Figures 4.4 and 4.5 show the gasification rates, r_s , for the range of conversions or carbon burn-off (X) for seven overseas coals, eight UK coals and two lignites. Table 4.1 lists the rates r_s , at 75% conversion. This conversion is the value adopted by CTDD for their gasifier model. The general trend of reactivity, r_s , with carbon conversion as illustrated, for example, in Figures 4.4 and 4.5 shows an increase in reactivity in the first stages of gasification followed by a maximum and finally a decrease in reactivity as the sample of char burns out. This trend is explained by the development of surface area as the char is gasified followed by a decrease in surface area and active sites as the pores enlarge and the char particles decrease in size in the later stages of gasification.

The reactivities, r_s , at 75% conversion for the range of coals are given in Table 4.1 in order to categorise the coals and to inspect the data for trends. The categories are given as follows:

Reactivity	r_s at 75% conversion (%/min)
Low	20-30
Medium low	30-40
Medium	40-60
High	60-100
Very high	100-300

Table 4.1: Reactivities at 75% Conversion for Various Coals

Coal	Reactivity at 75% Conversion	Category
Taff Merthyr	20	Low
El Cerrejon	22	Low
Rietspruit	28	Low
Hunter Valley	29	Low
Longannet	30	Medium Low
Drayton	33	Medium Low
Janowice	35	Medium Low
Maltby	40	Medium
Silverwood	42	Medium
Illinois No 6	43	Medium
Harworth	47	Medium
Daw Mill	49	Medium
Thoresby	58	Medium
Littleton	72	High
Gardanne	85	High
Teruel Mequinenza	180	Very High
Rheinbraun	255	Very High

The r_s at 75% conversion is the value used for the reaction rate in CTDD's gasifier model and is consequently of significance but the reactivity at other carbon conversions could also be used for ranking purposes.

As shown in Table 4.1, at the lower end of the arbitrary reactivity scale there are two bituminous southern hemisphere coals, Hunter Valley NSW, (Australia) and Rietspruit (South Africa) along with the low volatile steam coal from South Wales, Taff Merthyr and the Columbian coal, El Cerrejon. The other southern hemisphere coal, Drayton, had a medium low reactivity. Most of the UK coals are ranked in the medium reactivity group. The sub-bituminous French coal from the Gardanne region and the UK Littleton coal gave medium to high reactivities. As expected, the German Rheinbraun lignite was most reactive with an r_s at 75% conversion of 255%/minute.

There are obvious differences in the gasification reactivities of the various coals and it is useful to survey the factors which influence reactivity pertinent to the properties of the coal. Temperature, pressure, H_2 , CO , pyrolysis history and particle size were investigated in a previous report⁽²⁾ and whilst it is not the purpose here to review these factors again, the findings of the report may be briefly summarised as follows.

The pyrolysis conditions under which chars are produced have an important bearing on their subsequent gasification reactivity. For a given coal the longer the pyrolysis time and the higher the pyrolysis temperature (within certain limits) the lower the reactivity of the char. Particle size also influences char reactivity, the smaller the particle size, the more reactive the char. This seems to be due to the effects of pore

diffusion, rather than just increased surface area. The effects are similar with both CO_2 and H_2O . Gasification rate increases with temperature. It also increases with pressure up to a point. At pressures above about 1.7 MPa, pressure does not significantly affect gasification rate. Hydrogen inhibits the rate of gasification by steam and carbon monoxide inhibits the rate of gasification by carbon dioxide.

Properties of the coal which may influence reactivity are ash, calcium, carbon content, rank, oxygen content, porosity and maceral composition.

Miura et al ⁽⁴¹⁾ reviewed the literature on factors affecting gasification reactivity. They reported that no distinction was made between the gasification agents O_2 , CO_2 and steam because the factors controlling the gasification reaction rate seem to be the same for O_2 , CO_2 and steam. The differences are in the rates of carbon gasification reaction, eg, $\text{O}_2 \gg \text{H}_2\text{O} > \text{CO}_2$. Miura ⁽⁴¹⁾ used the data of Kasaoka et al ⁽⁶²⁾, Swjuki et al ⁽⁶³⁾, Takarada et al ⁽⁶⁴⁾ and Hashimoto et al ⁽⁶⁵⁾ from 95 chars prepared from 68 different coals and compared percent carbon with reaction rate at 50% conversion. It was shown that the relation between carbon content and reactivity changed at $\text{C} \approx 80\%$. The values of gasification reactivity rates of lower rank coals ($\text{C} < 80\%$) differ widely and are much larger than higher rank coals ($\text{C} > 80\%$) which have values differing by small amounts. Hashimoto et al ⁽⁶¹⁾ investigated the steam gasification of 25 coals and the only correlation found was with carbon content, again showing an abrupt change between 75-80% C (daf). The reactivity r_s of coals studied in this report are shown for different carbon contents (dmmf) in Table 4.2 and Figure 4.6. The two lignites clearly have the highest reactivity and the lowest carbon contents, though

Illinois No 6 coal also has a low carbon content, but has a very low reactivity. It stands apart from the main group of bituminous coals for which no correlation between carbon content and reactivity could be found. This group includes the southern hemisphere coals which all behave very similarly. They have carbon contents between 82.6 and 83.6% and quite low reactivities (r_s between 28 and 33% min^{-1}) At the end of the scale, low reactivity ($r_s = 20\% \text{ min}^{-1}$) was recorded for the anthracite, with a carbon content of 92%.

Linear regression was undertaken for each plot of coal property vs reactivity. Table 4.3 shows the R^2 values obtained. In most cases a linear relationship is not expected, however, linear regression is still an interesting way to compare the data. The R^2 value for the plot of carbon content vs reactivity is 0.67, which suggests a poor correlation, though still better than was obtained with most of the other properties studied.

Other measures of coal rank include volatile matter and mean random vitrinite reflectance. Table 4.2 shows that the volatile matters are low at 14% for the anthracite which has low reactivity, and high at 53 and 55% for the lignites, which have high reactivity. This can be seen in the plot of reactivity vs volatile matter given in Figure 4.7. Gardanne coal also stands apart from the main central group owing to its rather higher volatile matter. Its reactivity is somewhat higher than the bituminous coals, but much less than the lignites, though its volatile matter content is similar. However, whilst the trend of increasing reactivity with increasing volatile matter is apparent at extremes of reactivity, this does not seem to hold true for coals of

intermediate reactivity. Therefore, for most of the coals, volatile matter would not be a useful indicator of reactivity. The R^2 value for the plot of volatile matter vs reactivity is 0.48 which shows that the correlation is poor.

Miura ⁽⁴¹⁾ reported that the correlation between steam gasification reactivity and mean vitrinite reflectance (MVR) of the coal was unsatisfactory but the controlling factor changed at an MVR of 0.8%. This factor combined with the abrupt change of reactivity at percent carbon of 80% shows that factors related to coal rank control the gasification rates of higher rank coals.

Table 4.2: Reactivity of Various Coals vs Fundamental Coal Properties

Coal	Reactivity $r_s(\% \text{min}^{-1})$ at 75% conversion	Carbon (% dmmf)	VM (% daf)	Oxygen (% dmmf)	Mean Vitrinite Reflectance (%)	$\text{Na}_2\text{O}+\text{K}_2\text{O}$ + $\text{CaO}+\text{MgO}$ (% in coal)
Longannet	30	82.9	35.6	10.0	0.56	0.42
Daw Mill	49	81.3	42.1	11.5	0.60	0.89
Thoresby	58	84.3	38.7	7.9	0.71	0.55
Silverwood	42	85.6	37.3	6.3	0.88	0.48
Maltby	40	85.6	38.8	6.9	0.85	0.38
Harworth	47	86.6	36.8	5.2	0.87	0.70
El Cerrejon	22	82.2	39.3	10.4	0.72	0.85
Hunter Valley	29	83.4	36.9	9.1	0.67	0.31
Rheinbraun	255	67.5	53.0	27.2	0.28	1.87
Janowice	35	83.0	38.3	9.7	0.76	0.60
Illinois No 6	43	76.5	43.4	17.1	0.40	0.77
Gardanne	85	80.4	55.3	11.8	0.48	7.5
Rietspruit	28	83.6	36.3	9.2	0.73	0.41
Drayton	33	82.6	38.9	10.5	0.65	0.31
Teruel Mequinenza	180	76.1	60.6	13.8	0.29	3.51
Taff Merthyr	20	91.5	14.1	2.0	1.9	0.53
Littleton	72	83.3	37.1	8.7	0.72	0.61

Table 4.2 shows that a low reactive coal (the anthracite) had an MVR of 1.9% compared to two highly reactive coals (the two lignites) with MVRs of 0.48% and 0.28%. Again in the medium reactivity ranges, twelve of the selected bituminous coals had an average MVR of 0.7%. Figure 4.8 illustrates the trends in MVR against gasification reactivity in steam. These data appear to confirm the change in reactivity at 0.7% mean vitrinite reflectance reported by Miura⁽⁴¹⁾. Gradanne coal seems to follow the trend, with a somewhat lower MVR of 0.48% and slightly higher reactivity at the rest of the main group with $r_s = 85\% \text{min}^{-1}$. Illinois No.6 appears to buck the trend again with an MVR of 0.4% but only medium low reactivity. However, steam and CO₂ gasification reactivities of the char shown in Table 4.4 indicated a higher reactivity than exhibited by the coal (see section 4.2). It is likely that the low rank coals with low MVR have not aged as much as the high rank coals with higher MVR. The vitrinite reflectance is a direct observation of the coalification process with extremes for lignite (MVR=0.28%) and for the anthracite (MVR=1.9%). Linear regression of the plot of MVR vs reactivity gives an R^2 value of 0.27, showing very poor correlation. In fact, inspection of Figure 4.8 shows that the relationship between MVR and reactivity appears more exponential than linear. Therefore linear regression was undertaken of a plot of log reactivity vs MVR. However, the R^2 value for this plot was very low at 0.37 hence the relationship is not exponential.

Oxygen content can also be used as an indication of coal rank, typically decreasing as coal rank increases. Figure 4.9 shows a plot of oxygen content vs reactivity. The R^2 value for this plot is 0.6, which whilst showing poor correlation is still one of the best agreements of all the properties tested. The Rheinbraun lignite has the highest

oxygen content of any of the coals at 27.2%. It also has the highest reactivity at $r_s = 255\% \text{min}^{-1}$. The anthracite, Taff Merthyr, has the lowest oxygen content at 2.0, and the lowest reactivity at $r_s = 20\% \text{min}^{-1}$. The southern hemisphere coals are not markedly different from the other bituminous coals, but Illinois No6, once again stands out from the main group with a relatively high oxygen content (17.1%) and a relatively low reactivity. The reactivity of Teruel Mequinenza, the other lignite is much higher yet the oxygen content is slightly lower at 13.8%.

It is well established that minerals in the coal affect the reactivity of lower rank coals and calcium and magnesium oxides are the most important catalysts for this increase in reactivity. Takarada et al ⁽⁶⁴⁾ investigated the relationship between gasification reactivity for chars of lower rank coals and found that for non-caking coals with carbon less than 78%, the reactivity was directly proportional to the amount of Ca and Na ion exchanged by ammonium acetate. Miura ⁽⁴¹⁾ reported little difference in gasification reactivity for demineralised chars of lower rank coals. Van Heek and Mühlen ⁽¹⁷⁾ reported that reactivities of demineralised lignites showed a drastic decrease in gasification reactivity to values similar to low reactivity hard coals. They also reported that coal minerals did not affect the reactivity of hard coals. In lignite, the probable catalyst was calcium which needs to be in intimate contact with the carbon. It is likely that all the alkali and alkaline earth oxides or carbonates act as catalysts, eg, Na_2O , K_2O , CaO and MgO . The percentage of alkaline oxides in the coals investigated here is also shown in Table 4.2 along with gasification reactivity. The values are plotted out in Figure 4.10. The R^2 value for this plot, as expected from the previous work above, is very low at 0.21. The alkalis for low and medium

reactivity coals were in the range 0.3% to 0.9% whereas the three most reactive coals had alkalis at 8.2%, 4.2% and 2.3%. However, of these three coals the one with highest alkali content is least reactive and vice versa.

Three coals in this study have a carbon content of less than 80%, which is the value below which previous work (eg Miura et al) have shown that Ca content influences reactivity. The least reactive of this group is Illinois (76.5% carbon) which has relatively a very low Ca content at 0.433%. The lignite, Teruel Mequinenza, has an almost identical carbon content (76.1) but has a much higher Ca content and is very much more reactive. The most reactive of the group, the lignite Rheinbraun, has an intermediate Ca content, but a very much lower carbon content, suggesting that relatively speaking, carbon content exerts a bigger influence on reactivity than Ca content. Gardanne coal falls slightly outside the 80% carbon limit with a carbon content of 80.4%. However it has the highest Ca content of all and is the third most reactive coal. This again suggests that carbon content may override catalytic considerations in determining reactivity. The anthracite, Taff Merthyr, has a slightly higher alkali content than several of the other coals, but has the lowest reactivity of all.

The contribution of the above four components has also been considered individually. In many cases, and certainly for the three most reactive coals, it is CaO which forms the bulk of the total alkali content. Hence a plot of CaO content against reactivity (Figure 4.11) has a very similar form to the plot of total alkali content against reactivity. For the majority of coals there is no clear correlation between CaO and

reactivity. Of the two coals with the lowest CaO content, <0.1%, one is classified as low reactivity and one as medium. The three coals with very high CaO content are the three most reactive, but with reactivities which *decrease* with *increasing* CaO content, and as stated for total alkali content, consideration of the carbon content of these coals suggests that it is that which exerts the stronger influence over reactivity.

A particularly interesting result is that for K_2O which is shown in Figure 4.12. In general the level of K_2O seemed to have no effect on reactivity, however, it is noticeable that the two lignites which are most reactive, and the anthracite which is least reactive, have some of the lowest K_2O levels (<0.05%).

The plot of MgO vs reactivity (Figure 4.13) shows a strong correlation between MgO levels and reactivity. The two highly reactive lignites both have high MgO contents, and the anthracite and the southern hemisphere coals have low MgO contents and low reactivity. However, when only the bituminous coals are considered the trend is far less clear.

There is clearly no relationship between the Na_2O content of the coals studied and their reactivity. Rheinbraun coal has a low Na_2O content but very high reactivity whereas the southern hemisphere coals have a low Na_2O content and low reactivity. The anthracite has an intermediate Na_2O content but low reactivity but Teruel Mequinenza has intermediate Na_2O content and high reactivity.

Linear regression was undertaken for Figures 4.11 to 4.14 and the R^2 values were low

in all cases except for MgO which had an R² value of 0.87. The R² value for the Na₂O plot was 0.0.

Table 4.3 Correlation Between Reactivity and Various Coal Properties

Coal Property	R²
Carbon	0.67
Volatile matter	0.48
Mean Vitrinite Reflectance	0.27
Oxygen	0.60
Total Alkalis	0.21
Na ₂ O	0.00
K ₂ O	0.12
CaO	0.17
MgO	0.87
MVR vs log reactivity	0.37
K ₂ O vs log reactivity	0.07

4.2.1 Char Reactivity

Chars have been produced from the eight overseas coals, and two of the UK coals. A comparison of the steam gasification reactivities of the chars can be made with the parent coals from Figures 4.4 and 4.5. The reactivities at 75% conversion are given in Table 4.4, together with the reactivities of the parent coals for comparison.

The reactivities of most of the chars tend to follow the trends of the parent coals, though there are some exceptions. El Cerrejon and Drayton are still low/medium low reactivity. Janowice and Thoresby are medium low/medium and Gardanne is still quite reactive but has changed to medium from high. The char made from Illinois No.6 coal has developed more reactivity shown both in steam and CO_2 . The reduction of reactivity (r_s) for CO_2 from that of steam is clear in Table 4.4. Gasification in CO_2 appears to show differences between the chars more demonstratively than gasification in steam. The most dramatic change in reactivity occurred with the Rheinbraun lignite, which was reduced from 255%/min for the parent coal in steam, down to 32%/min for the char in steam.

Table 4.4: Comparison of Reactivities for Coals and Chars to Steam, and for Chars to Steam and CO₂

	r_s Steam (coal) % min ⁻¹	r_s Steam % min ⁻¹	r_s CO ₂ % min ⁻¹
Daw Mill	49	38.5	10.7
Janowice	35	46.5	11.5
El Cerrejon	22	35	6
Illinois No 6	43	48	30
Thoresby	58	53	12.5
Rietspruit	28	46	8
Gardanne	85	52	23.5
Pittsburgh	nd	53.5	-
Drayton	33	30	7
Rheinbraun	255	32	7

Relationships have also been sought between char reactivity, and the properties of the char, or if appropriate, the parent coal. Char analysis for this work was very limited, primarily because of the small quantities of coal produced in the f.b.r. but also due to time and cost considerations. The char analysis undertaken for this project was confined to microproximate analysis, details of which are given in chapter 3 and reference 60 and 61 but which is claimed to give good agreement with BS1016. The results of the microproximate analysis are given in Table 4.5.

Table 4.5: Microproximate Analysis of Chars

	Ash %	Moisture %	Volatile Matter %
Daw Mill	28.6	5.2	nd
Janowice	23.8	0.1	0.9
El Cerrejon	26.7	0.1	2.2
Illinois No 6	19.3	3.4	3.6
Thoresby	51.4	0.0	0.6
Rietspruit	18.7	0.6	2.0
Gardanne	45.2	1.4	nd
Pittsburgh	69.1	0.0	nd
Drayton	43.7	0.2	nd
Rheinbraun	nd	nd	nd

Figure 4.17 shows the reactivity to both steam and to CO₂ of the chars, plotted against the mean vitrinite reflectance of the parent coal. As with the coals themselves there is a general trend for reactivity to decrease with increasing MVR, however whilst the agreement is poor for steam, it is better for CO₂.

It was thought that ash constituents might remain relatively unchanged during pyrolysis, and it would therefore be interesting to compare char reactivity with total alkalis in the parent coal to discover whether there were still any obvious effects on the char. The results are shown in Figure 4.18. The correlations are poor but there is evidence of a trend of reactivity increasing with increasing alkali content especially in CO₂.

Finally char reactivity was plotted against volatile matter of the parent coal. It was thought higher volatile coals might lead, on pyrolysis, to the formation of a more porous char. This increased might lead in turn to greater reactivity. The results are shown in Figure 4.19, and again, whilst there is a trend of reactivity increasing with increasing volatile matter, the correlation is poor.

One striking feature of the results for the char gasification tests is that the reactivity of some coals had increased compared with their parent coals, and yet some had decreased. The pyrolysis process is usually very rapid compared with gasification, and since the p.t.g.a. samples are in the heated zone for some moments before weight readings are first logged, it had been thought that during coal tests even the first weight loss readings are due primarily to gasification rather than pyrolysis. However, one partial explanation for the differences in reactivity between chars and their parent chars is that in high volatile coals complete pyrolysis takes longer and therefore some of the weight changes being measured are due to pyrolysis. This would explain the decreases in reactivity but would not explain the increases.

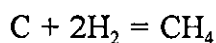
Figures 4.20 to 4.22 show carbon content, volatile matter, and mean vitrinite reflectance plotted against the difference in reactivity between the coal and the char. These figures show a trend whereby the change in gasification rate can be estimated approximately from coal properties related to its rank. For example, in general, coals with carbon contents less than about 83% show a decrease in reactivity when pre-pyrolised and coals with carbon contents above 83% show an increase. This cut off point corresponds to an MVR of about 0.7%, where a similar trend is observed. The trend is less clear when volatile matter is considered but the data do suggest that pre-pyrolysis of high volatile coals causes gasification rates to decrease compared with the parent coal, whereas pre-pyrolysis of low volatile coals causes the gasification rate to increase.

4.3 Gasification in Steam/Hydrogen Mixtures, and in Carbon Dioxide/Carbon Monoxide Mixtures

Chars produced from two of the coals, Gardanne and Rietspruit, were also gasified using steam/hydrogen mixtures and carbon dioxide/carbon monoxide mixtures.

4.3.1 Gasification in H_2O/H_2

Although H_2 is a gasification agent in its own right via the reaction



this reaction is very much slower than the $C-H_2O$ reactions. Previous work by Van Heek et al ⁽¹⁸⁾ has demonstrated that H_2 inhibits the rate of gasification of coals and chars in H_2O . H_2 is able to combine with active sites within the char, rendering them unavailable for the with H_2O . Also, in a closed system, the addition of hydrogen, a product of the steam gasification reaction, can alter the equilibrium position according to Le Chatelier's principle. In the p.t.g.a. however, product gases are swept away so that equilibrium is not established.

Samples of char were gasified at 950°C and 2.5 MPa pressure using mixtures 20% H_2 /80% H_2O , and 40% H_2 /60% H_2O in the p.t.g.a. and their reactivities to these mixtures were measured for comparison with their reactivities in pure steam under similar conditions.

Figure 4.23 shows the reactivity of Gardanne char to the above gas mixtures. Gardanne is one of the most reactive of all the chars tested. In pure steam the initial reactivity is about $37\% \text{ min}^{-1}$, which decreases to about $29\% \text{ min}^{-1}$ in 20% H_2 and 15% in 40% H_2 .

There is a pronounced difference between the shape of the curves for $\text{H}_2\text{O}/\text{H}_2$ mixtures and that for pure steam. In pure steam the reactivity increases with increasing carbon conversion until it reaches a maximum at approximately 70% conversion. In $\text{H}_2\text{O}/\text{H}_2$ the reactivity decreases with conversion. In the case of the 40% H_2 /60% H_2O mixture the reactivity decreases to 0 at about 72% conversion.

Figure 4.24 shows the reactivity of Rietspruit char under the same conditions used for Gardanne. Rietspruit is less reactive under these conditions, with an initial reactivity in pure steam of about $29\% \text{ min}^{-1}$. The effect of H_2 upon reactivity is far more dramatic, with the reactivity falling to about $6\% \text{ min}^{-1}$ in 20% H_2 /80% H_2O , and about $3\% \text{ min}^{-1}$ in 40% H_2 /60% H_2O .

The shapes of the graphs are similar for both chars, with the reactivity increasing with increasing conversion in steam, and decreasing with increasing conversion in $\text{H}_2\text{O}/\text{H}_2$ mixtures.

It is also noticeable that the reactivity falls to zero (ie the reaction stops) well before 100% conversion is reached when $\text{H}_2/\text{H}_2\text{O}$ mixtures are used with Rietspruit as well as with Gardanne. This may be due to H_2 combining with active sites in the char

without gasification, but precluding gasification by H_2O .

4.3.2 Gasification in CO_2/CO

CO is known to inhibit to inhibit CO_2 gasification and the reasons are thought to be similar to those for the inhibition of H_2O gasification by H_2 , although the active sites involved may be different.

Samples of the chars were gasified using the following gas mixtures: 20% $\text{CO}/80\%\text{CO}_2$, 40% $\text{CO}/60\%\text{CO}_2$, 60% $\text{CO}/40\%\text{CO}_2$ and 80% $\text{CO}/20\%\text{CO}_2$. In most cases there was no reaction with 80% $\text{CO}/20\%\text{CO}_2$, or at least the reaction rate was too slow to be measured. Clearly there can be no reaction with pure CO , unlike the case with pure H_2 . The reactivities of the chars in these mixtures were compared with their reactivity in pure CO_2 . The reactions conditions used, as before, were a temperature of 950°C and a pressure of 2.5 MPa.

Figure 4.25 shows the reactivity of Gardanne char to the above mixtures under these conditions. In pure CO_2 the reactivity at 0% conversion is about $16\% \text{ min}^{-1}$. In 20% $\text{CO}/80\%\text{CO}_2$, this has fallen to about $7\% \text{ min}^{-1}$ and a similar result is obtained with 40% $\text{CO}/60\% \text{ CO}_2$. With 60% $\text{CO}/40\%\text{CO}_2$ the initial reactivity drops to about $2\% \text{ min}^{-1}$.

Unlike the case with $\text{H}_2/\text{H}_2\text{O}$ gasification the shapes of the curves using CO_2/CO mixtures are similar to that using pure CO_2 , with 100% conversion being obtained in

every case.

Figure 4.26 shows the reactivities of Rietspruit char under the same conditions. Rietspruit is considerably less reactive than Gardanne with an initial reactivity of 5.6% min⁻¹. In 20%CO/80%CO₂ the reactivity decreases to 1.8% min⁻¹ and in 40%CO/60%CO₂ it decreases further to 0.9% min⁻¹. In 60%CO/40%CO₂ the initial reactivity is about 0.3% min⁻¹. 100% conversion is achieved in 100% CO₂ and 20%CO/80%CO₂, however in 40%CO/60%CO₂ and 60%CO/40%CO₂, the maximum conversion appears to be about 80%. However, this is not absolutely clear because the reaction rates are so slow.

4.4 Gasification of Maceral Concentrates

The reactivities to steam of the maceral concentrates described in Section 3.2.1 were measured in the p.t.g.a. (Section 3.5.1). Chars were produced from the maceral concentrates in the f.b.r., and the reactivities of these chars to steam and to CO₂ were also measured. However, the results show that there are large differences between the behaviour of macerals of the same type from different sources. This is particularly true for vitrinites. This range of behaviour means that it is difficult to generalise about the results and the situation is complicated by the poor separation achieved with some of the samples. It was not possible to obtain any pure macerals, so all the samples contained varying proportions of the other macerals which would obviously have influenced their behaviour. The maceral concentrates produced were all subjected to microproximate analysis, the results of which are given in Table 4.5

Figure 4.27 shows the reactivities to steam of the parent coals from which the maceral concentrates were derived. The conditions used were 2.5 MPa steam at 950°C. It shows that Daw Mill is the most reactive of the coals and Longannet is the least reactive. These reactivities may be compared with those of the maceral concentrates which are presented below.

Figure 4.28 shows the reactivities of all the maceral concentrates studied using the same conditions. The trend is for the vitrinite concentrates to be the most reactive. This is contrary to earlier expectations, since the literature ⁽⁴⁾ suggests that liptinites are most reactive. The inertinite concentrates tended to be the least reactive, with liptinites being of intermediate reactivity. There are exceptions to this however.

Figure 4.29 compares the reactivities of all the different vitrinite concentrates. Drayton is the most reactive with a maximum reactivity of almost 70 %/min. However it is of great significance that the Longannet sample has the lowest reactivity with a maximum of about 35%/min. This sample is almost pure vitrinite with over 97% vitrinite and less than 1% inertinite, compared to the Drayton sample which has only 86% vitrinite and 9% inertinite. Since the reactivity of the Drayton inertinite concentrate is only 30%/min a sample of pure Drayton vitrinite might be expected to have a very high reactivity. The least pure sample is Daw Mill, which has a vitrinite content of only 78%, yet this has the second highest reactivity, with a maximum of almost 60%/min.

Figure 4.30 shows the reactivity of the liptinite concentrates. Again the most reactive

of the samples is Drayton with a maximum reactivity of about 50%/min. In fact however, this sample is predominantly vitrinite, with a liptinite concentration of only 9%, which probably accounts for its relatively high reactivity. The reactivities of Silverwood and Rietspruit are very similar, although the composition of the samples is quite different. Rietspruit has a relatively high inertinite content (32%) and at 7% the liptinite concentration is less than half of that in the Silverwood sample. Silverwood has the highest liptinite content (15%) and the highest reactivity of the three samples. It also has the lowest vitrinite content.

Figure 4.31 shows the reactivities of the inertinite concentrates for all the coals. The Rietspruit sample has a high initial reactivity of 40%/min at 10 % conversion, which decreases rapidly to 12%/min at 90% conversion. This sample has the highest inertinite concentration (58%) and the lowest vitrinite concentration (3%). The Daw Mill sample is also quite reactive having a maximum reactivity of about 40%/min. The reactivities of the Drayton and Silverwood samples are similar, though their maceral compositions are quite different. Silverwood has the lowest inertinite content of all the samples at 37%. It also has the highest vitrinite content. The inertinite content of the Drayton sample is relatively high at 53% and the vitrinite content is relatively low at 37%. Figures 4.32 to 4.36 show the reactivities of the different fractions for each coal. In all cases the vitrinite concentrates are more reactive than the other fractions. There are insufficient data from the liptinite and inertinite concentrates to say conclusively which is more reactive. All the liptinite concentrates contained more vitrinite than liptinite, making the results more difficult to interpret.

It is clear from these figures that the reactivities of all the coals tested were increased by increasing the vitrinite concentration. Increasing the concentration of the other macerals seems to decrease the reactivity to some extent.

One of the problems with interpreting these figures is that the lines indicating the reactivity of the different samples often cross at various degrees of conversion. Thus the relative reactivity of the samples can be different depending on the degree of conversion under consideration. CTDD have used 75% conversion as a standard, for comparing the reactivities of different samples when using their gasification model. 75% is thought to be about the average degree of conversion of the coal particles in the gasifier.

Table 4.7 gives the reactivity of all the samples at 75% conversion. These data are presented in the form of a bar chart in Figure 4.37. With Silverwood the vitrinite concentrate has a slightly lower reactivity than the parent coal at this particular conversion, though at other conversions it is higher. All the other vitrinite concentrates have significantly higher reactivities than the parent coals. The inertinite and liptinite concentrates have lower reactivities than the parent coals. Overall this work suggests that whilst the reactivity of a coal can be affected greatly by altering the proportions of particular macerals. However, the results have not shown that a maceral analysis by itself would be an especially useful tool for predicting reactivity. The work has suggested, however, that there may be a tendency for coals from the southern hemisphere to contain liptinites which are more reactive than their counterparts from the northern hemisphere, however, only tentative conclusions can

be drawn, with for example, the Drayton liptinite sample being mainly composed of vitrinite. The vitrinites from southern hemisphere coals also appear to be fairly reactive. The relatively high reactivity of the macerals from the southern hemisphere coals is surprising given the generally low reactivity of the parent coals.

Because of the difficulty and expense of maceral separation, only minimal quantities of maceral concentrate were obtained in each case. This greatly restricted the amount of analysis which could be carried out on each sample. Therefore the only analysis undertaken was microproximate analysis. Had a wider range of analyses been available, it would have been possible to attempt to relate maceral properties to their reactivity as was done for the whole coals in section 4.2. Here, however it was only possible to plot reactivity against volatile matter and this is done in Figure 4.38. There is no clear relationship, but as for the whole coals (see Figure 4.7) there is clearly a trend whereby reactivity increases with increasing volatile matter. Linear regression of the data gives an R^2 value of 0.26, rather lower than that for the equivalent case with the whole coals where the R^2 value was 0.48.

As noted earlier, one of the major difficulties in interpreting the influence of maceral concentration on reactivity stemmed from the incomplete separation. Therefore a multiple linear regression technique was used to calculate a theoretical reactivity value for pure macerals from each coal. This technique could only be applied to three coals, since only these three coals had at least four points for the regression. The four points represent the three maceral concentrates obtained from each coal and the parent coal itself. The reactivity of each of these samples, together with its actual maceral

composition, given in Tables 3.5 and 3.8 was used in each case for the calculation. The calculation was done using Microsoft Excel, and the spreadsheets containing the data are given in Appendices 2a, 2b, and 2c.

The regression calculates the constants (m_1 , m_2 and m_3) for an equation of general form

$$y = m_1x_1 + m_2x_2 + m_3x_3 + b$$

Here, y represents reactivity and x_1 , x_2 and x_3 are the percentages of each of the three maceral groups. In order to calculate a theoretical reactivity for a pure maceral, the appropriate x value is set at 100%, the other x values then of course must be 0. Thus to calculate the theoretical value of, for example, pure Rietspruit vitrinite, using the constants from appendix 2a, the calculation would be,

$$y = (1.688 \times 100) + -119.116 = 49.7$$

The calculated reactivities are given in Table 4.6 below.

Table 4.6: Theoretical Values for Reactivities of Pure Macerals

	Vitrinite	Liptinite	Inertinite
Drayton	91.8	-353.9	96.2
Silverwood	81.7	-176.5	-92.0
Rietspruit	49.7	-78.9	29.0

Clearly many of the results obtained are quite meaningless. This is probably due to the very limited amount of data available, four results for each coal is barely adequate for the multiple linear regression technique. Had more data been available, it is likely that more realistic results could have been obtained.

4.4.1 Gasification of Chars Derived from Maceral Concentrates

In the p.t.g.a., pyrolysis and gasification occur simultaneously, though the pyrolysis reactions occur more quickly.

Samples of all the maceral concentrates tested previously were pyrolysed in the laboratory scale f.b.r. to produce chars. The reactivity of these chars to steam and to CO₂ was measured in the p.t.g.a. at a temperature of 950°C and a pressure of 2.5 MPa. The pyrolysis conditions in the f.b.r. will be quite different to those in the p.t.g.a., where the heating rate is much slower.

4.4.1.1 Steam Gasification

Figure 4.39 shows the reactivities of all the char samples to steam at 950°C and 2.5 MPa. It is apparent that pyrolysis has completely changed the relative reactivities of the samples. For example the Drayton vitrinite concentrate which was previously the most reactive sample is now one of the least reactive. Also the range of reactivities of the chars is much smaller. At 75% conversion, the most reactive char, Daw Mill Vitrinite, has a reactivity of about 48%/min and the least reactive, the Longannet

liptinite/inertinite sample, has a reactivity of about 18%/min. For the unpyrolysed coals, this range extends from about 10%/min up to about 68%/min. Figures 4.40 to 4.44 show the reactivities of the maceral concentrates plotted for each coal. Table 4.6 shows the reactivities at 75% conversion of all the samples, and these values are plotted in Figure 4.45. 75% conversion was again chosen as the basis of comparison for the reactivities, since this is thought to be an average of conversion of coal in the gasifier. However the choice of degree of conversion is somewhat arbitrary, and the results could appear different if a different value were chosen. For chars, a case can be made for choosing 0% conversion as the basis of comparison, which has been done extensively in the past. This option is not usually available for coals studied in the p.t.g.a., as the weight loss during the first few seconds cannot be recorded. During these few seconds, there is often a significant weight loss due to pyrolysis.

Pyrolysis in the f.b.r has clearly reduced the reactivity of almost all the samples. With the raw coals the vitrinite concentrates were the most reactive, however this is not always true for the chars. The most dramatic change has occurred for the Drayton samples. Whilst the reactivity of the inertinite concentrate has remained virtually unchanged following pyrolysis, the reactivity of the vitrinite concentrate has decreased dramatically. It is possible to speculate that, since the inertinite concentrate contains 39.1% vitrinite, the reactivity of the inertinite itself has actually increased, and this has been offset by the reduction in reactivity of the vitrinite. This view is reinforced by consideration of the results for the Silverwood samples. Here the reactivity of the inertinite concentrate has increased from 33%/min to 41%/min. The reactivity of the vitrinite concentrate has decreased from 43%/min to 36%/min.

It is apparent that some of the vitrinite concentrates undergo a much more dramatic reduction in reactivity during pyrolysis than others. In order to examine this further, the ratio of reactivity after pyrolysis to the reactivity before pyrolysis was plotted against mean vitrinite reflectance (MVR) which may be taken as an indication of rank. The results of this are shown in Table 4.9 and depicted in Figure 4.46. There may be a trend of the reactivity ratio decreasing with increasing MVR, though two of the coals fall well outside the trend.

One possible explanation for this would be the fact the high volatile coals might produce more porous chars, due to the formation of pores by escaping volatile matter which could occur if the coal goes through a highly plastic stage on pyrolysis. Chars may have a high reactivity ratio, (ie, the char is very reactive compared to the parent coal) if they are very porous, since they will have a lower resistance to pore diffusion. However it is known that in practice there is only a poor correlation between reactivity and porosity or total surface area ⁽⁶⁾. It is therefore more likely that pyrolysis affects the active surface area, by the destruction of active sites. The extent of this destruction will depend upon the nature of these sites and their relative abundance in the parent coals.

4.4.1.2 CO₂ Gasification

Figure 4.47 shows the reactivity of chars produced from maceral concentrates. The range of reactivities is fairly small, roughly 3 to 10% min⁻¹ at 75% conversion, with the exception of the Longannet vitrinite concentrate which has a reactivity of 23%/min by comparison with the other samples this sample is so reactive that there seems to be a possibility that the result is spurious.

Figures 4.48 to 4.52 show the reactivities of all the char samples for each coal. The reactivities at 75% conversion are shown in Table 4.10 and plotted in the form of a bar chart in Figure 4.53. As with steam gasification the relative reactivities of the coals has changed. In the case of Daw Mill the vitrinite concentrate is still the most reactive, however in many cases, the vitrinite sample is the least reactive. For example with Rietspruit, in steam the inertinite sample is most reactive and in CO₂ the liptinite sample is most reactive, but in both cases, the vitrinite sample is least reactive. With Drayton it is the inertinite sample which is most reactive to CO₂ and the liptinite sample which is most reactive to steam, but still the vitrinite sample which is least reactive. This is perhaps the most surprising result since before the Drayton Vitrinite concentrate was the most reactive sample before pyrolysis.

A recent study by Chatzakis ⁽⁶⁸⁾ measured the reactivity of maceral concentrates to CO₂ in a 'hot rod' fixed bed reactor. The samples were heated in this reactor at a constant heating rate of 10 K s⁻¹ until a desired maximum temperature (1000°C) was reached. The samples were then maintained at this temperature for a pre-determined

'hold time'. Two hold times were chosen, namely 10 s and 200 s. With the shorter hold time, it was found that the gasification reactivity decreased in the order vitrinite>liptinite>inertinite, which is the same trend given by the p.t.g.a. measurements on the unpyrolysed maceral concentrates. The longer hold time gave a trend of decrease in reactivity of Inertinites>vitrinites>liptinites which was said to be due to the more open pore structure of the inertinite chars and their higher ash content, and the highly fused morphologies and limited surface areas of the liptinites. The trend can be compared with the p.t.g.a. measurements on the chars derived from the maceral concentrates although this is less clear.

In a previous study, Czechowski and Kidawa ⁽⁶⁹⁾ gasified pyrolysis chars of Janina coal in a thermobalance at 900°C and atmospheric pressure, and the reactivity to both steam and CO₂ decreased in the order vitrinite>coal>liptinite>inertinite, the same trend as for the unpyrolysed maceral concentrates tested in the p.t.g.a.. The results were explained in terms of the higher porosity of the vitrinite compared to the other macerals and the large concentration of catalytically active species (Ca, K, Na) in the vitrinite.

4.5 Conclusions

The following conclusions can be drawn from this survey of gasification reactivities and coal properties:

- Coals can be grouped into low, medium and high reactivities in steam gasification. The lignites studied exhibited the highest reactivity, and the anthracite exhibited the lowest reactivity. The southern hemisphere Coals studied also showed fairly low reactivity.
- Trends in reactivities are empirical with those coal properties which reflect coal rank and extent of coalification in the ground. Of these properties, it is the carbon content which shows the best correlation with reactivity for the coals studied.
- There appears to be an abrupt change in reactivity at carbon content of 80% above which coals and their chars lose reactivity.
- Coals with high levels of alkali and alkaline earth compounds show high catalytic reactivity.
- Where two properties both have an effect on reactivity, it is sometimes possible to suggest which of these effects is the overriding one. For example, increased carbon content in excess of 80% tends to result in a decrease in reactivity, regardless of mineral matter content, ie increased mineral matter

content does not compensate for the decrease in reactivity associated with very high carbon contents.

- The effects of H_2 and CO were to inhibit the rates of gasification reactions in steam and CO_2 . H_2 appeared not only to inhibit the rate of reaction but also to prevent full carbon conversion from being achieved. This may also be true for CO, though this is less clear from the results.
- The effect of pre-pyrolysis on coal reactivity seems to be dependent on coal rank. Coals with a carbon content of less than about 83% showed a decrease in reactivity compared to the parent coal when pre-pyrolysed, whereas those with a carbon content above 83% showed an increase. Other indicators of coal rank such as MVR, and, to a lesser extent, volatile matter, could also be used to show a similar effect.
- The limitations of the maceral separation technique used make the results obtained somewhat difficult to interpret; the poor separations have to some extent masked the behaviour of the macerals.
- Increasing the vitrinite concentration of a coal tends to increase its reactivity to steam whereas increasing the liptinite or inertinite concentrations tends to decrease its reactivity to steam.

- The results obtained from this work suggest that maceral analyses alone may be of limited use in predicting gasification reactivity.
- Following pre-pyrolysis, the reactivity of the macerals can alter significantly. The vitrinite tends to become less reactive but there is a wide range of variation in the extent of this reduction. In some cases the reduction is slight, in others a dramatic drop is observed.
- Liptinite and inertinite seem to be less affected by pre-pyrolysis. The reactivity decreases slightly in some cases and actually increases in others.
- Despite the limitations of the separation technique, it is clear that there are great differences between macerals of the same type derived from different coals. The classifications of vitrinite, liptinite and inertinite may be too broad to be meaningful in terms of gasification behaviour.

4.6 Recommendations for Further Work

There are many areas in which the work described above could usefully be extended. Firstly, the number of coals studied here is relatively small and it would be of interest to study a larger number to see if the same trends are confirmed. It would also be possible to make a more informed choice of coals based on the results of this work. Though a wide range of coal properties were considered, the coals chosen were predominantly 902 and 802 rank meaning that they are high volatile, non or weakly

caking coals. It would be interesting to study more higher rank coals, although the coals used here were chosen as much for practical as theoretical considerations.

In order to determine whether any coal property could be used to predict gasification performance, reactivity was plotted against each of the properties analysed. These plots were subjected to linear regression analysis which is not entirely appropriate since linear relationships are not really expected. Had more sophisticated software been available, this might have been used to determine a relationship between reactivity and other coal properties, which could have been used in the prediction of gasification performance.

The maceral separation technique used here was time consuming and expensive, however, it would have been preferable if all of the coals used could have been subjected to maceral separation. The number of coals separated was too low to base firm conclusions on, and made trends difficult to see. Nevertheless, some of the findings, eg that the vitrinite fractions tend to be most reactive agrees with the findings of other workers such as Czechowski and Kidawa ⁽⁶⁹⁾. If it were possible to achieve more complete separations, either by refining and improving the maceral separation technique, or by using an alternative technique such as density centrifugation, the results of the gasification tests would then presumably be more reliable and easier to interpret.

Table 4.7 Microproximate Analysis of Maceral Concentrates

	Ash	Moisture	Volatile Matter
Daw Mill V	2.5	5.1	39.9
Daw Mill I	2.4	2.7	30.2
Longannet V	3.3	5.7	23.9
Longannet L/I	25.6	1.8	2.5
Silverwood V	4.4	0.4	32.6
Silverwood L	7.6	0.3	34.4
Silverwood I	10.9	0.5	29.2
Rietspruit V	5.0	3.0	31.7
Rietspruit L	8.9	1.5	39.7
Rietspruit I	10.3	2.0	29.3
Drayton V	5.3	1.9	35.1
Drayton L	4.2	1.2	43.5
Drayton I	16.9	1.5	24.9

Table 4.8 Reactivities of Maceral Concentrates in Steam at 950°C and 2.5 MPa (75% Conversion)

	Reactivity (%/min)			
	Coal	Vitrinite	Liptinite	Inertinite
Silverwood	42	41	29	33
Drayton	33	66	52	30
Longannet	30	38	25	25
Daw Mill	49	56	-	36
Rietspruit	28	48	29	22

Table 4.10 Reactivity of Char Samples to Steam at 950°C and 2.5 MPa (75% Conversion)

	Reactivity (%/min)		
	Vitrinite	Liptinite	Inertinite
Silverwood	36	-	41
Drayton	22	36	29
Longannet	32	21	21
Daw Mill	48	-	33
Rietspruit	37	42	47

Table 4.9 Microproximate Analysis of Chars Derived From Maceral**Concentrates**

	Ash	Moisture	Volatile Matter
Daw Mill V	9.3	4.1	4.0
Daw Mill I	16.3	4.0	2.9
Longannet V	7.5	2.4	3.3
Longannet L/I	30.9	1.7	2.9
Silverwood V	49.5	0.1	1.4
Silverwood L	42.8	0.0	0.4
Silverwood I	33.6	1.4	2.3
Rietspruit V	56.1	0.0	1.0
Rietspruit L	39.8	0.0	1.8
Rietspruit I	29.5	2.2	1.2
Drayton V	23.9	1.3	3.2
Drayton L	35.4	0.4	0.1
Drayton I	29.3	1.2	2.1

**Table 4.11 Ratio of Vitrinite Reactivity Before and After Pyrolysis in the
f.b.r.**

	$r_s \text{ char}/r_s \text{ coal}$	MVR
Silverwood	0.84	0.88
Drayton	0.65	0.63
Longannet	1.07	0.56
Daw Mill	1.0	0.6
Rietspruit	1.23	0.73

**Table 4.12 Reactivity of Char Samples to CO₂ at 950°C and 2.5 MPa (75%
Conversion)**

	Reactivity (%/min)		
	Vitrinite	Liptinite	Inertinite
Silverwood	5.6	0.9	1.9
Drayton	3.8	7.0	7.7
Longannet	24	-	-
Daw Mill	12	-	8
Rietspruit	7.2	10.2	8.6

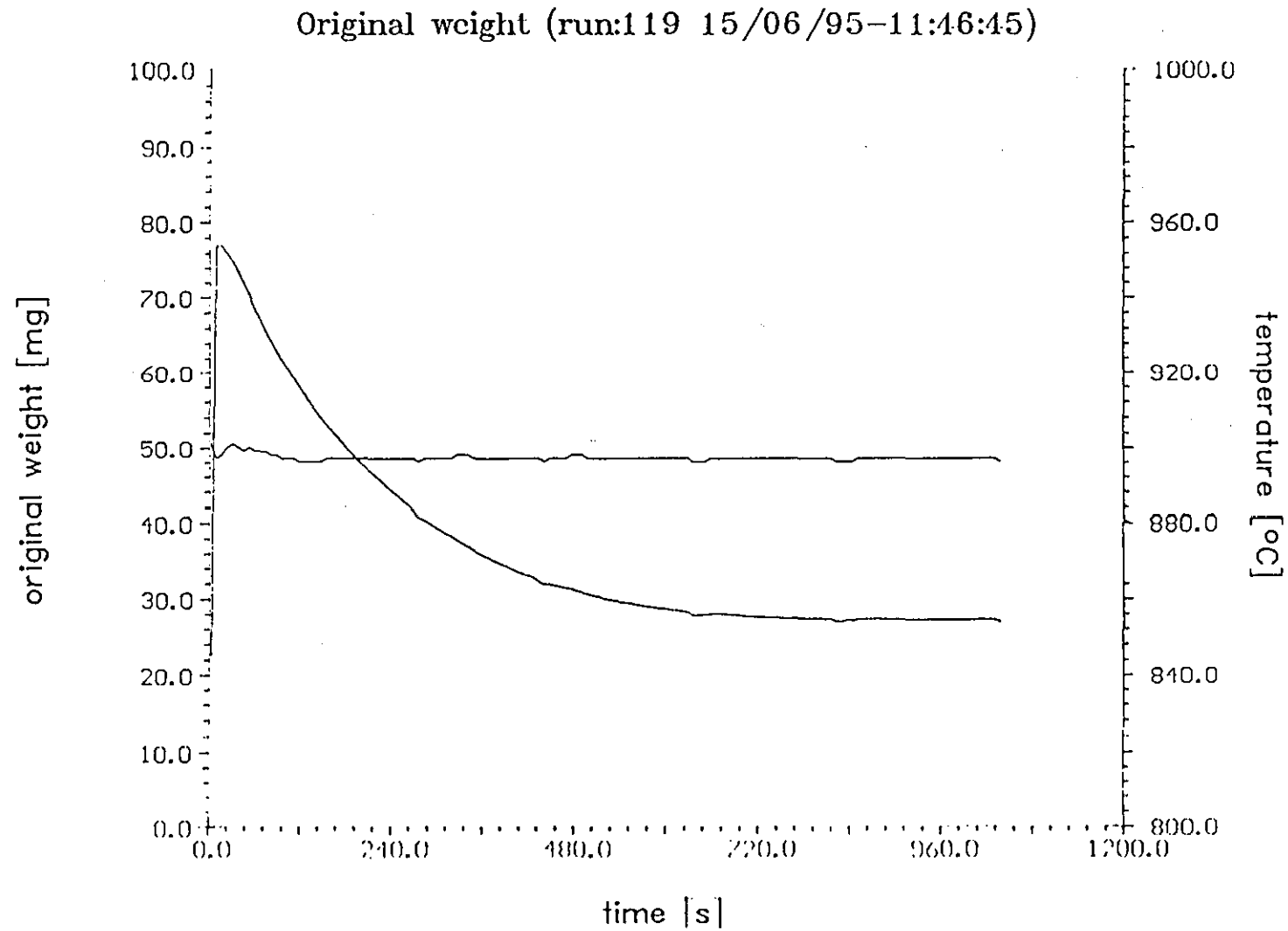


Figure 4.1 Typical Weight Loss Curve from the PTGA

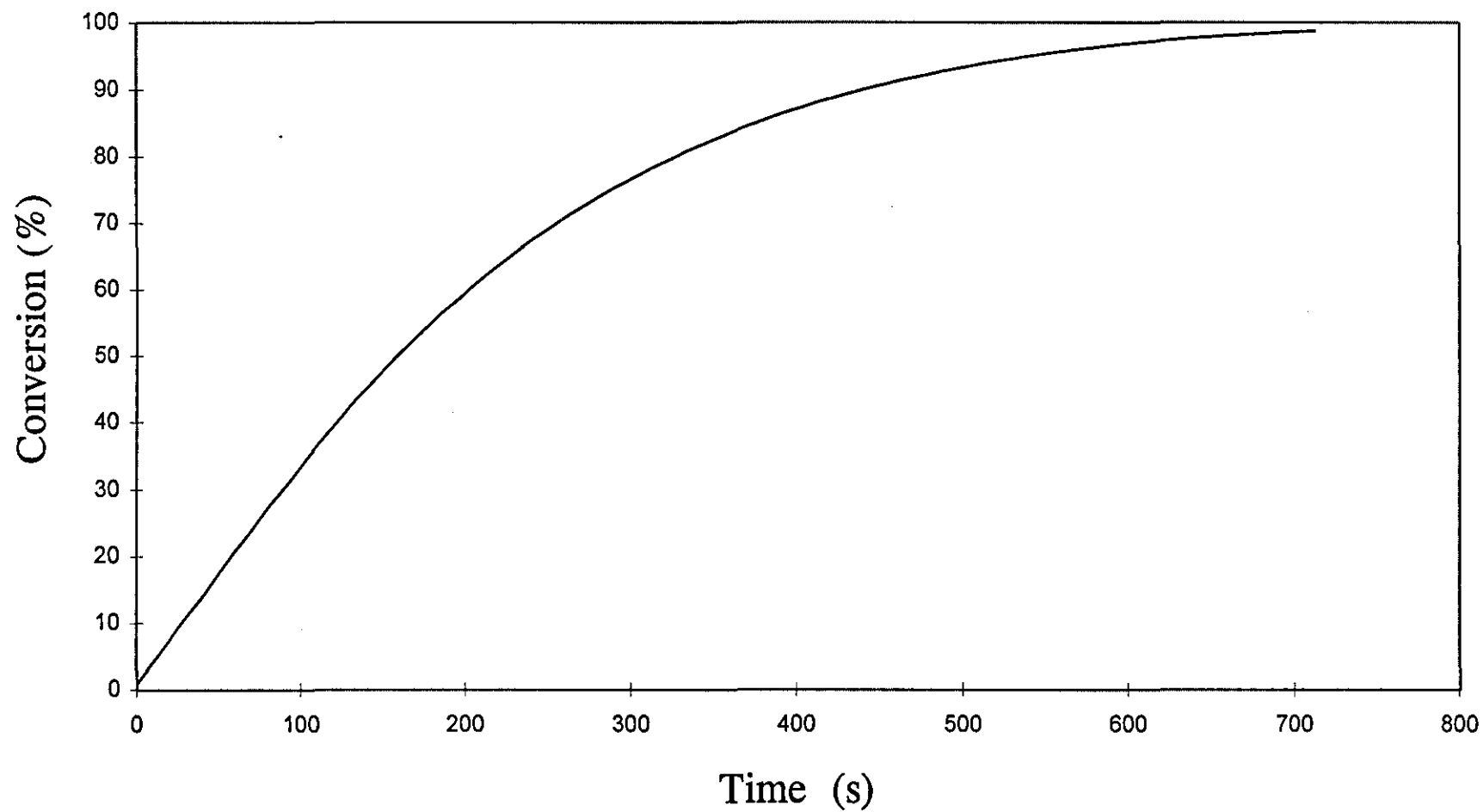


Figure 4.2 Conversion versus Time Plot Derived from Figure 4.1

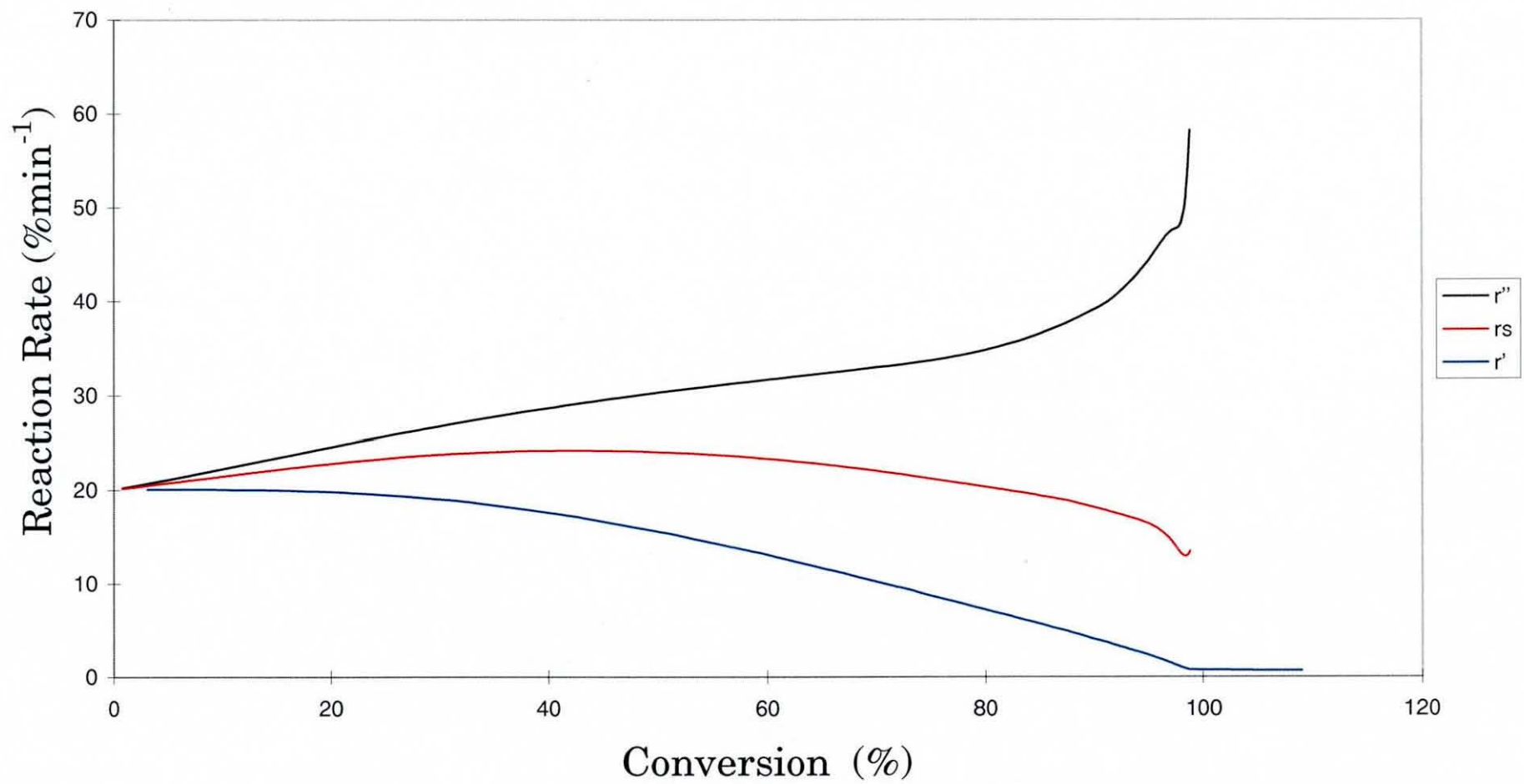


Figure 4.3 Comparison of Reactivity Parameters

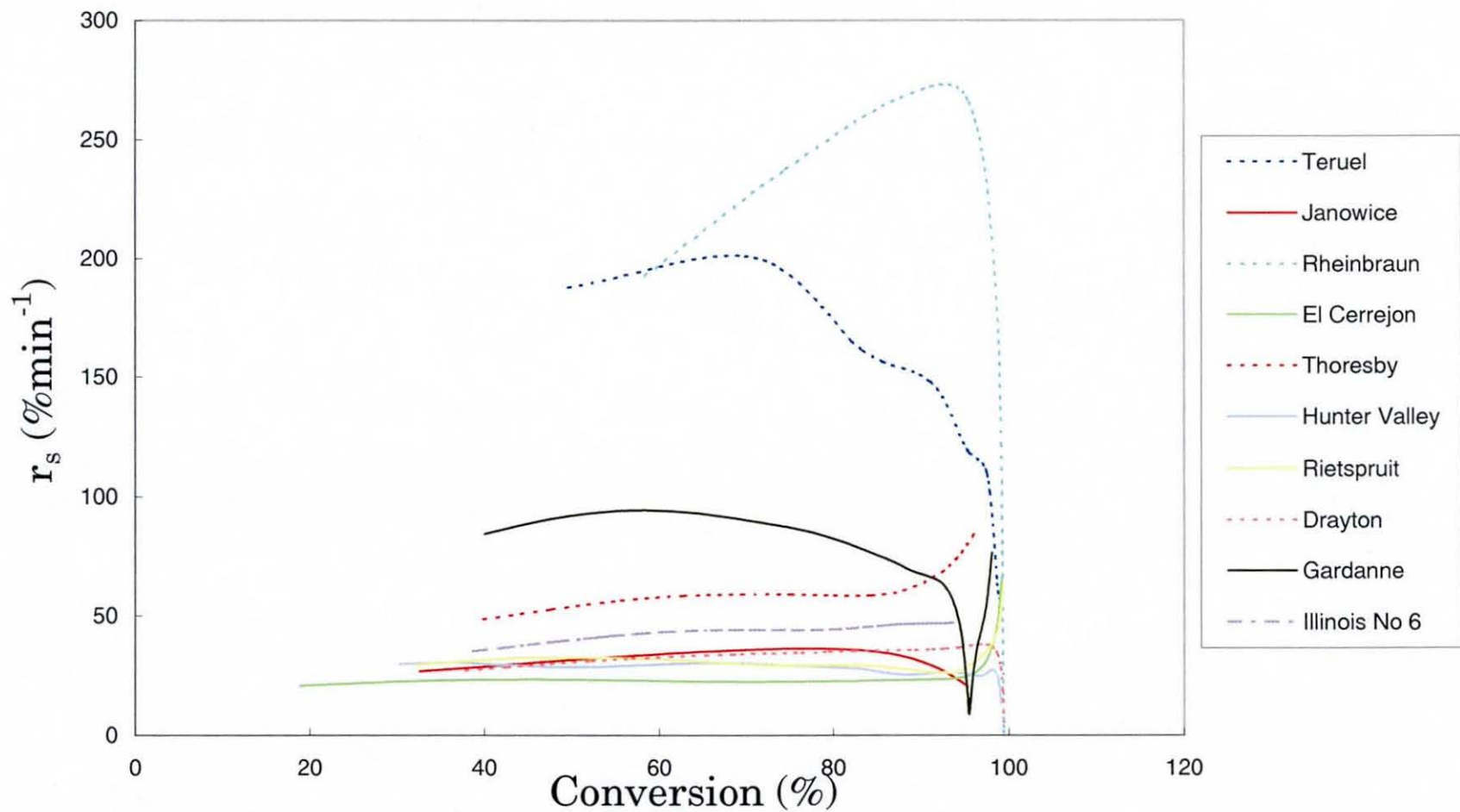


Figure 4.4: Reactivity of Non UK Coals To Steam at 950°C and 2.5 MPa

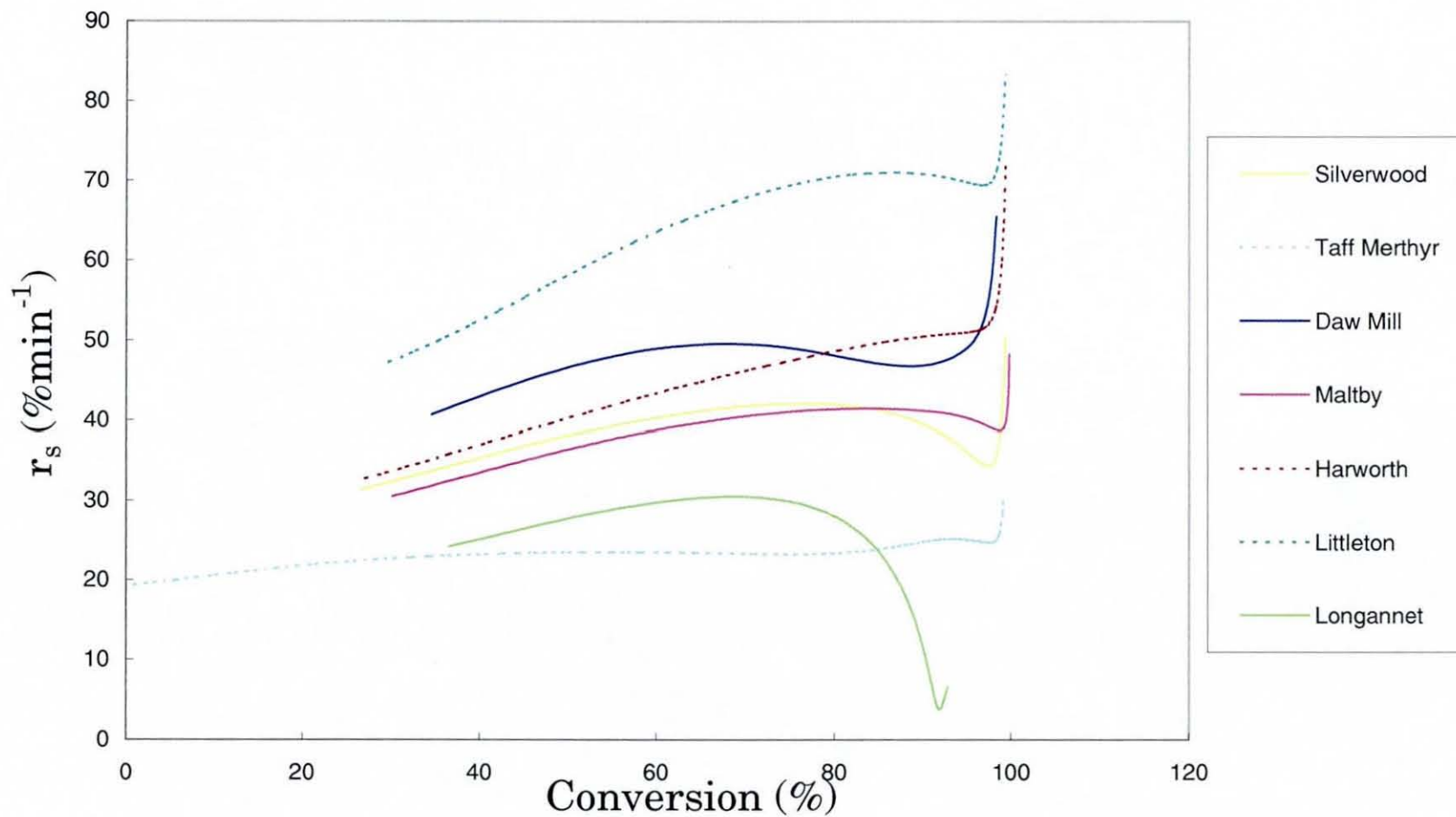


Figure 4.5: Reactivity of UK Coals To Steam at 950°C and 2.5 MPa

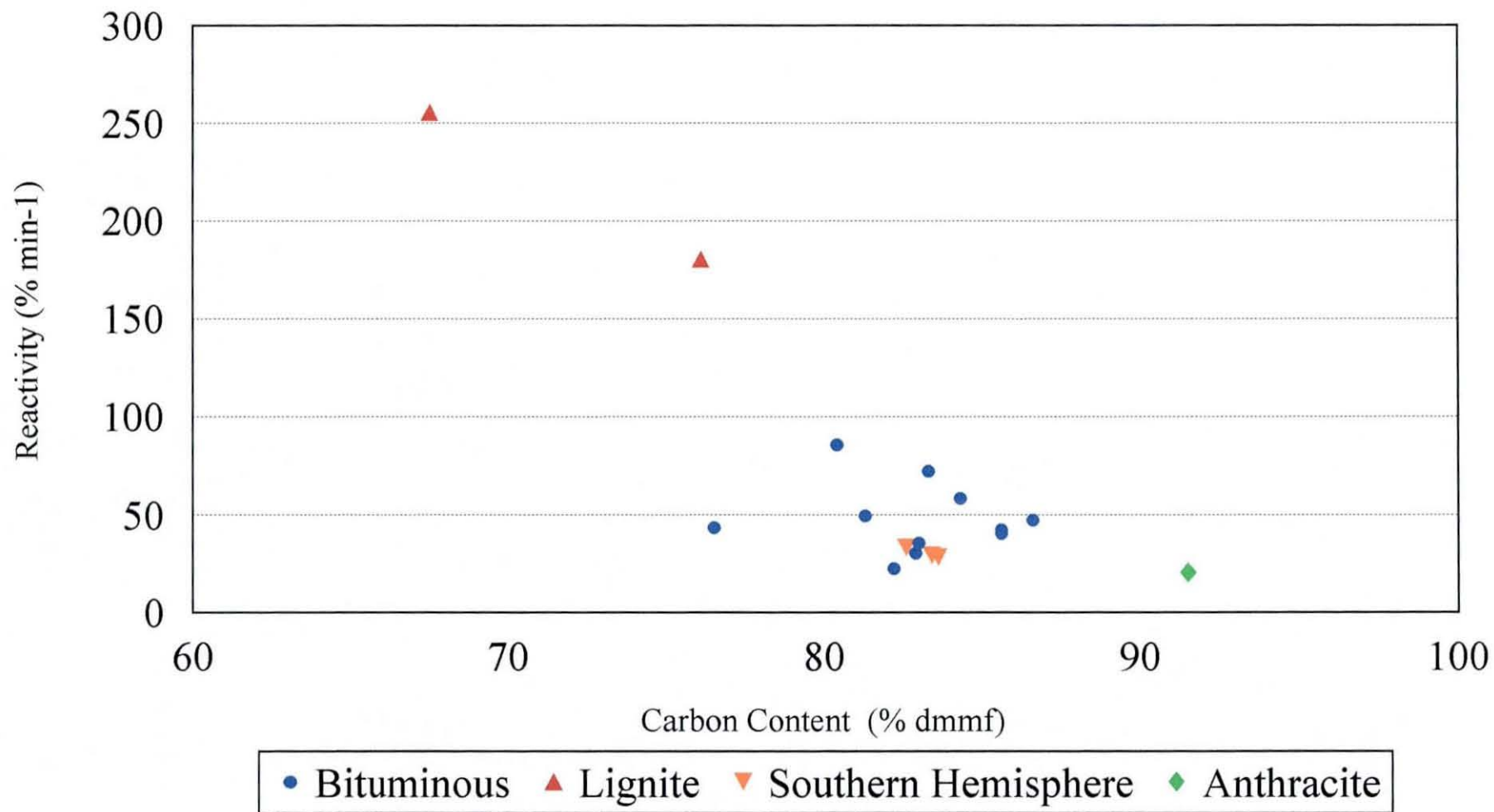


Figure 4.6: Reactivity vs Carbon Content in Coal

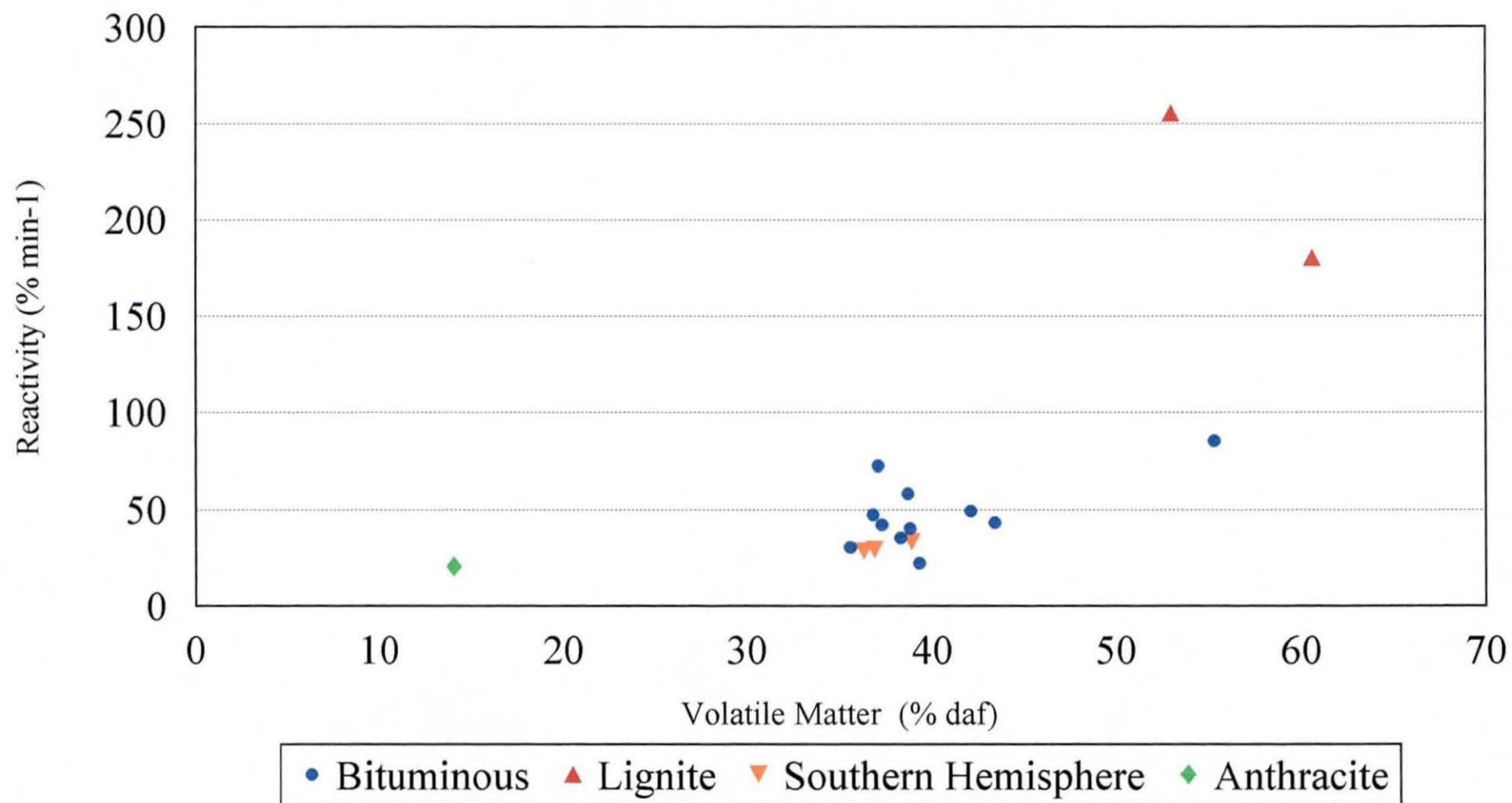


Figure 4.7: Reactivity vs Volatile Matter in Coal

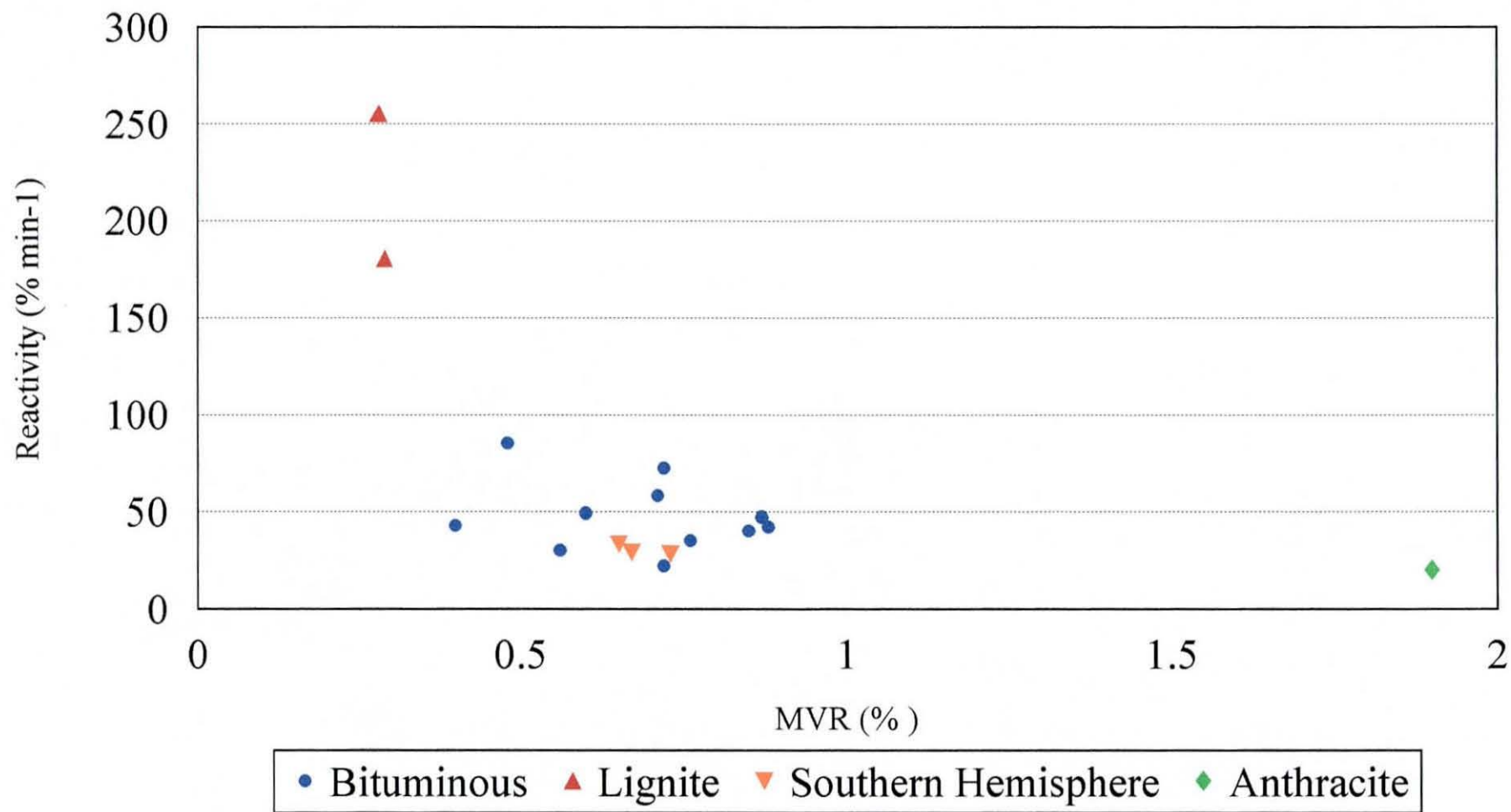


Figure 4.8: Reactivity vs Mean Vitrinite Reflectance

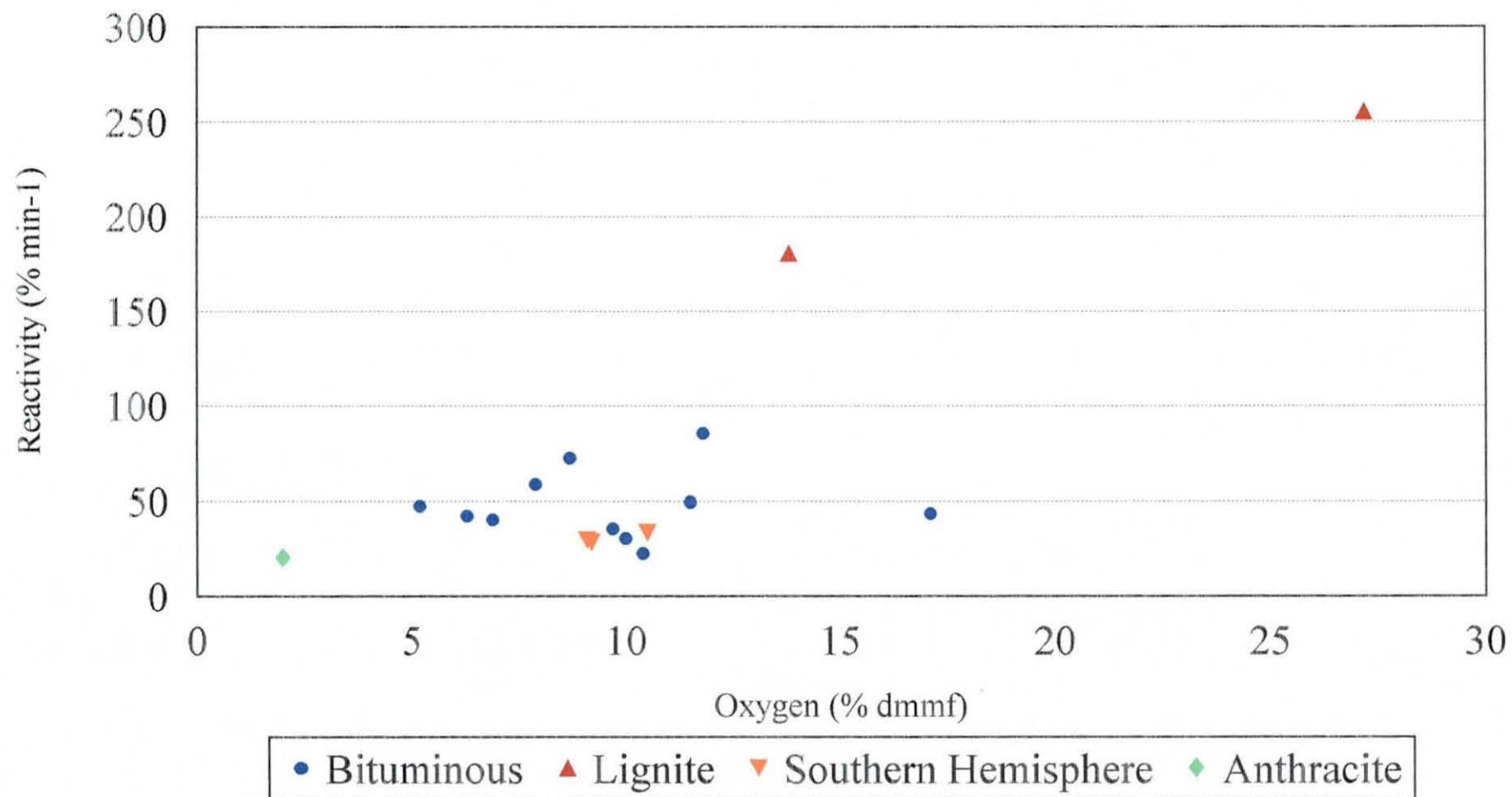


Figure 4.9: Reactivity vs Oxygen in Coal

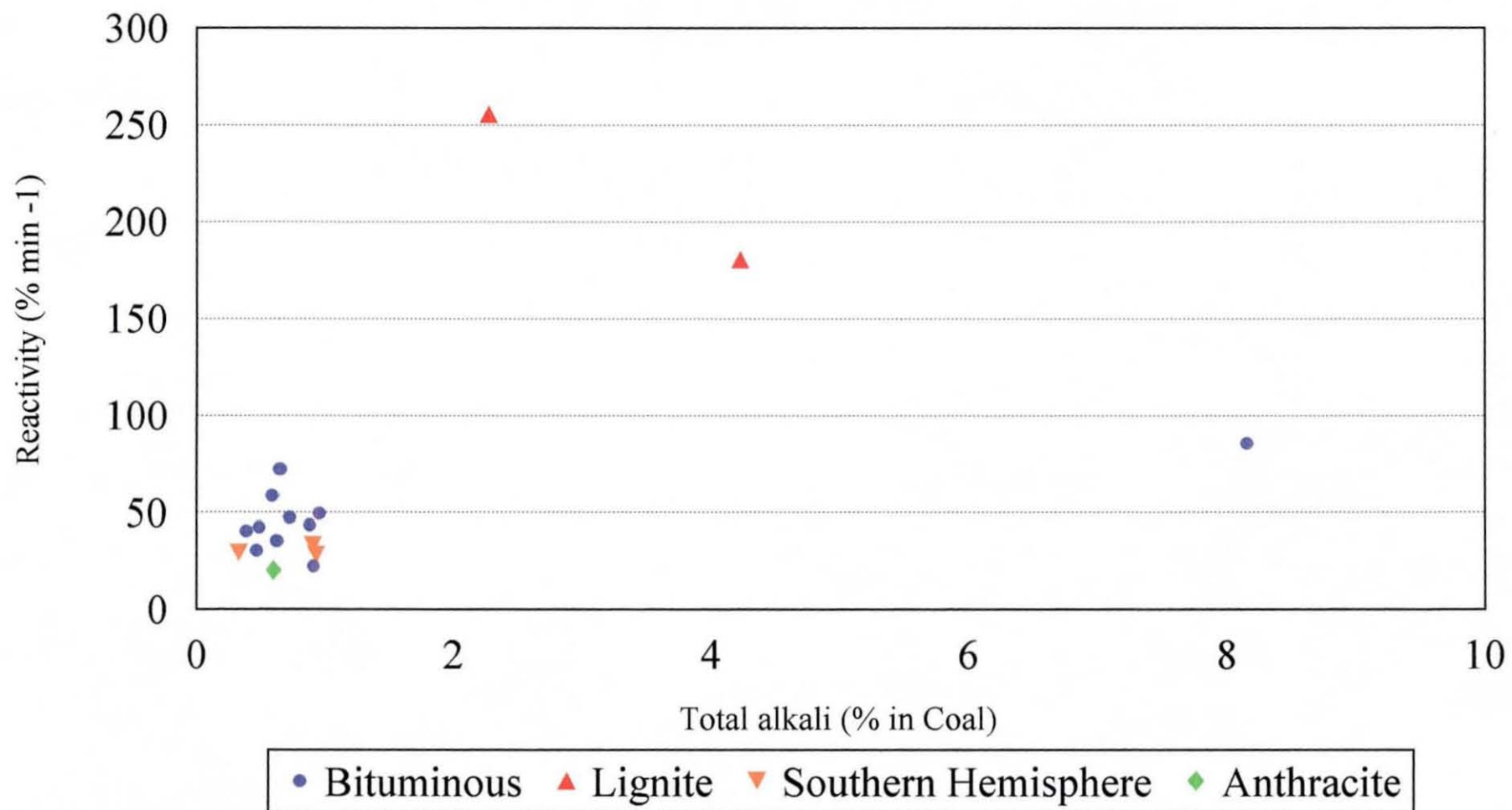


Figure 4.10: Reactivity vs Total Alkalis in Coal

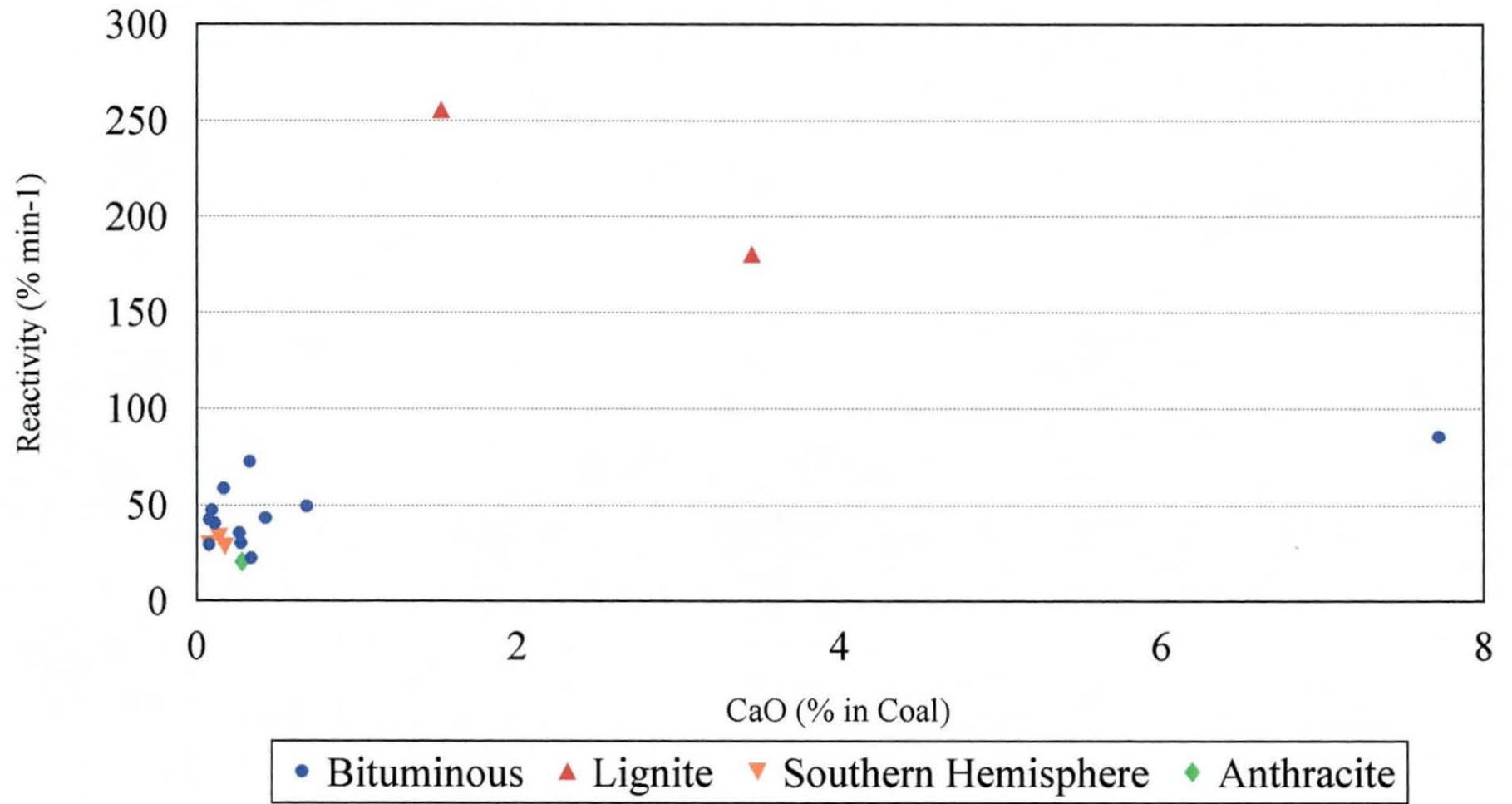


Figure 4.11: Reactivity vs CaO in Coal

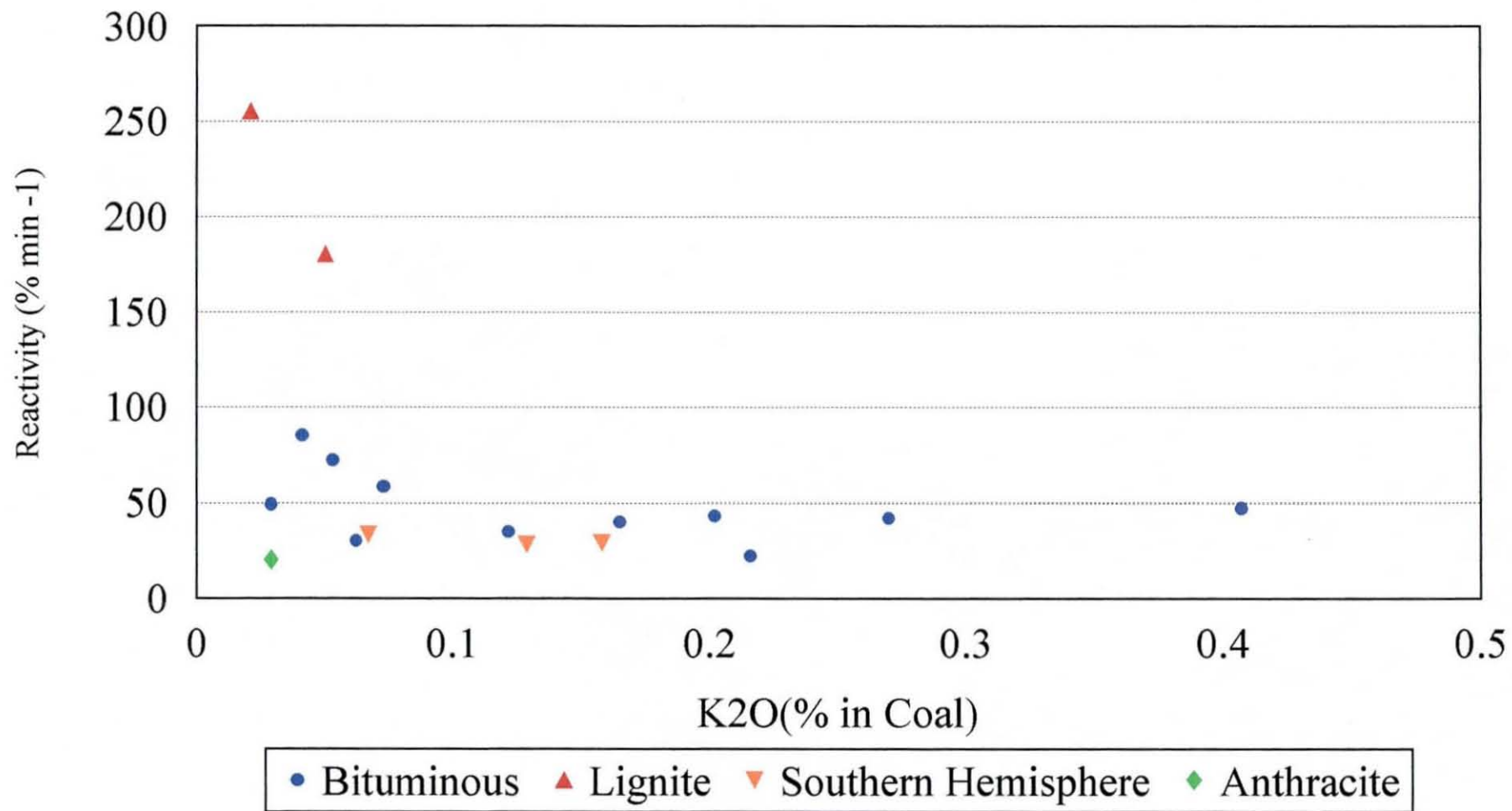


Figure 4.12: Reactivity vs K₂O in Coal

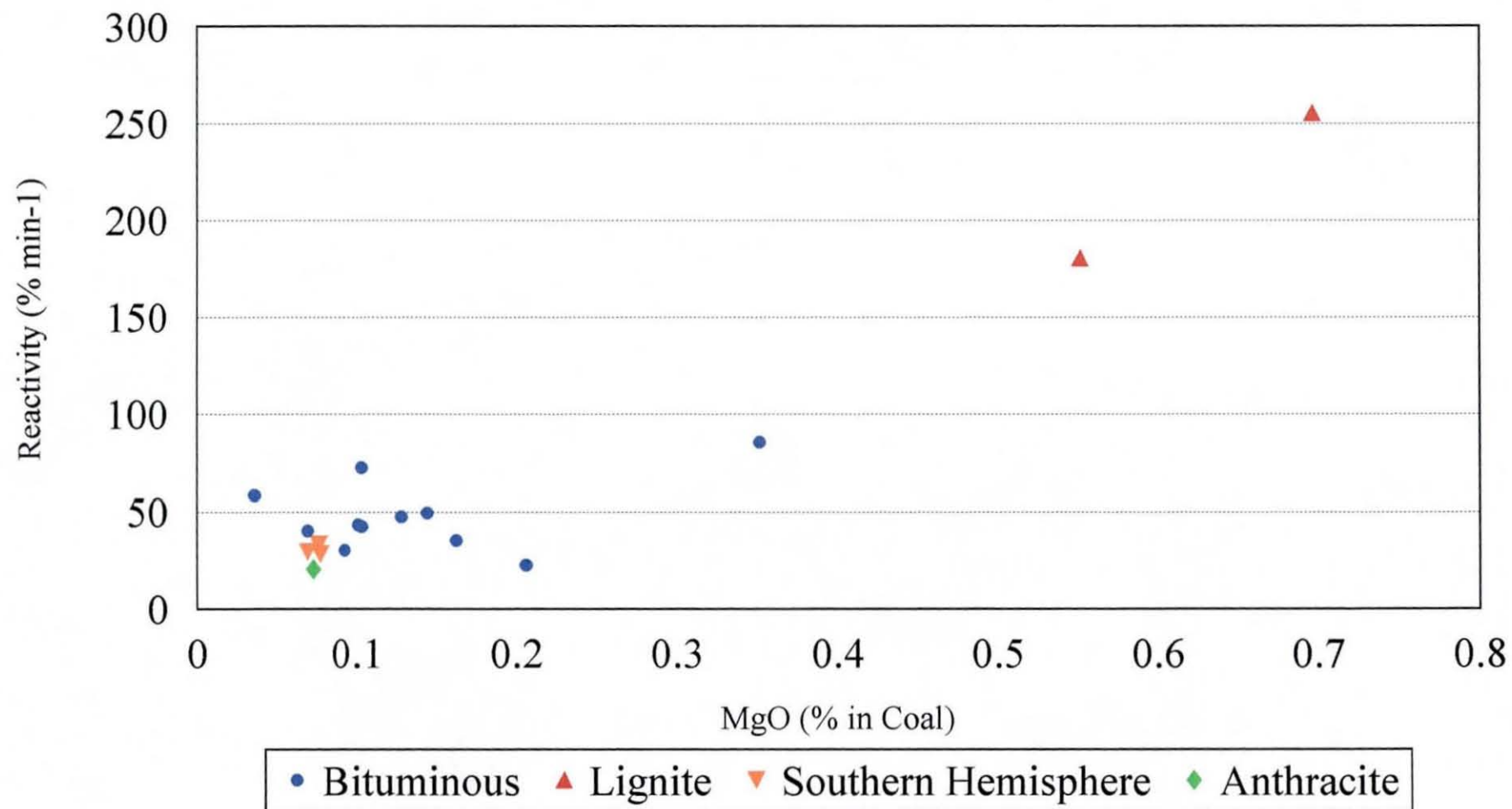


Figure 4.13: Reactivity vs MgO in Coal

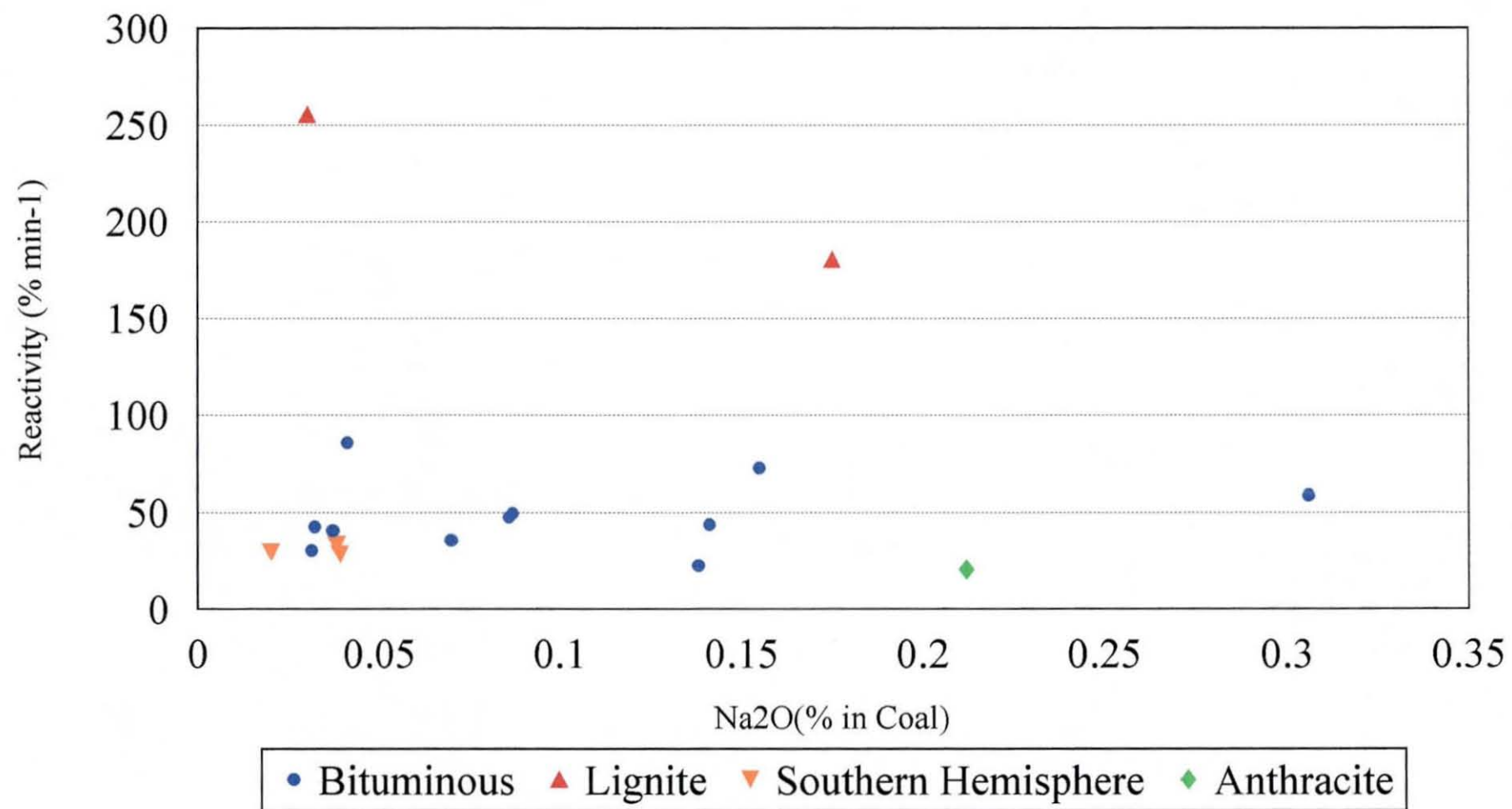


Figure 4.14: Reactivity vs Na₂O in Coal

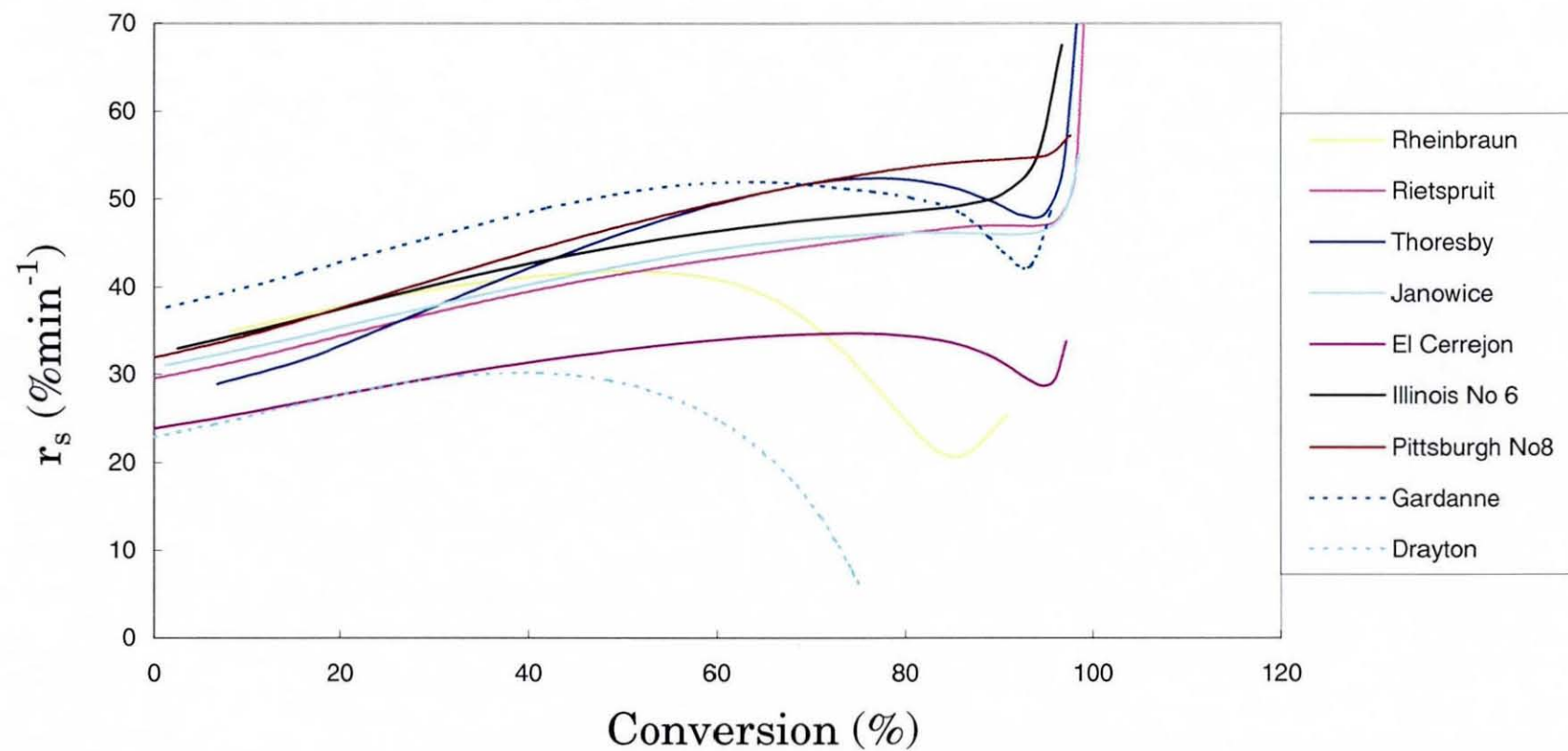


Figure 4.15: Reactivity of Various Char Samples
at 950°C and 2.5 MPa in Steam

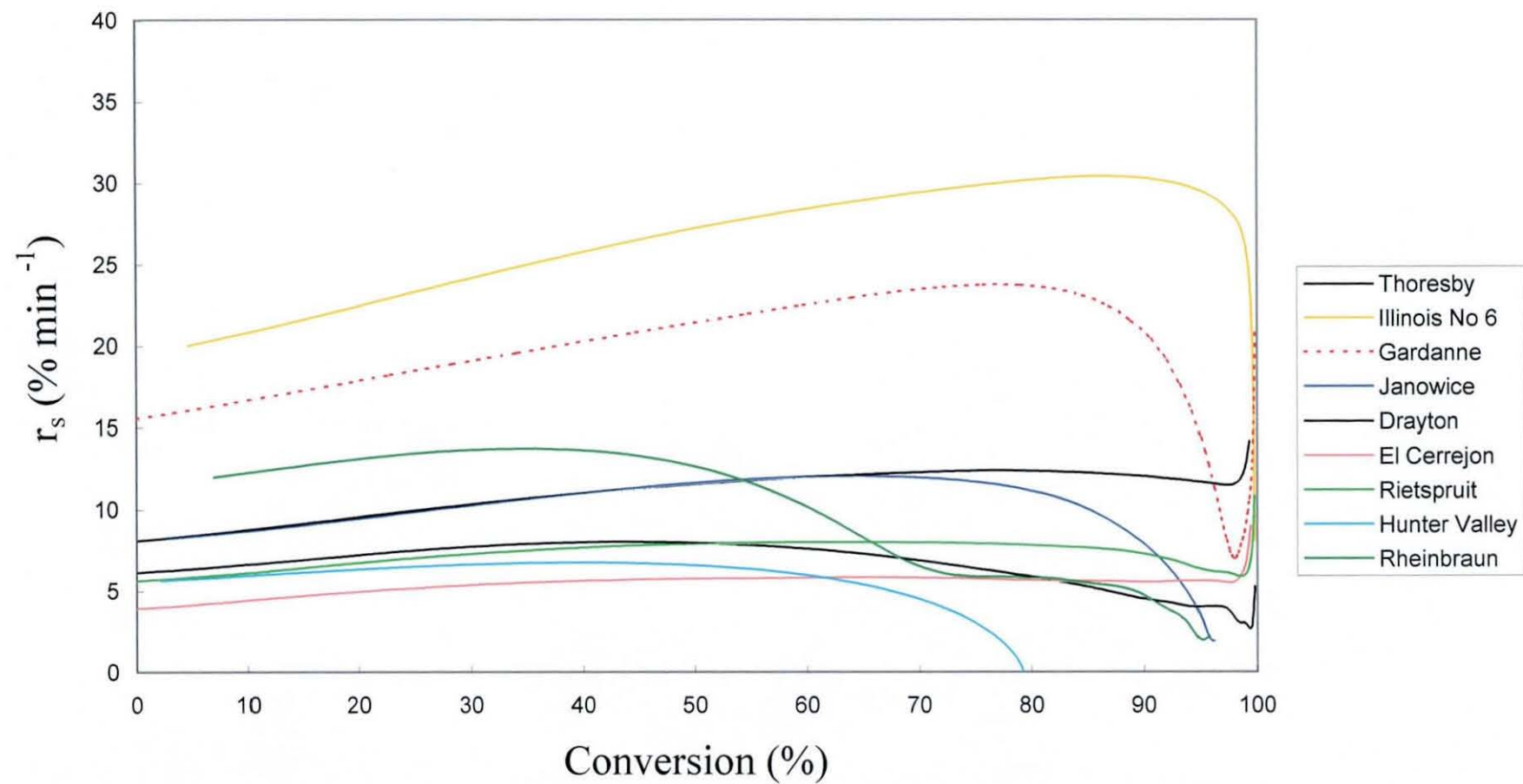


Figure 4.16: Reactivity of Various Char Samples at 950°C and 2.5 MPa in CO₂

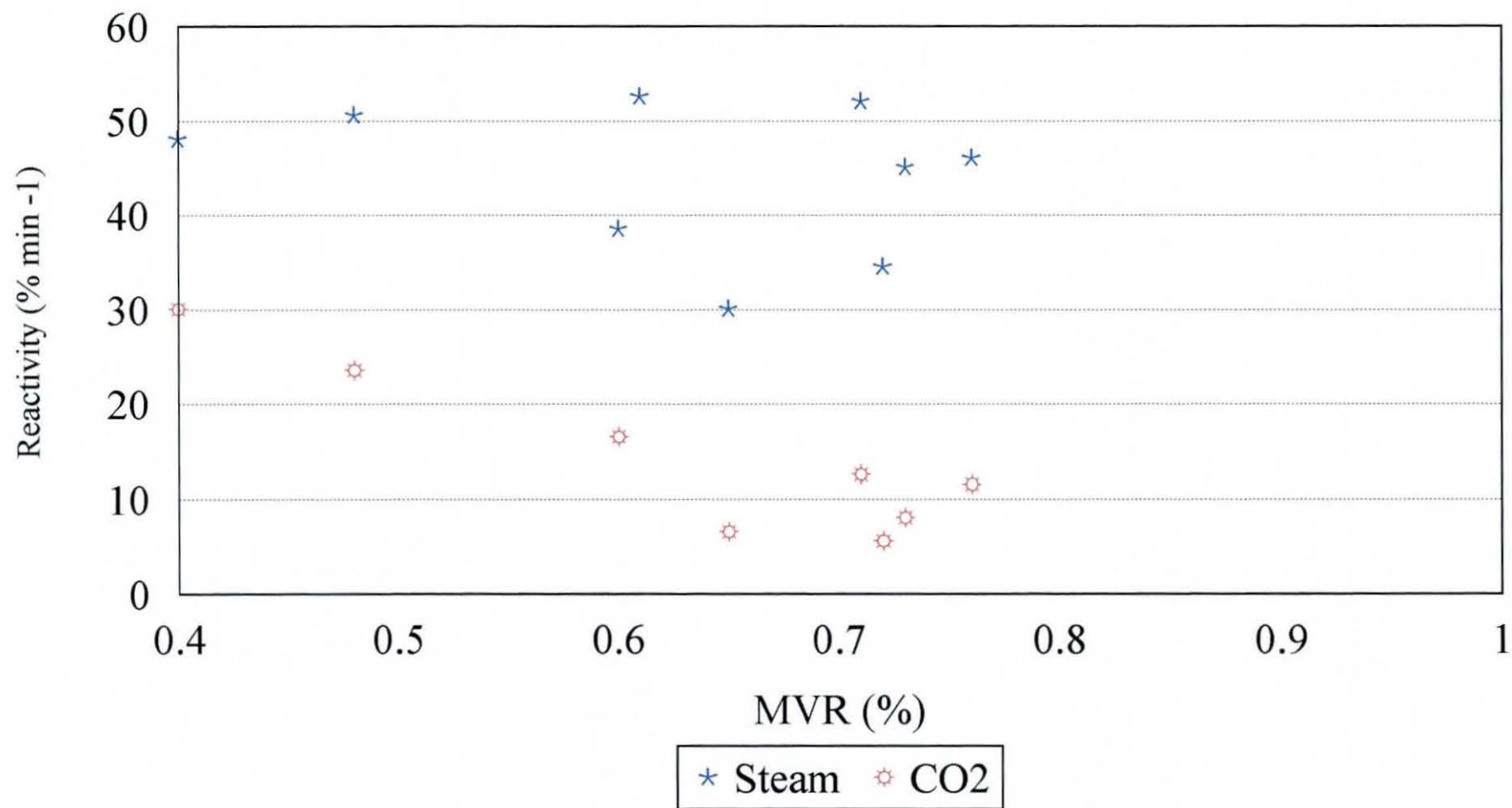


Figure 4.17: Reactivity vs MVR for Chars

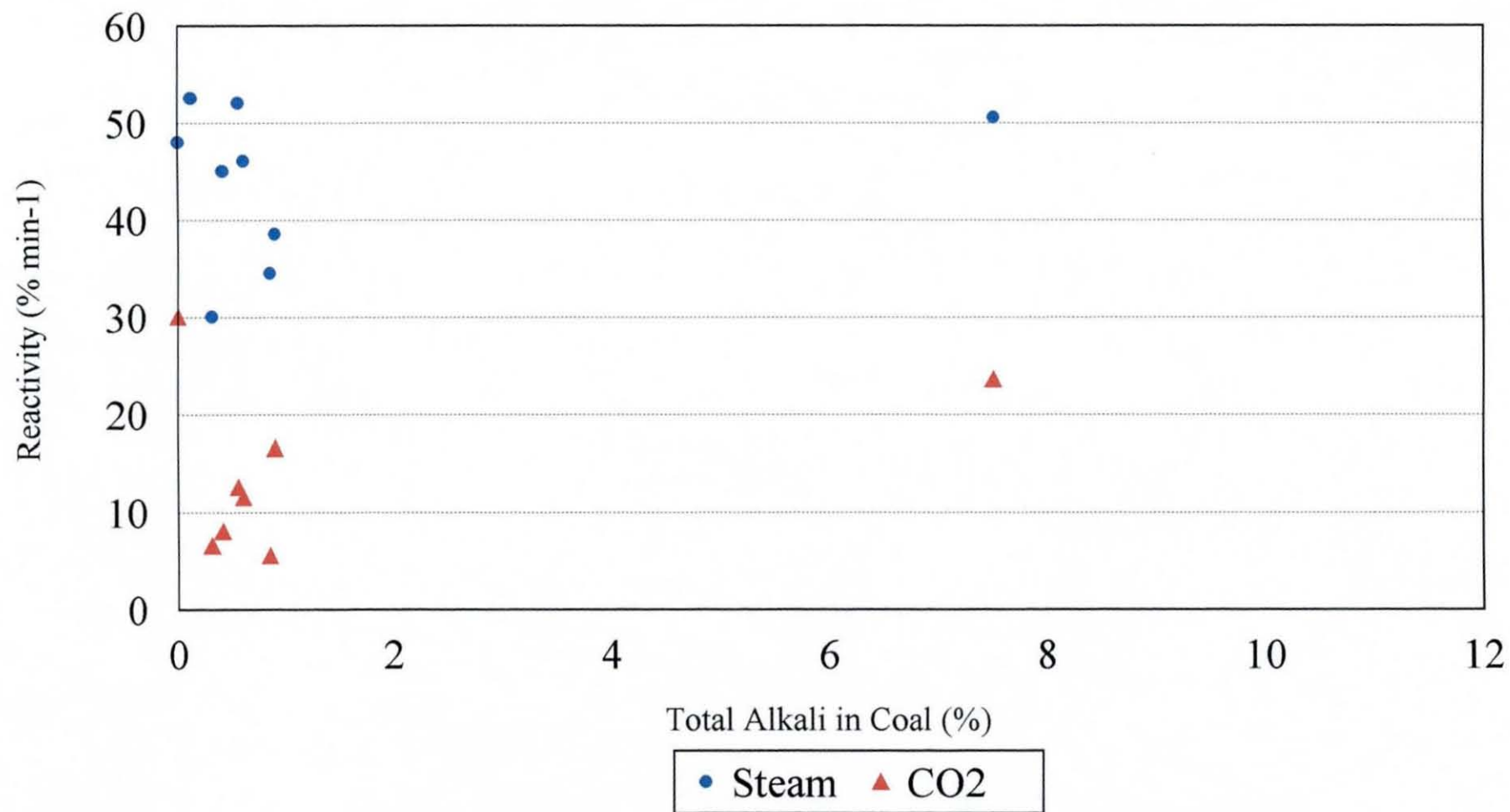


Figure 4.18: Reactivity of Char vs Total Alkali in Coal

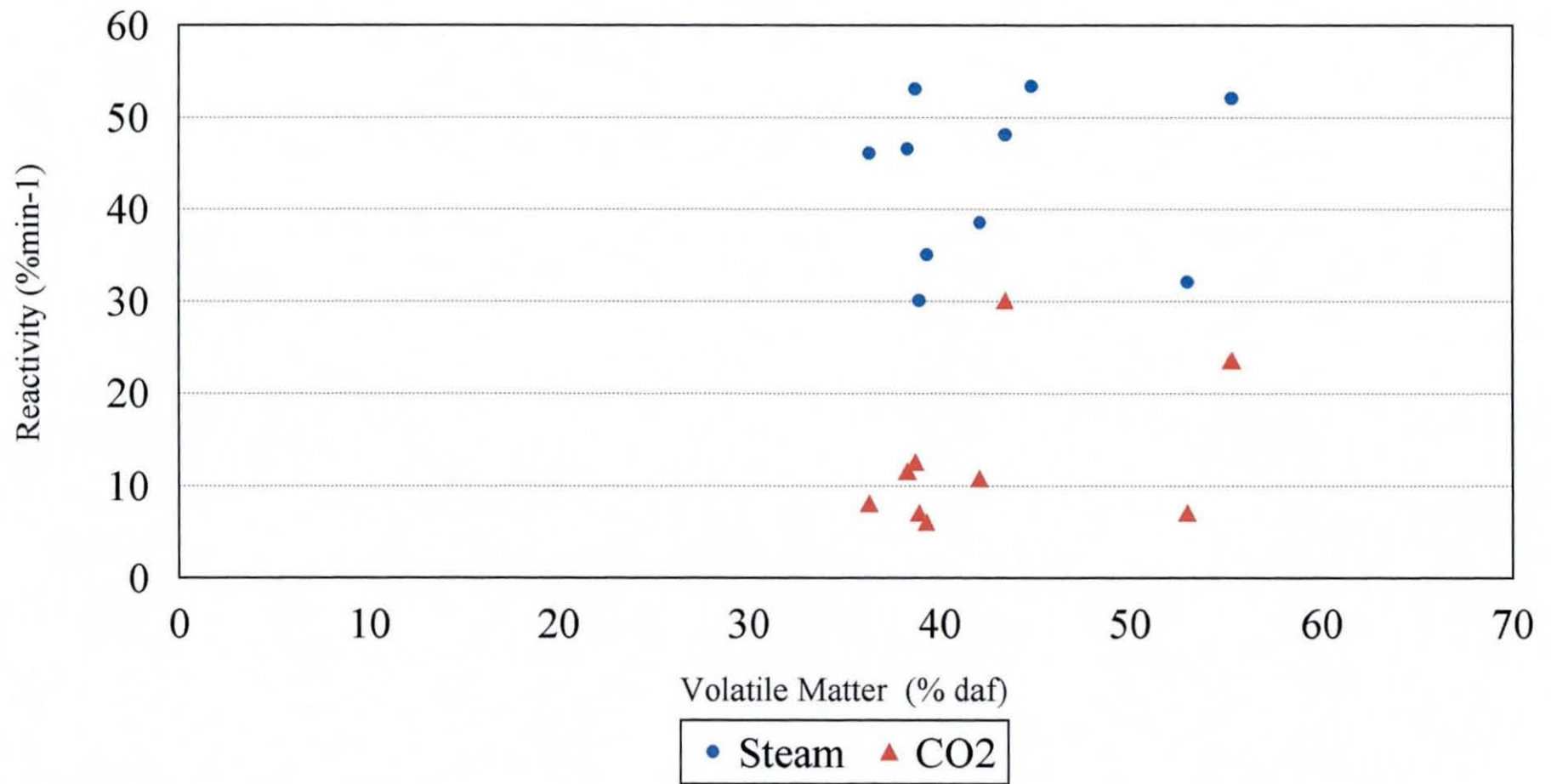


Figure 4.19: Reactivity of Char vs Volatile Matter in Coal

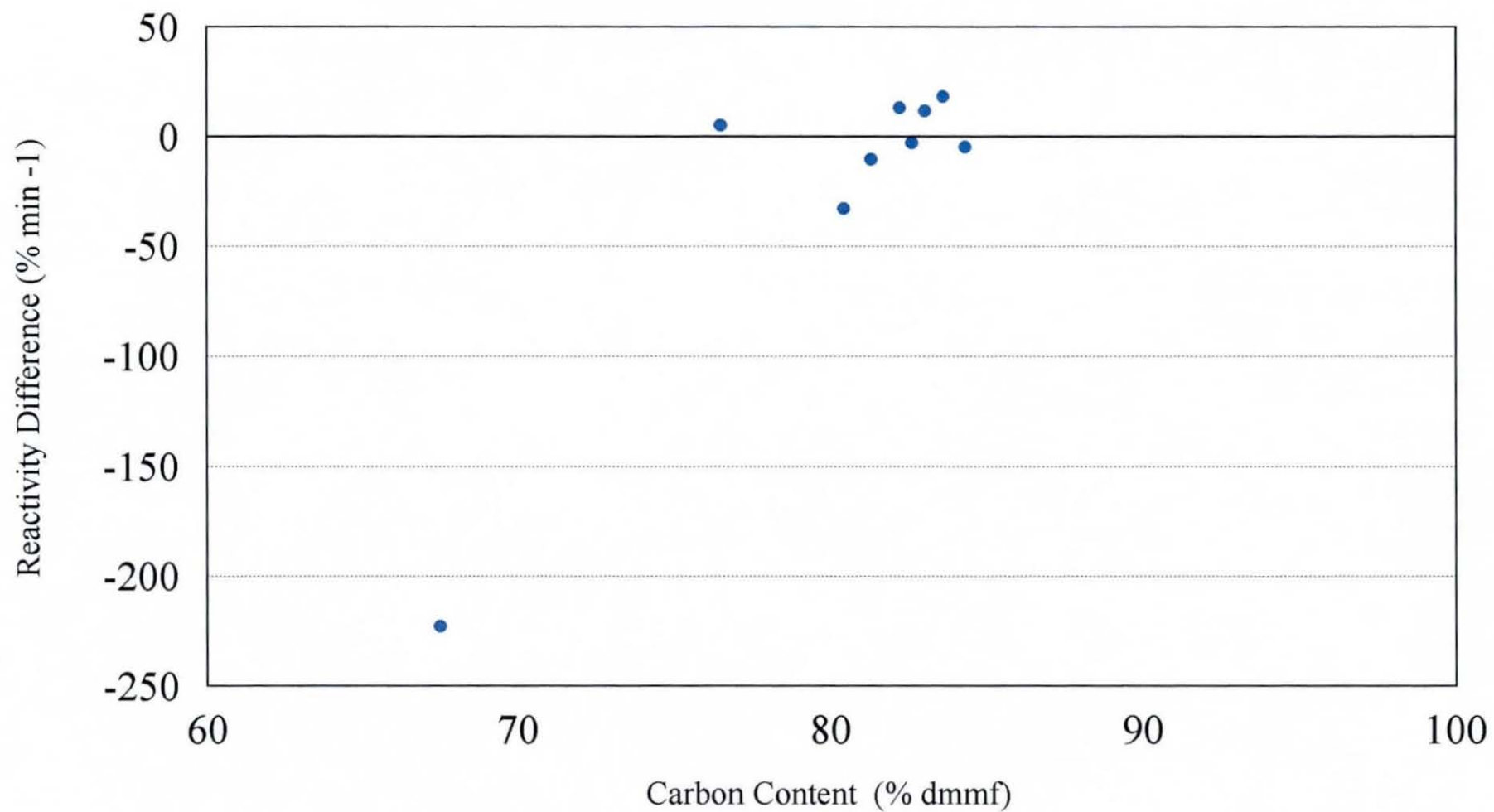


Figure 4.20: Difference in Coal and Char Reactivity vs Carbon Content of Coal

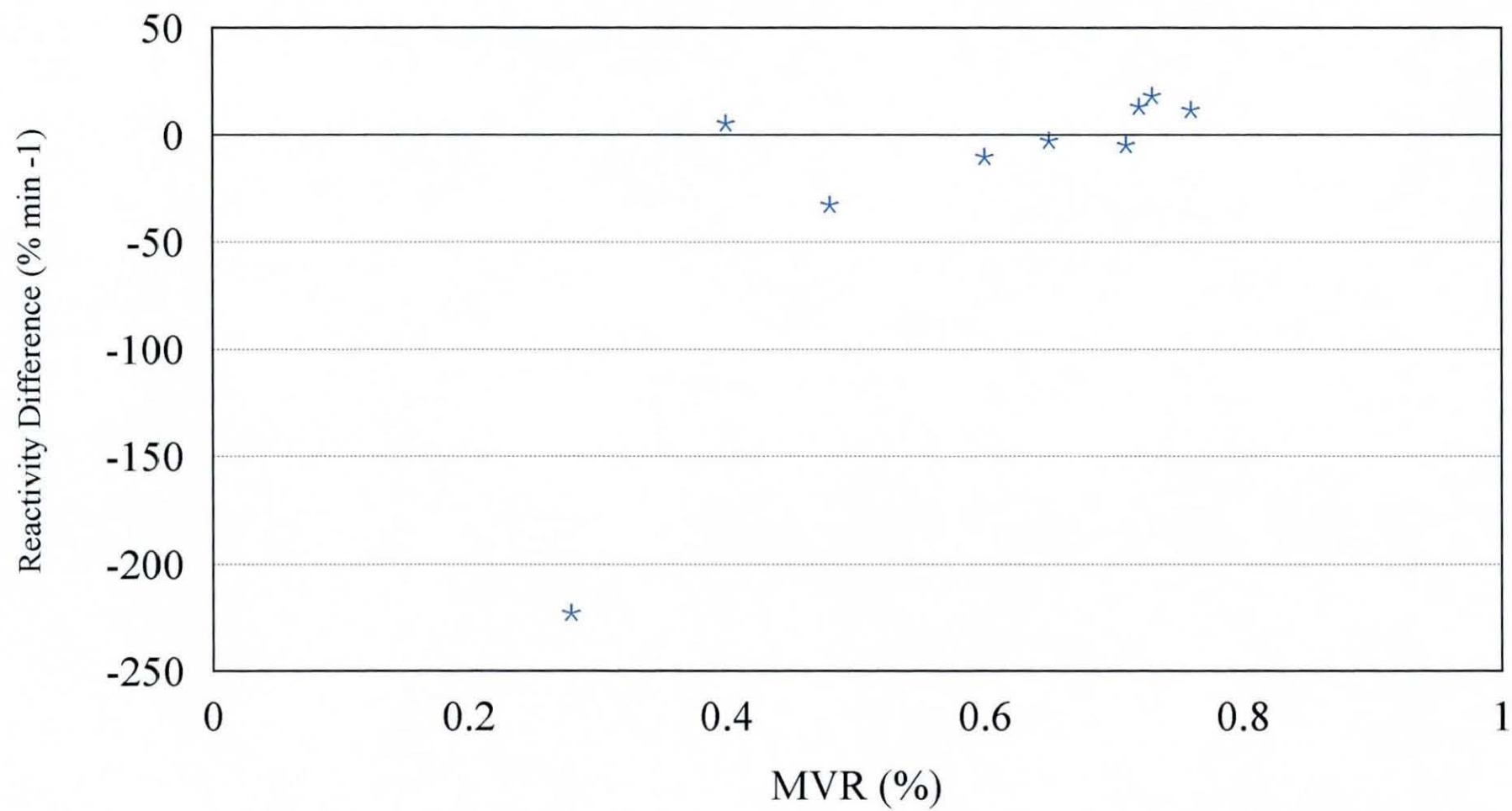


Figure 4.21: Difference in Coal and Char Reactivity vs MVR

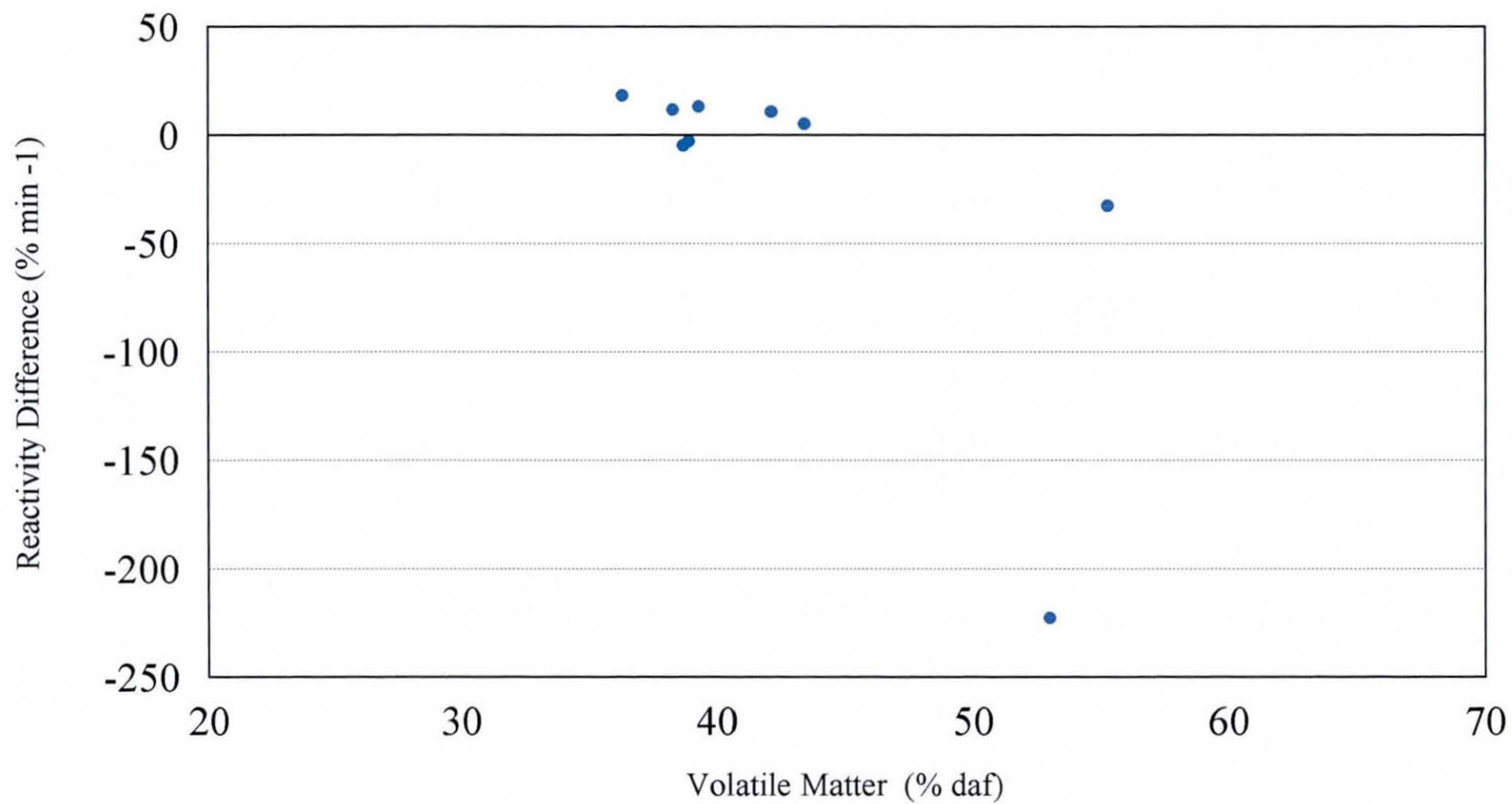


Figure 4.22: Difference in Coal and Char Reactivity vs Volatile Matter

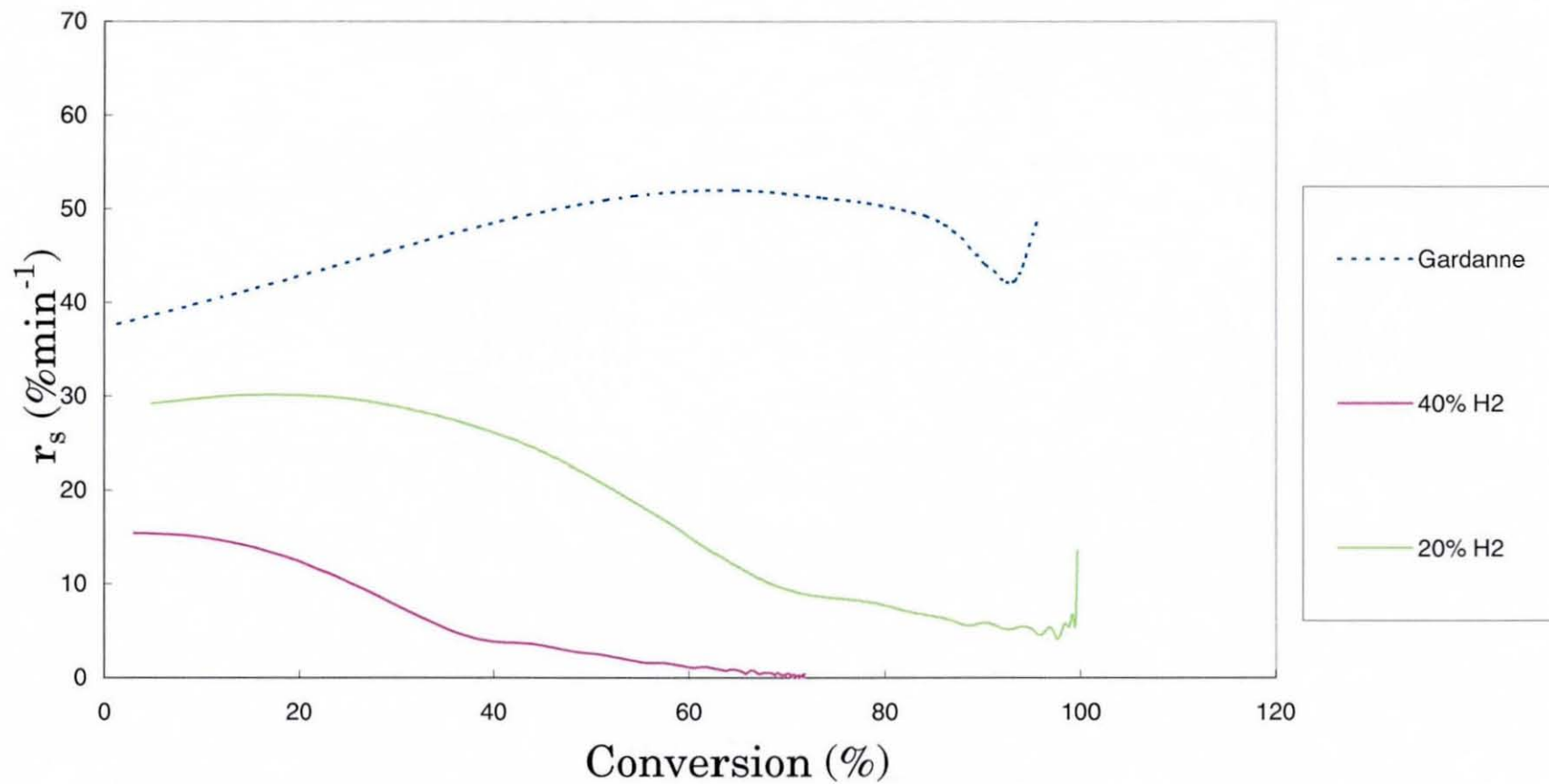


Figure 4.23: Reactivity of Gardanne Char at 950°C and 2.5 MPa in Steam/H₂ Mixtures

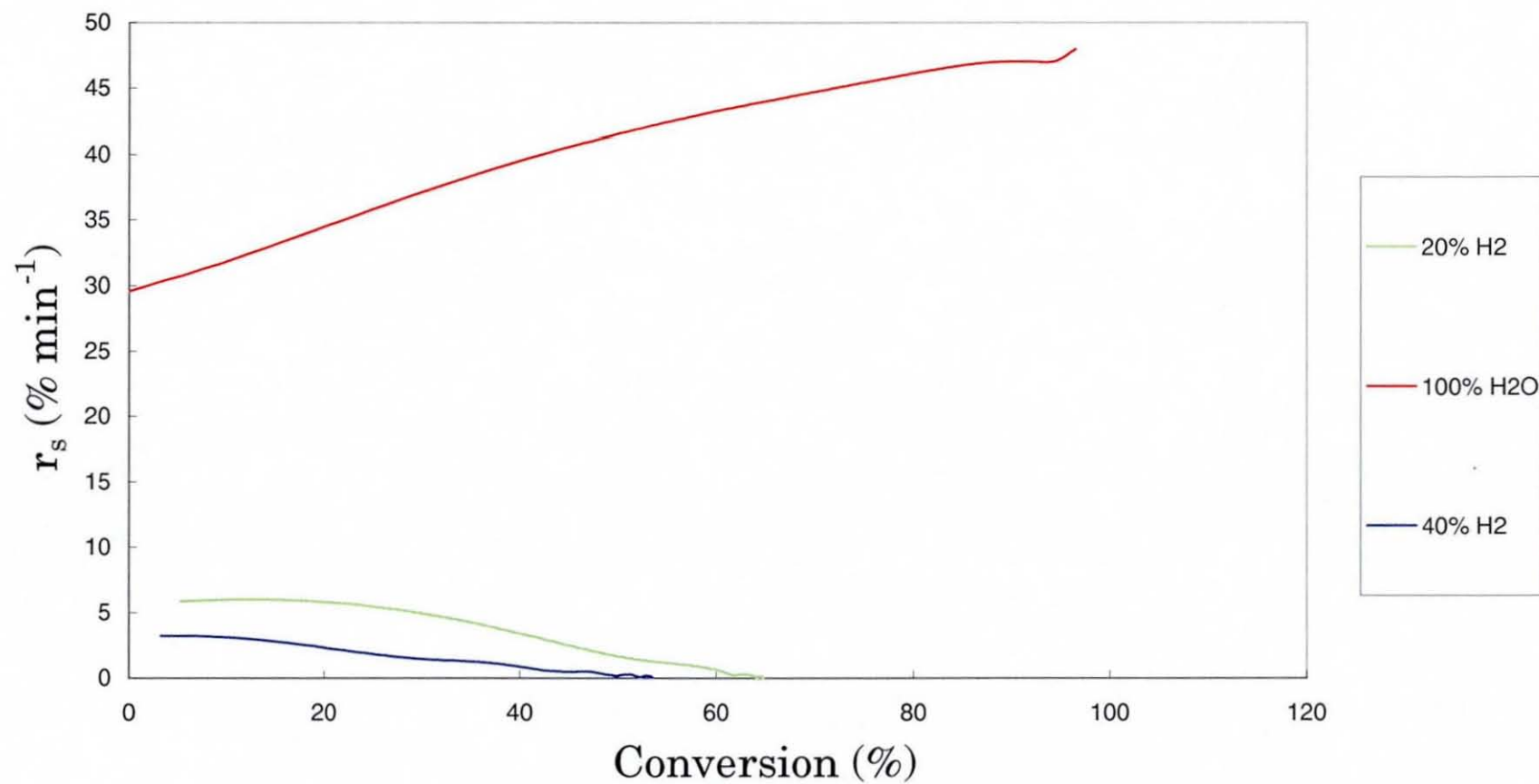


Figure 4.24 Reactivity of Rietspruit Char at 950°C and 2.5 MPa in H₂O/H₂ Mixtures

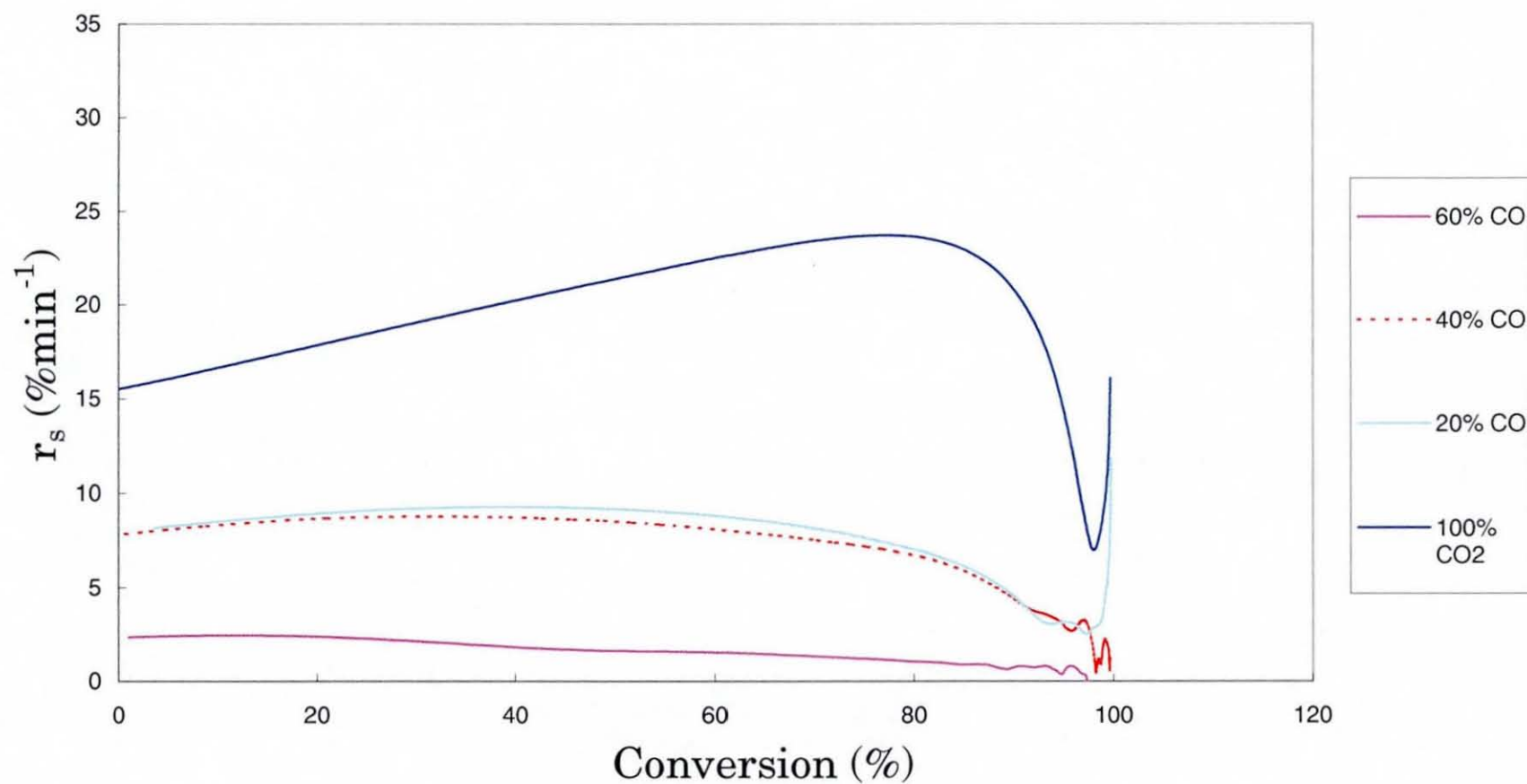


Figure 4.25: Reactivity of Gardanne Char at 950°C and 2.5 MPa in CO_2/CO Mixtures

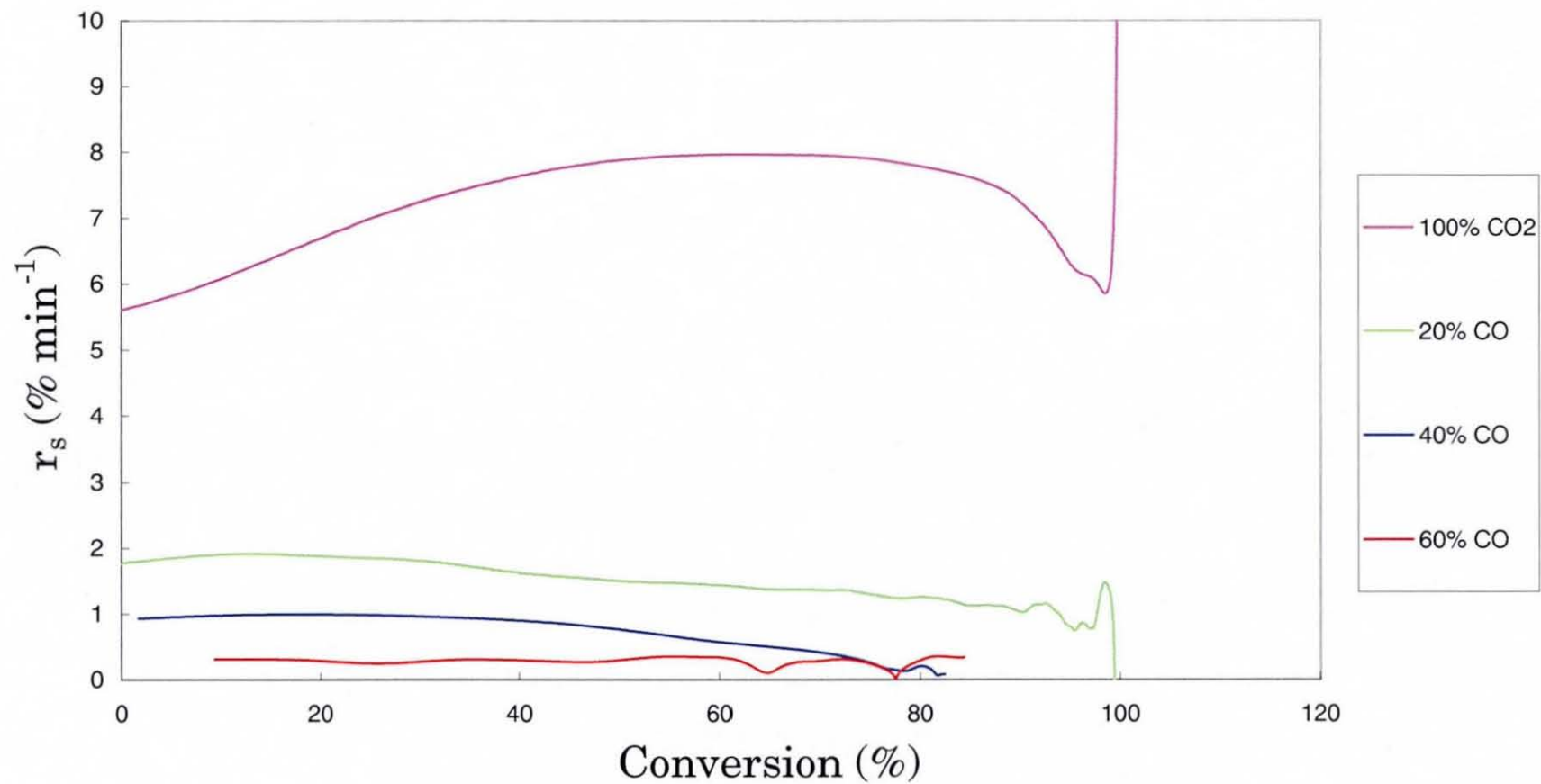


Figure 4.26: Reactivity of Rietspruit Char at 950°C and 2.5 MPa in CO_2/CO Mixtures

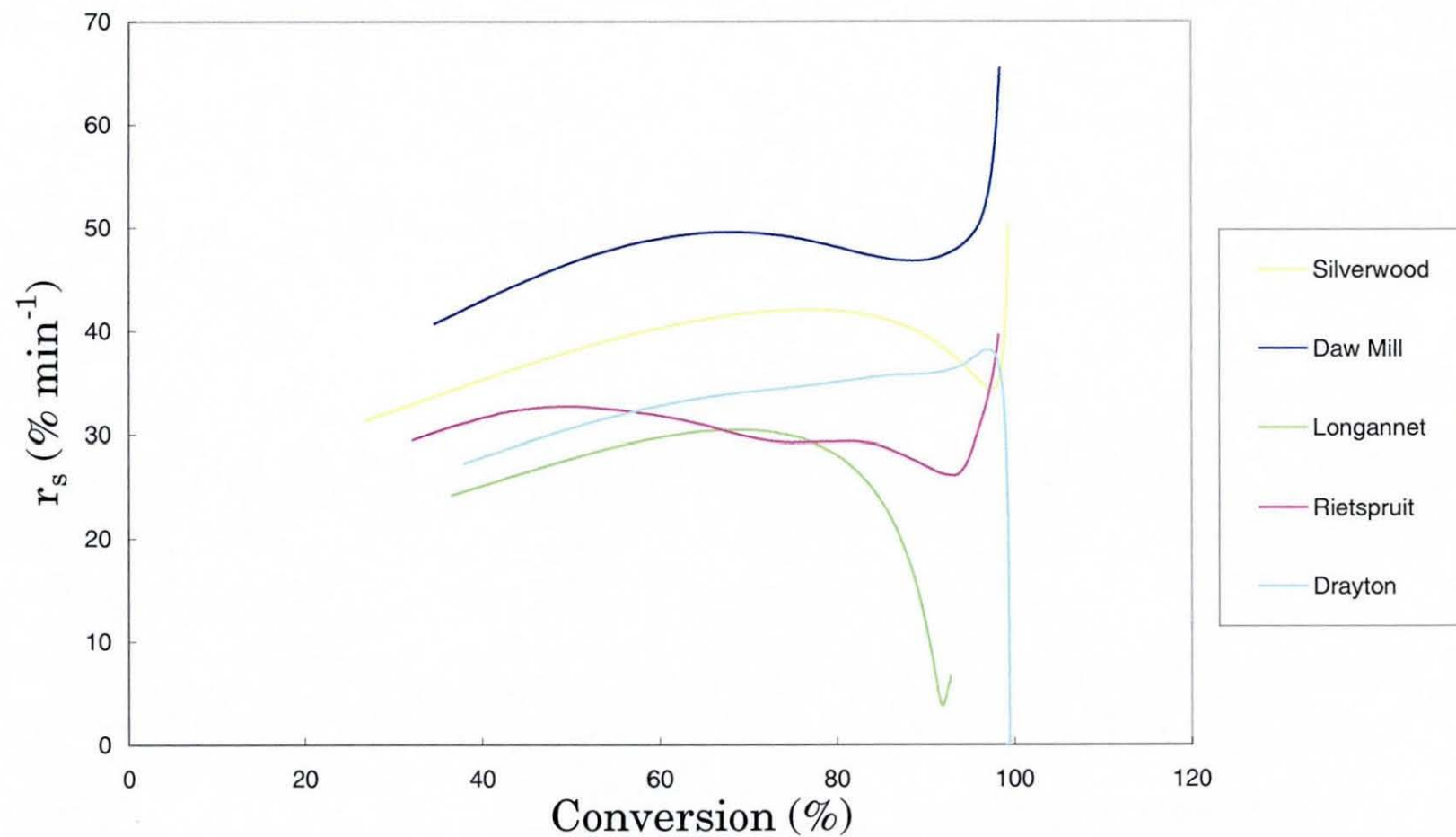


Figure 4.27: Reactivity of Various Coals To Steam at 950°C and 2.5 MPa

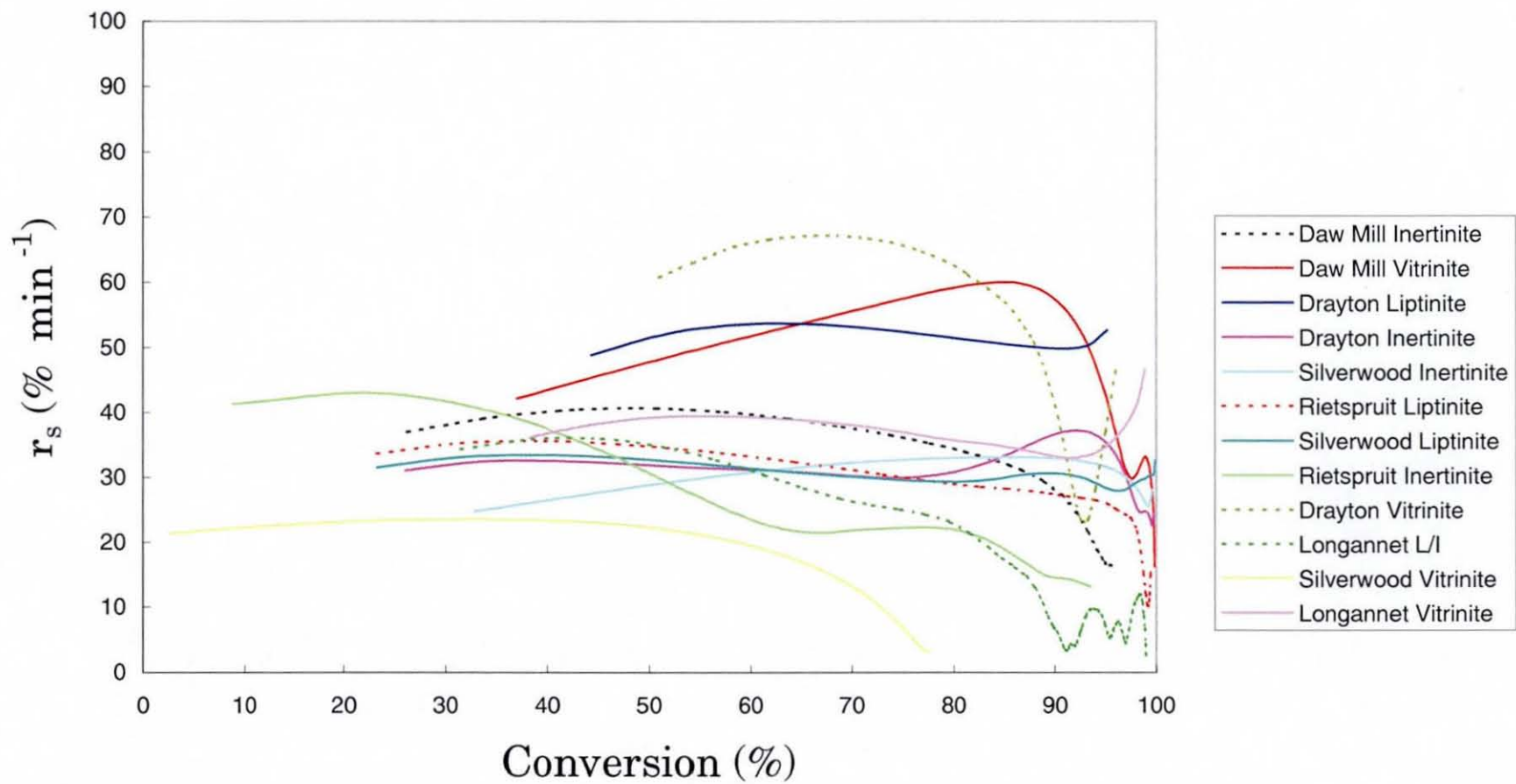


Fig 4.28: Reactivity of Macerals to Steam at 950°C and 2.5 MPa

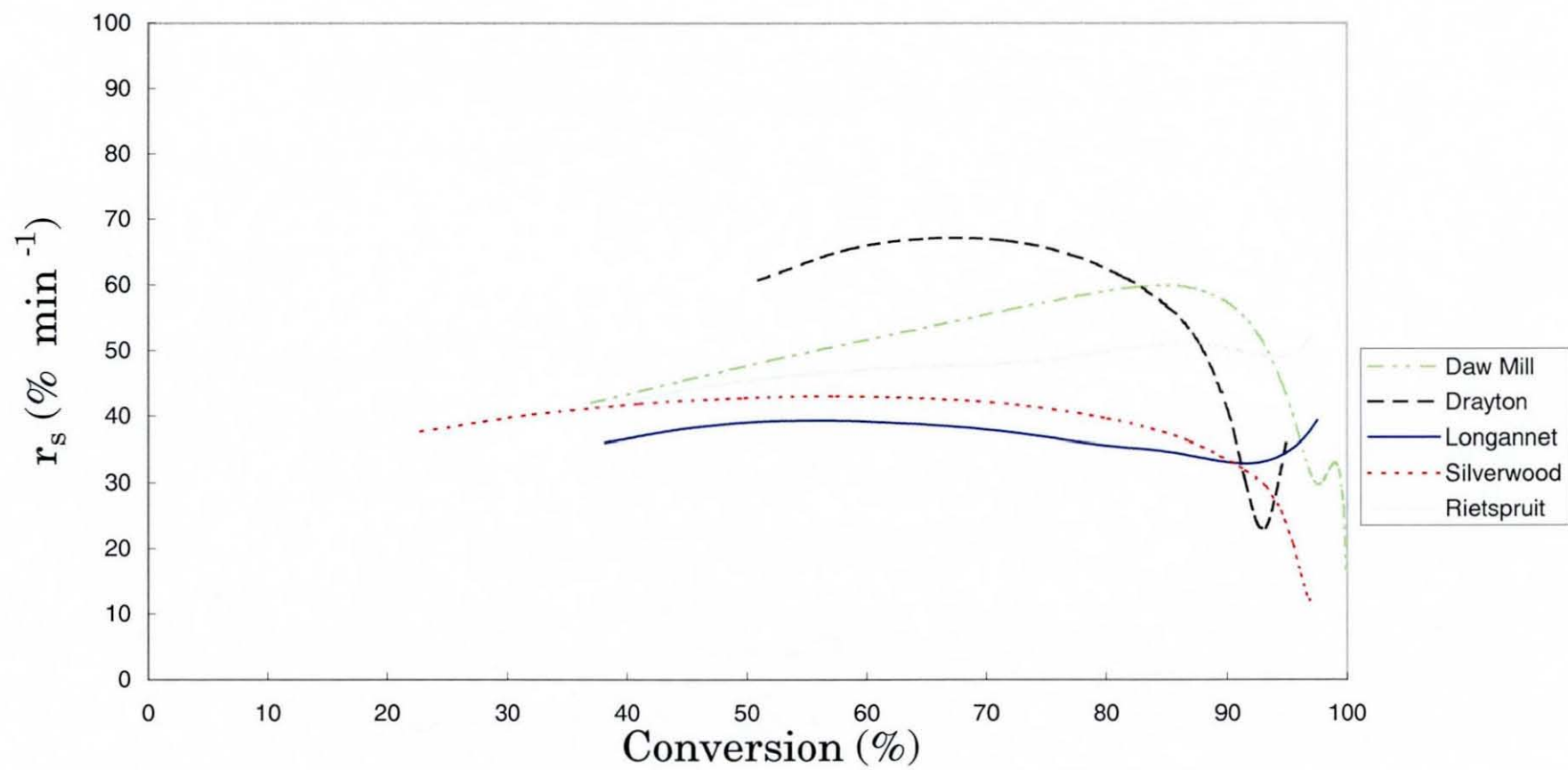


Figure 4.29: Reactivity of Vitrinite Samples to Steam at 950°C and 2.5 MPa

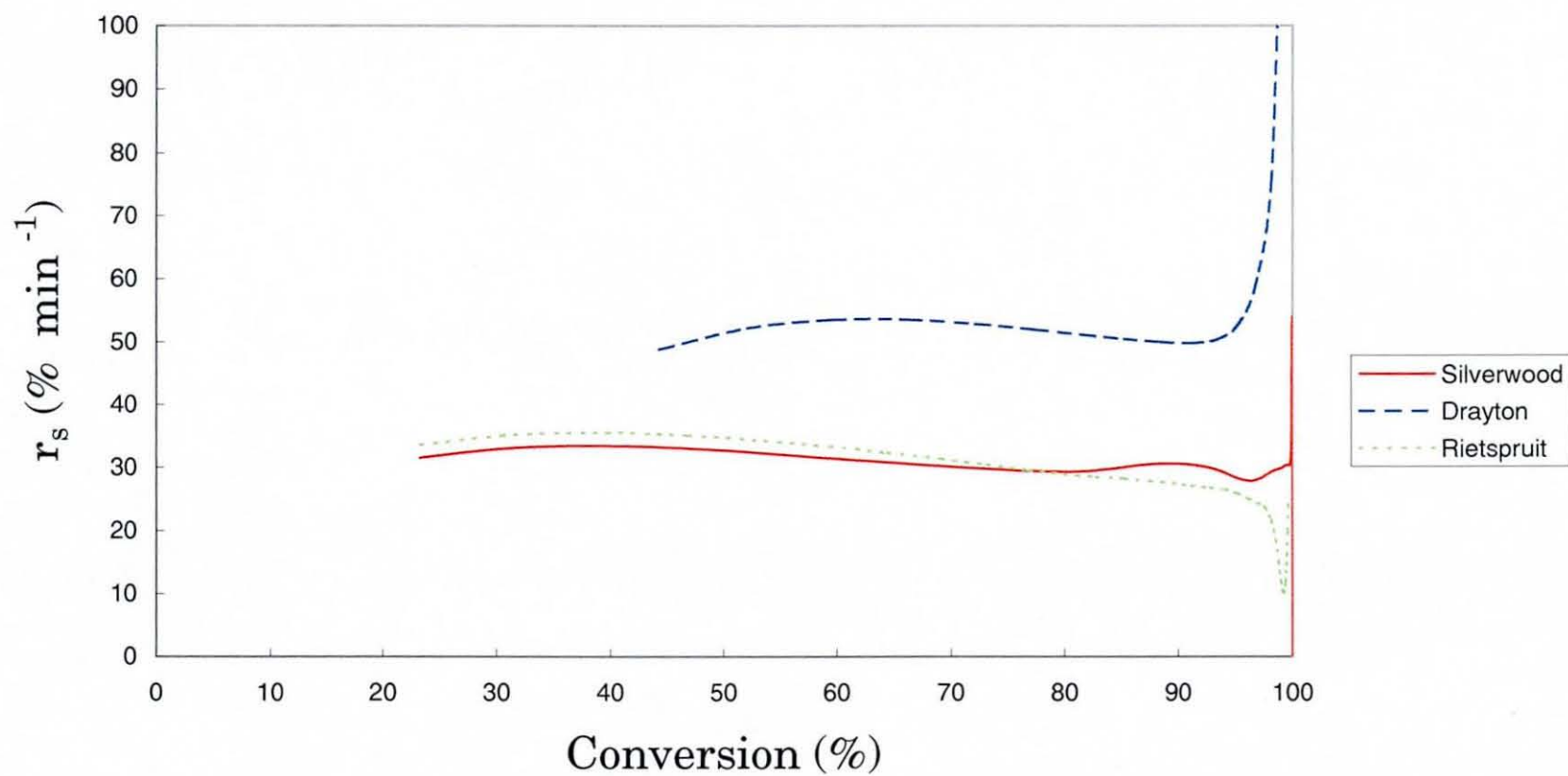


Figure 4.30: Reactivity of Liptinite Samples to Steam at 950°C and 2.5 MPa

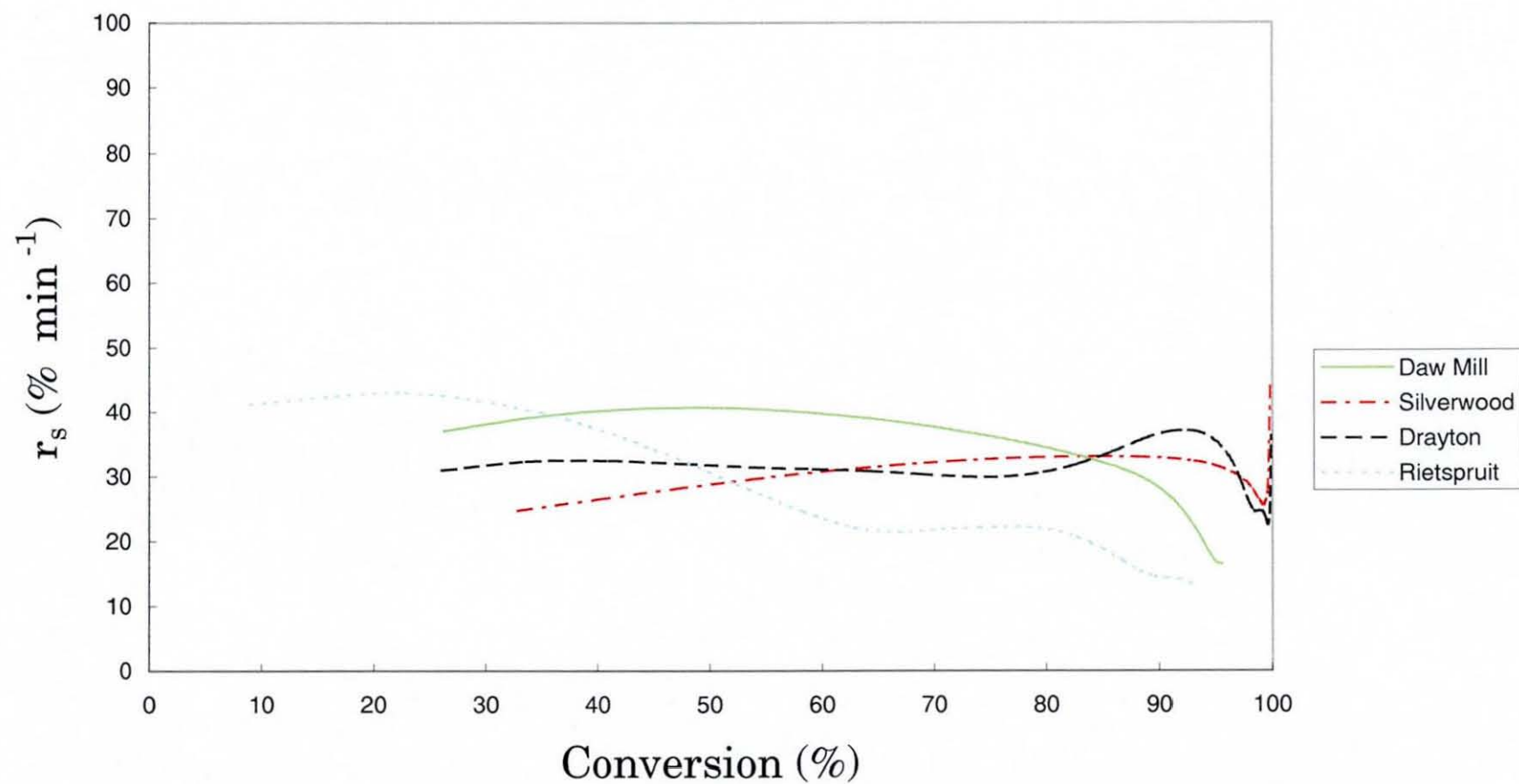


Figure 4.31: Reactivity of Inertinite Samples to Steam at 950°C and 2.5 MPa

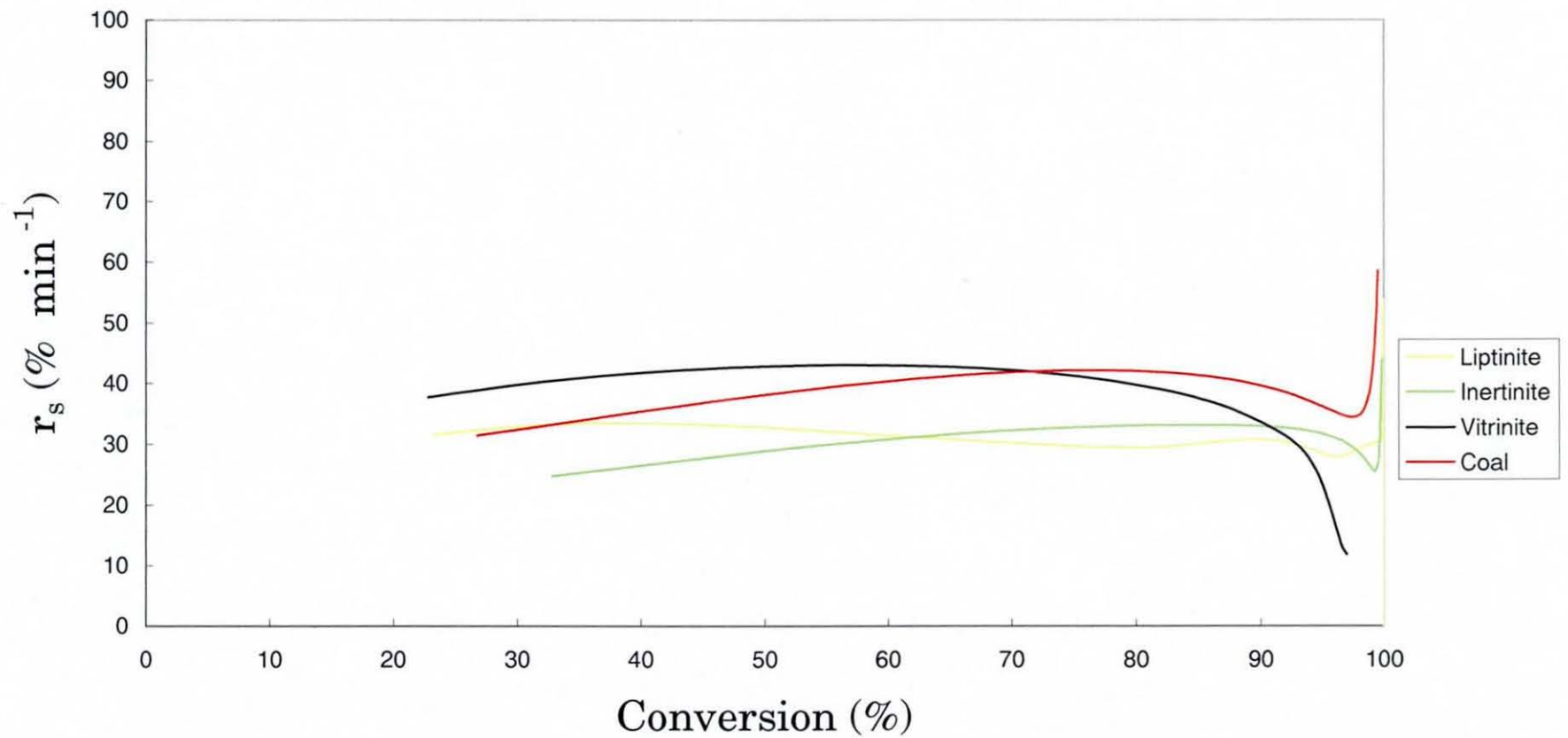


Figure 4.32: Reactivity of Silverwood Macerals to Steam at 950°C and 2.5 MPa

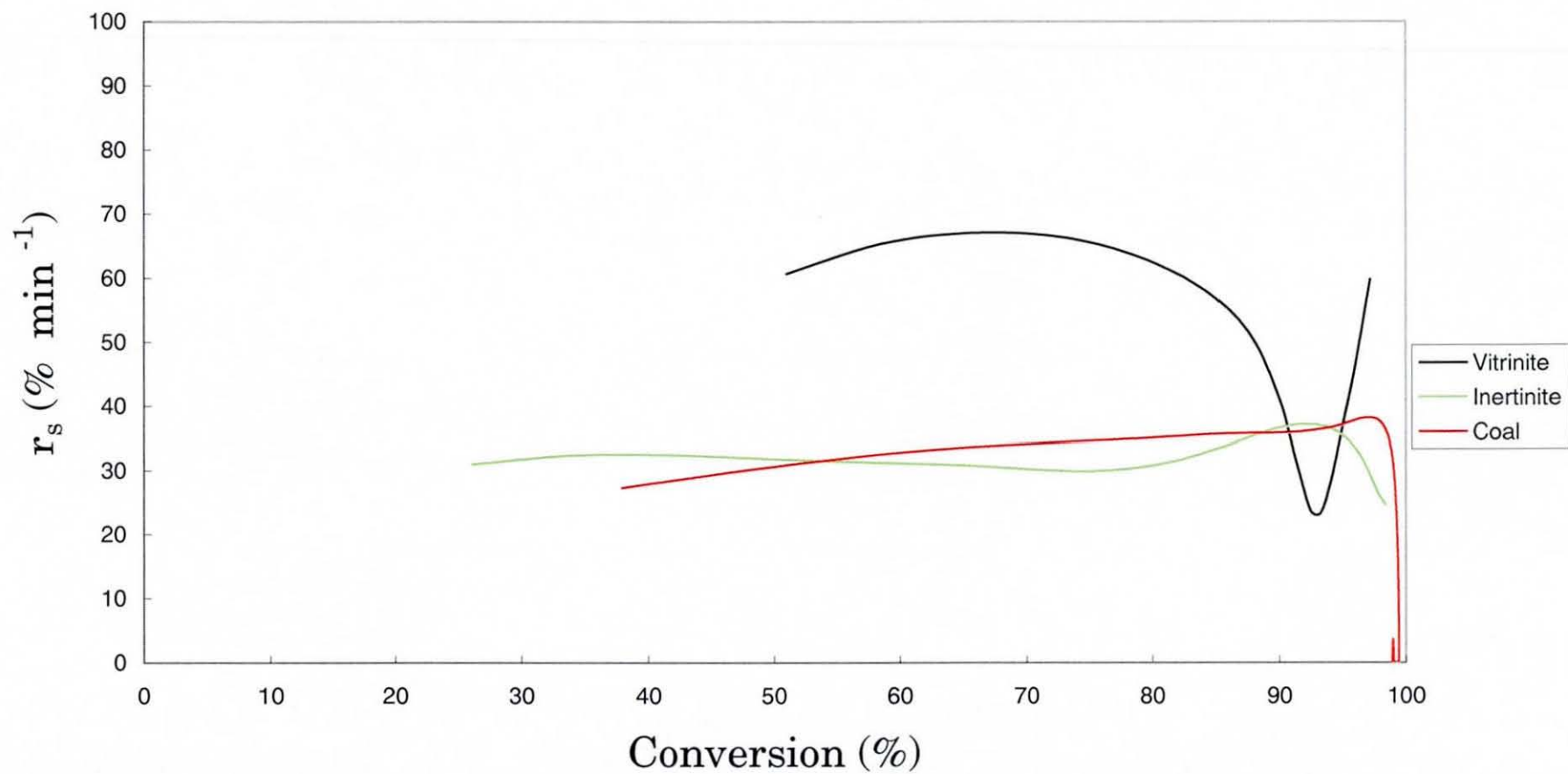


Figure 4.33: Reactivity of Drayton Macerals to Steam at 950°C and 2.5 MPa

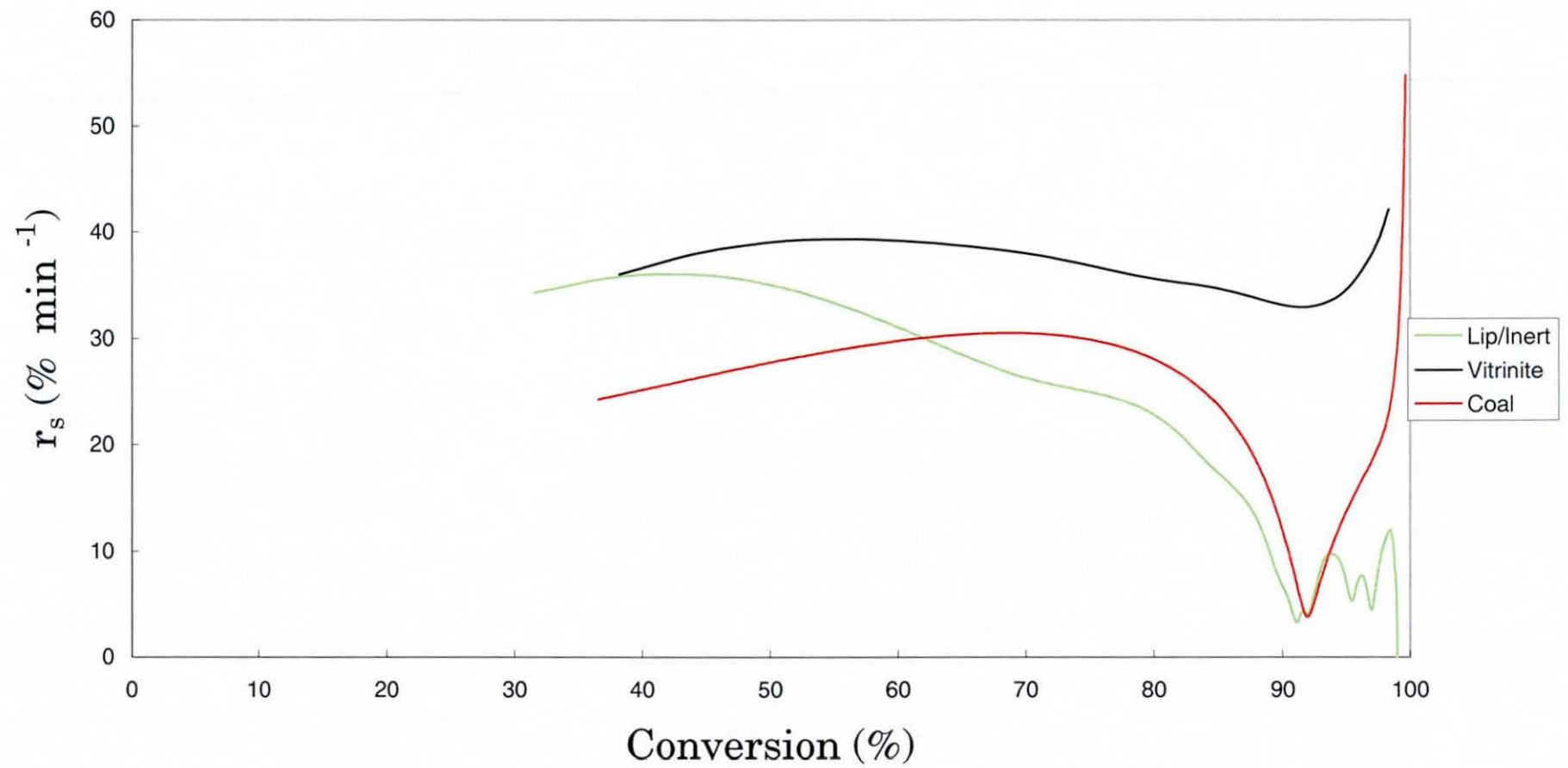


Figure 4.34: Reactivity of Longannet Macerals to Steam at 950°C and 2.5 MPa

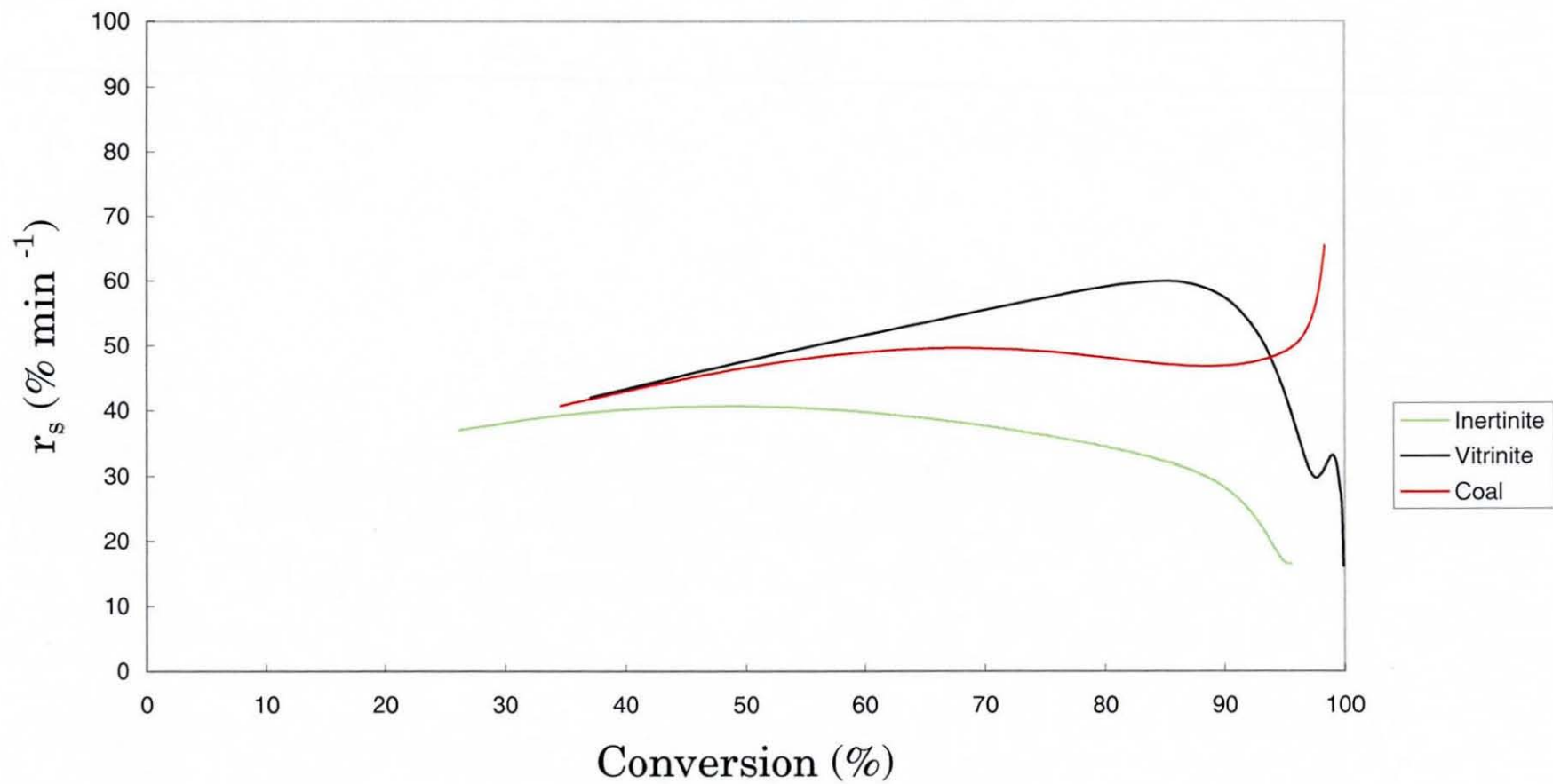


Figure 4.35: Reactivity of Daw Mill Macerals to Steam at 950°C and 2.5 MPa

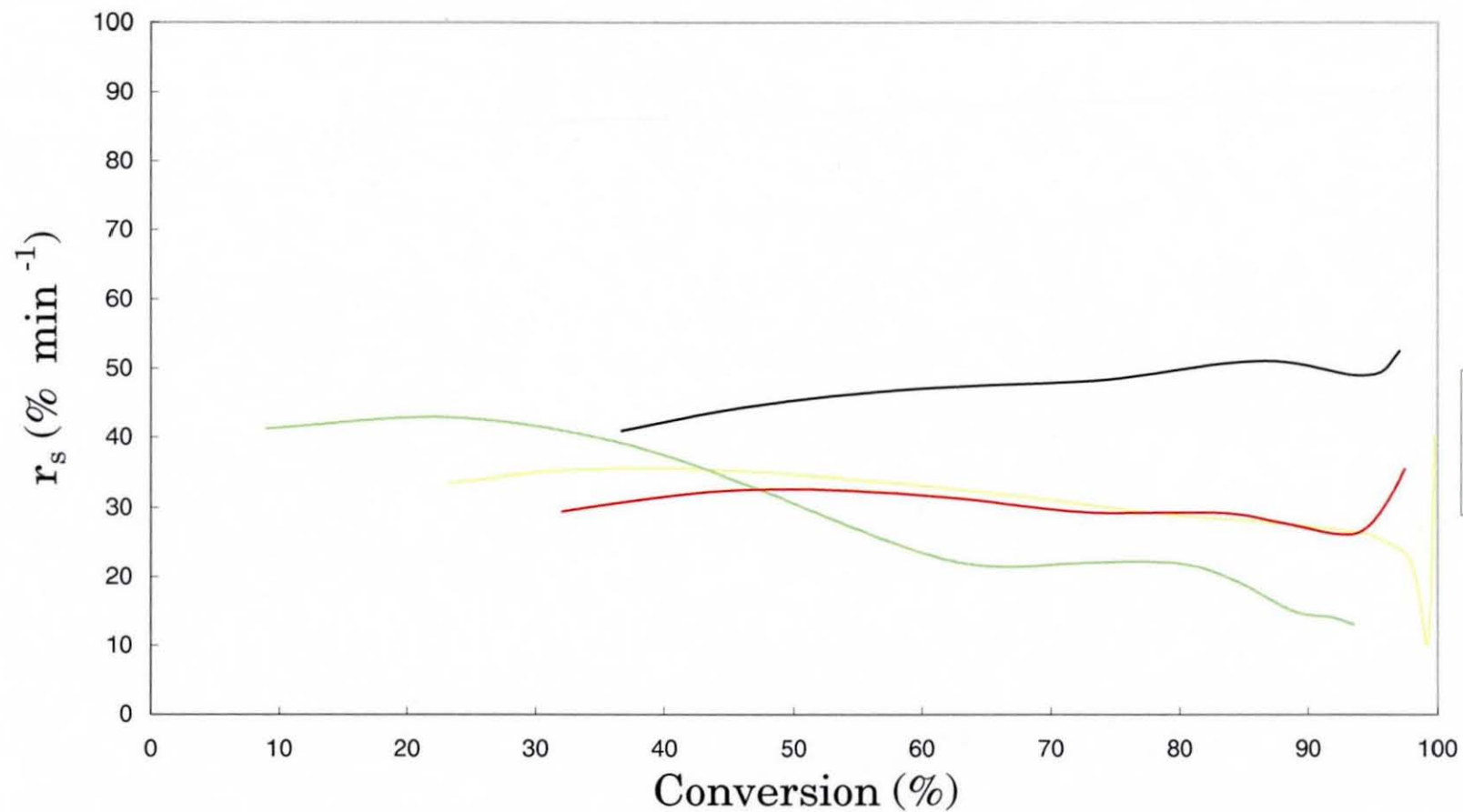


Figure 4.36: Reactivity of Rietspruit Macerals to Steam at 950°C and 2.5 MPa

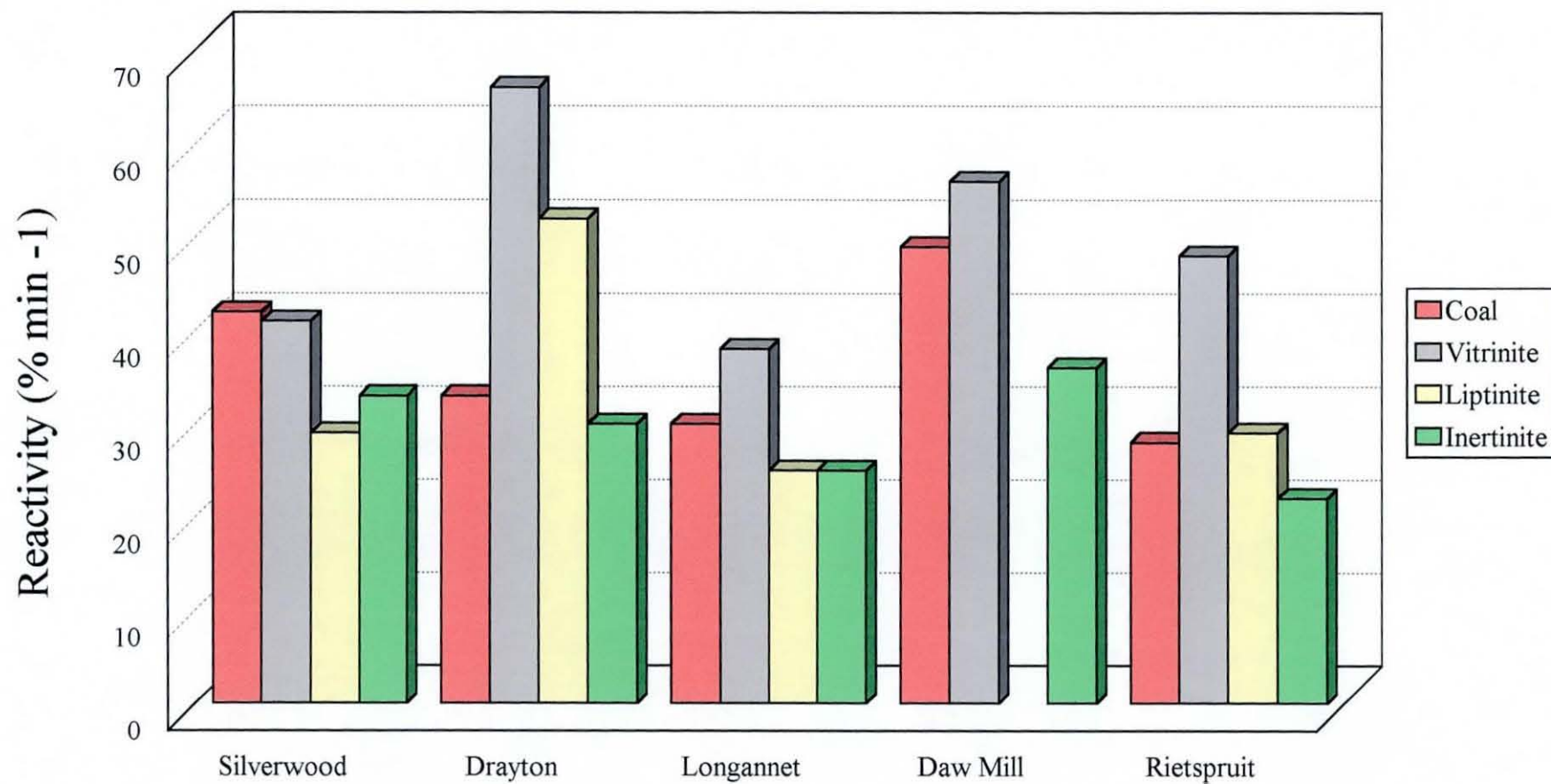


Figure 4.37: Variation of Reactivity with Maceral Type
Coal in Steam at 950°C and 2.5MPa

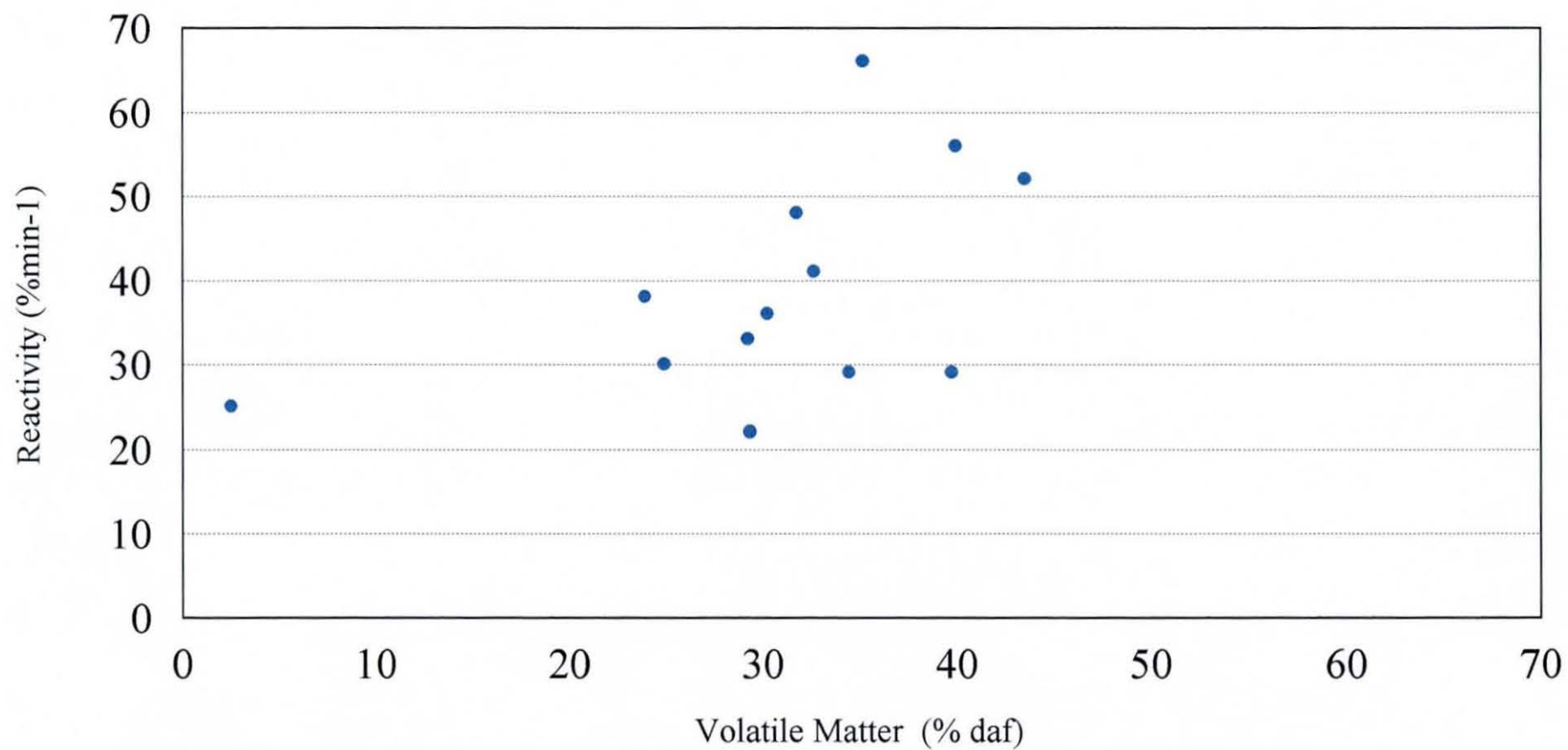


Figure 4.38: Reactivity to Steam vs Volatile Matter for Maceral Concentrates

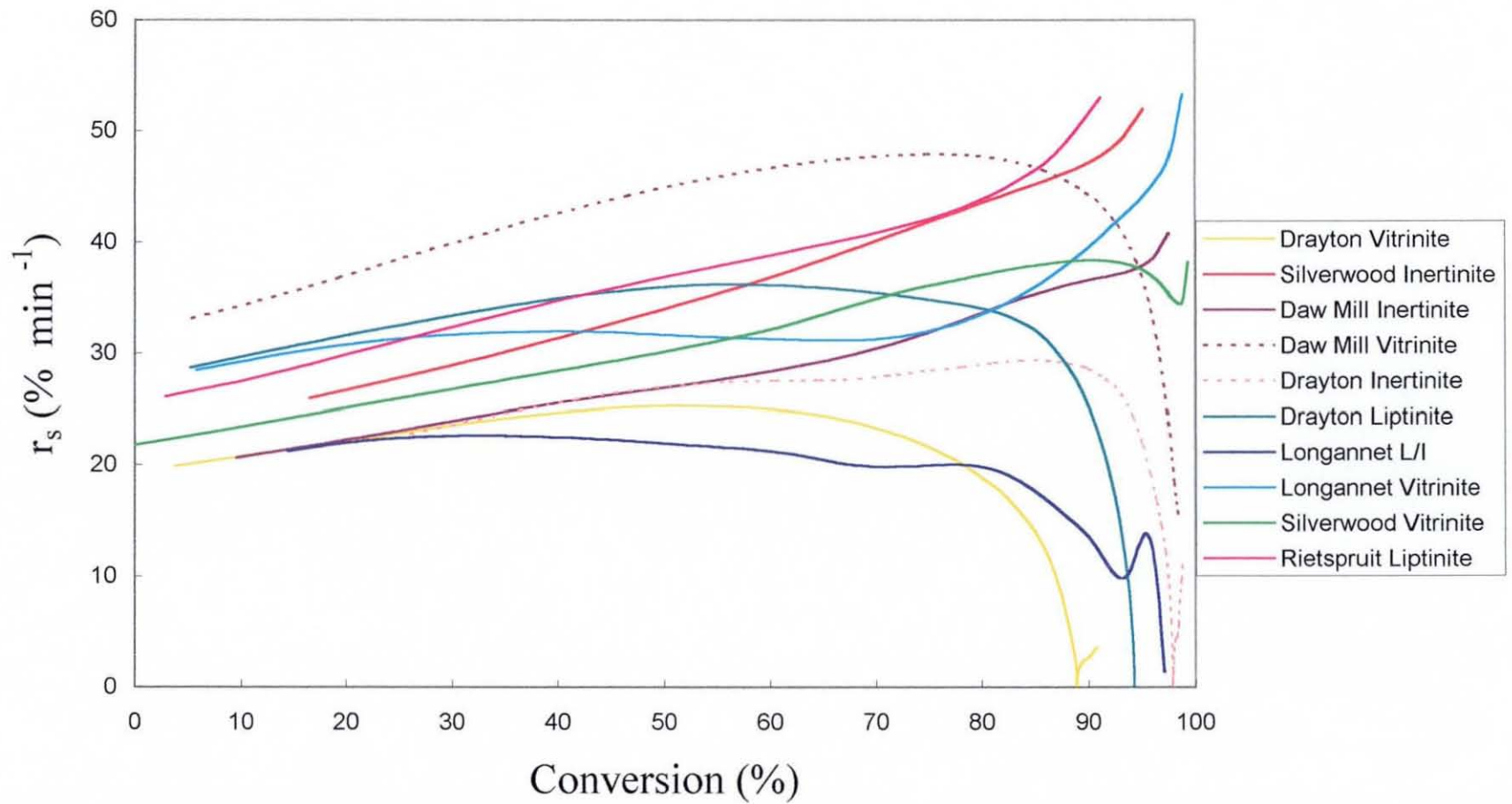


Fig 4.39: Reactivity of Char Samples to Steam at 950°C and 2.5 MPa

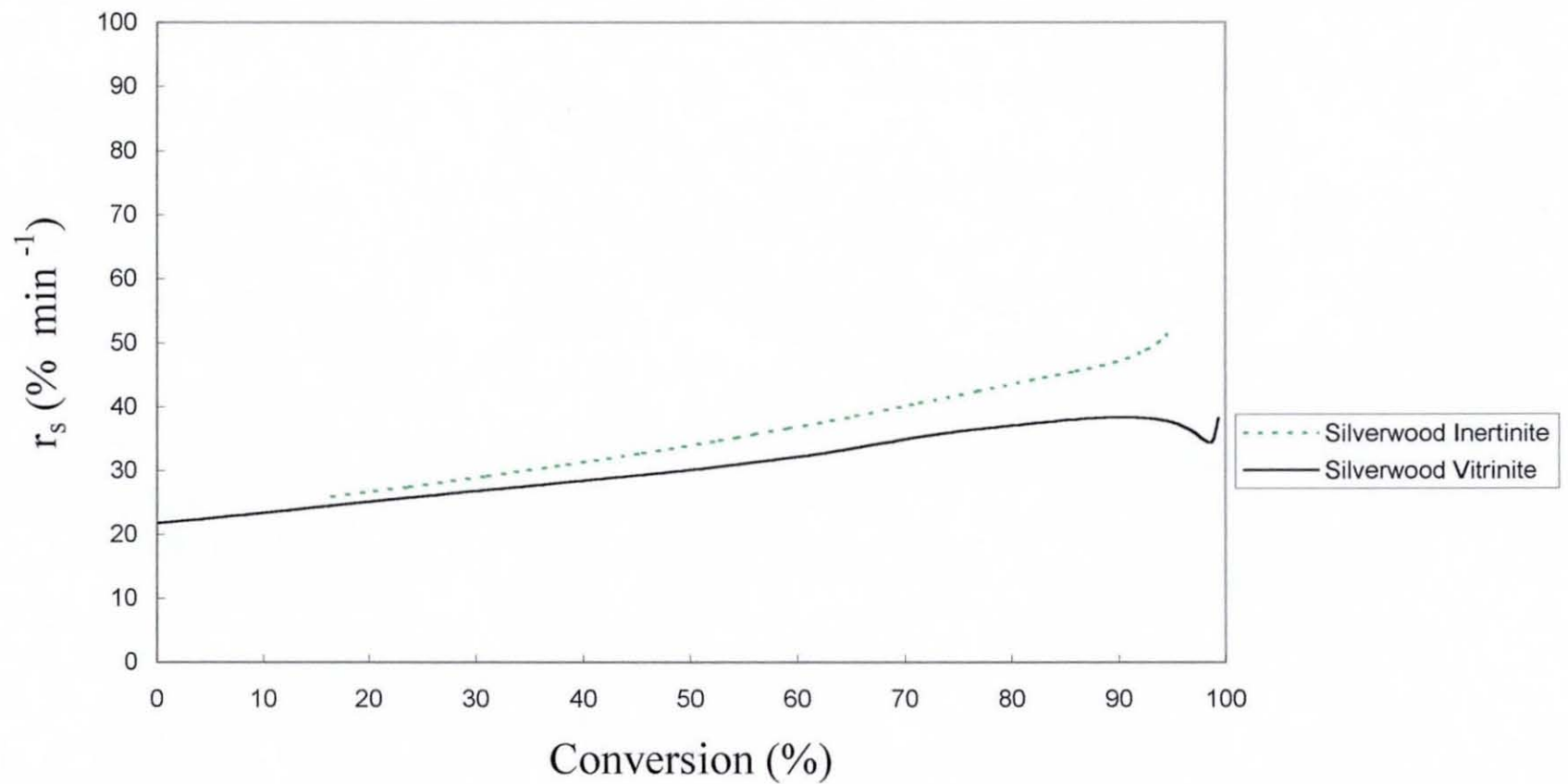


Figure 4.40: Reactivity of Silverwood Char Samples to Steam at 950°C and 2.5 MPa

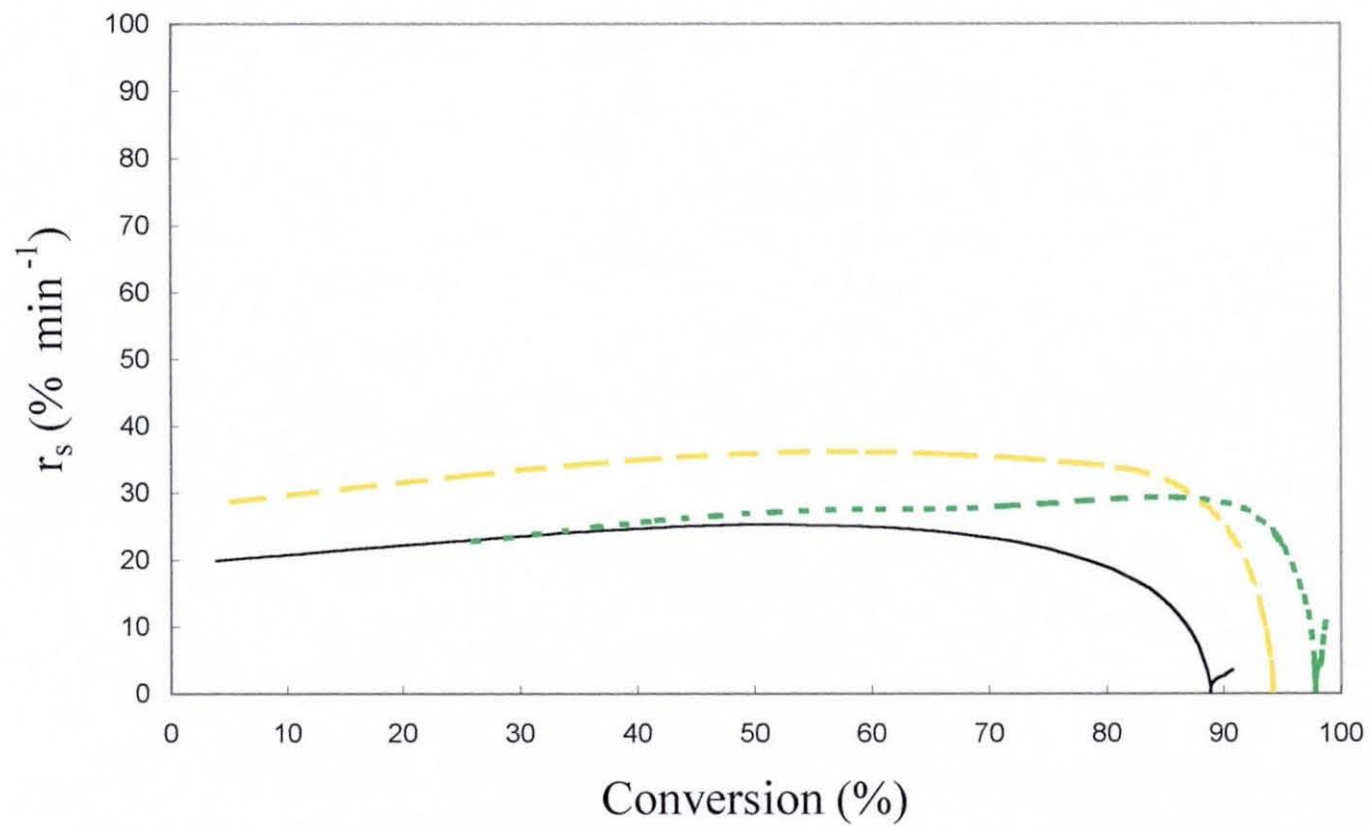


Figure 4.41: Reactivity of Drayton Char Samples to Steam at 950°C and 2.5 MPa

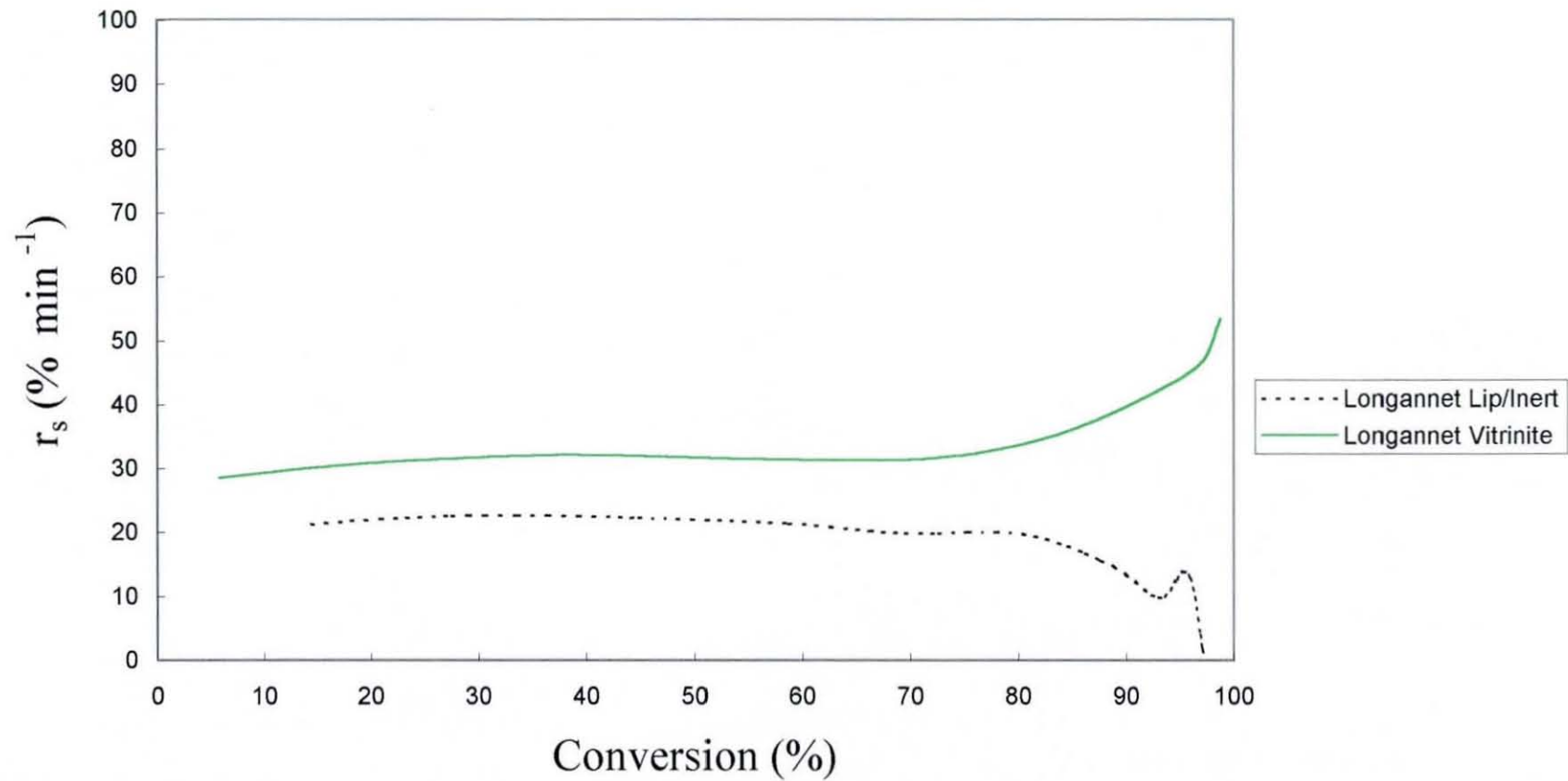


Figure 4.42: Reactivity of Longannet Char Samples to Steam at 950°C and 2.5 MPa

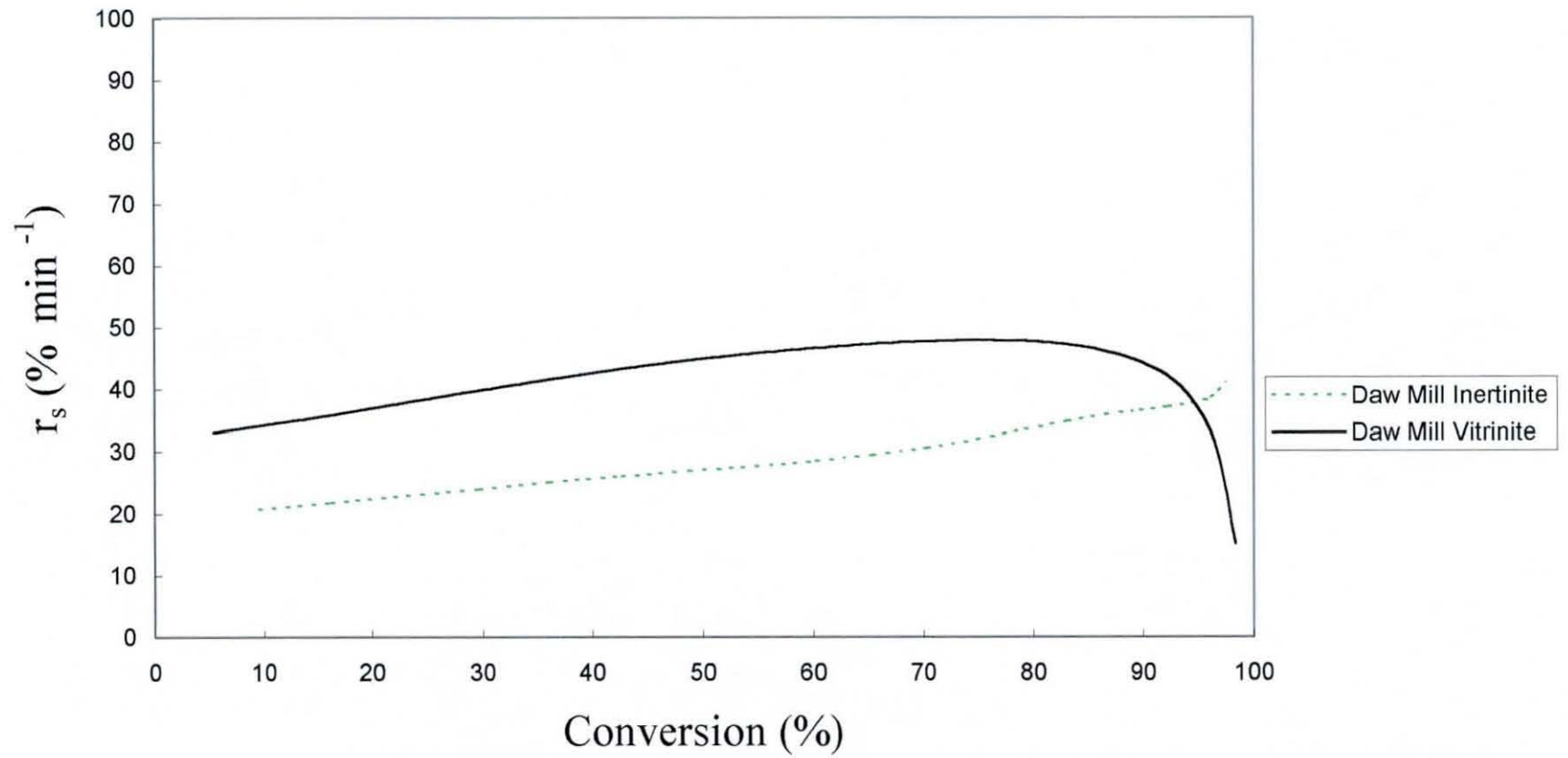


Figure 4.43: Reactivity of Daw Mill Char Samples to Steam at 950°C and 2.5 MPa

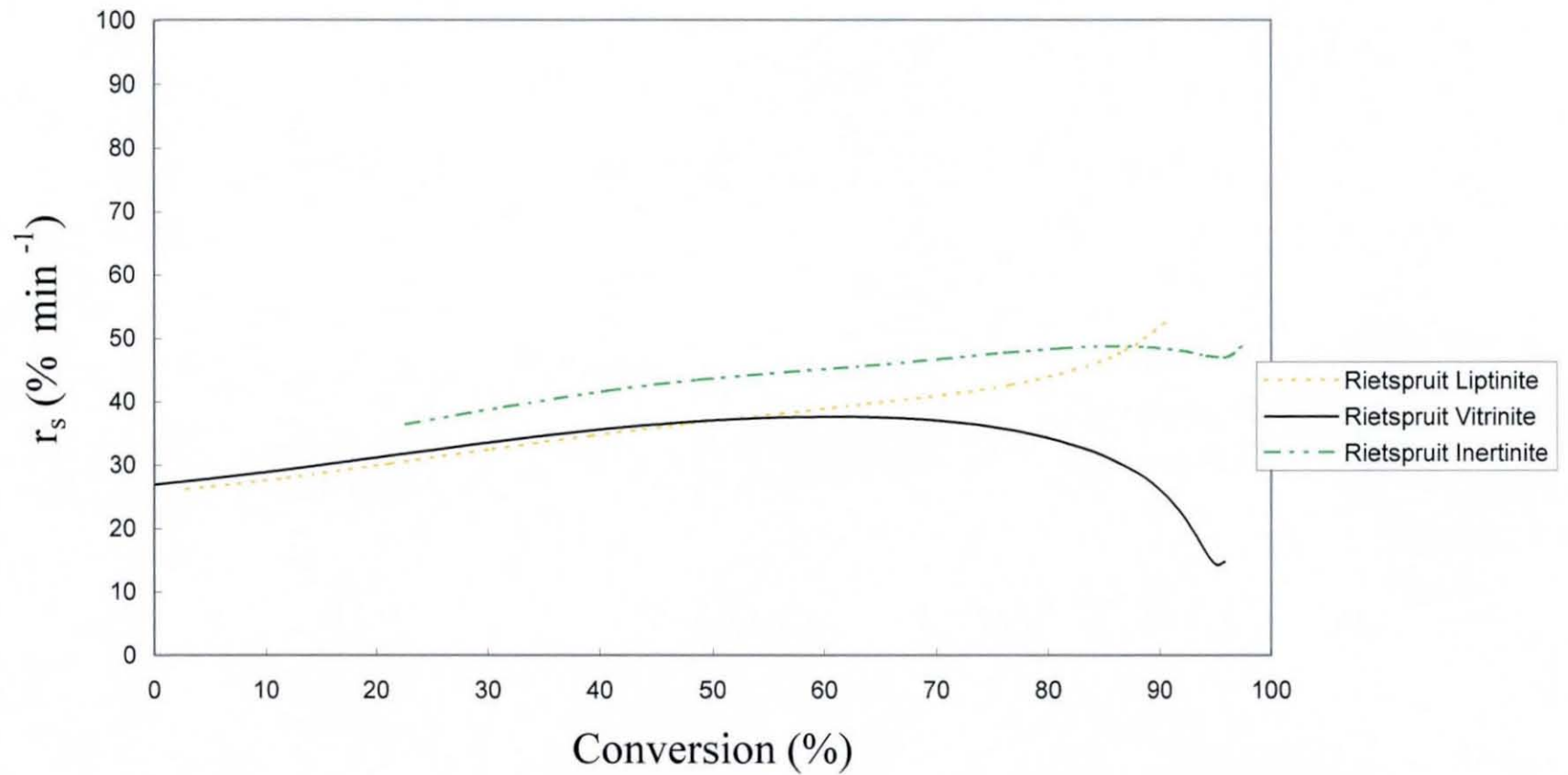


Figure 4.44: Reactivity of Rietspruit Char Samples to Steam at 950°C and 2.5 MPa

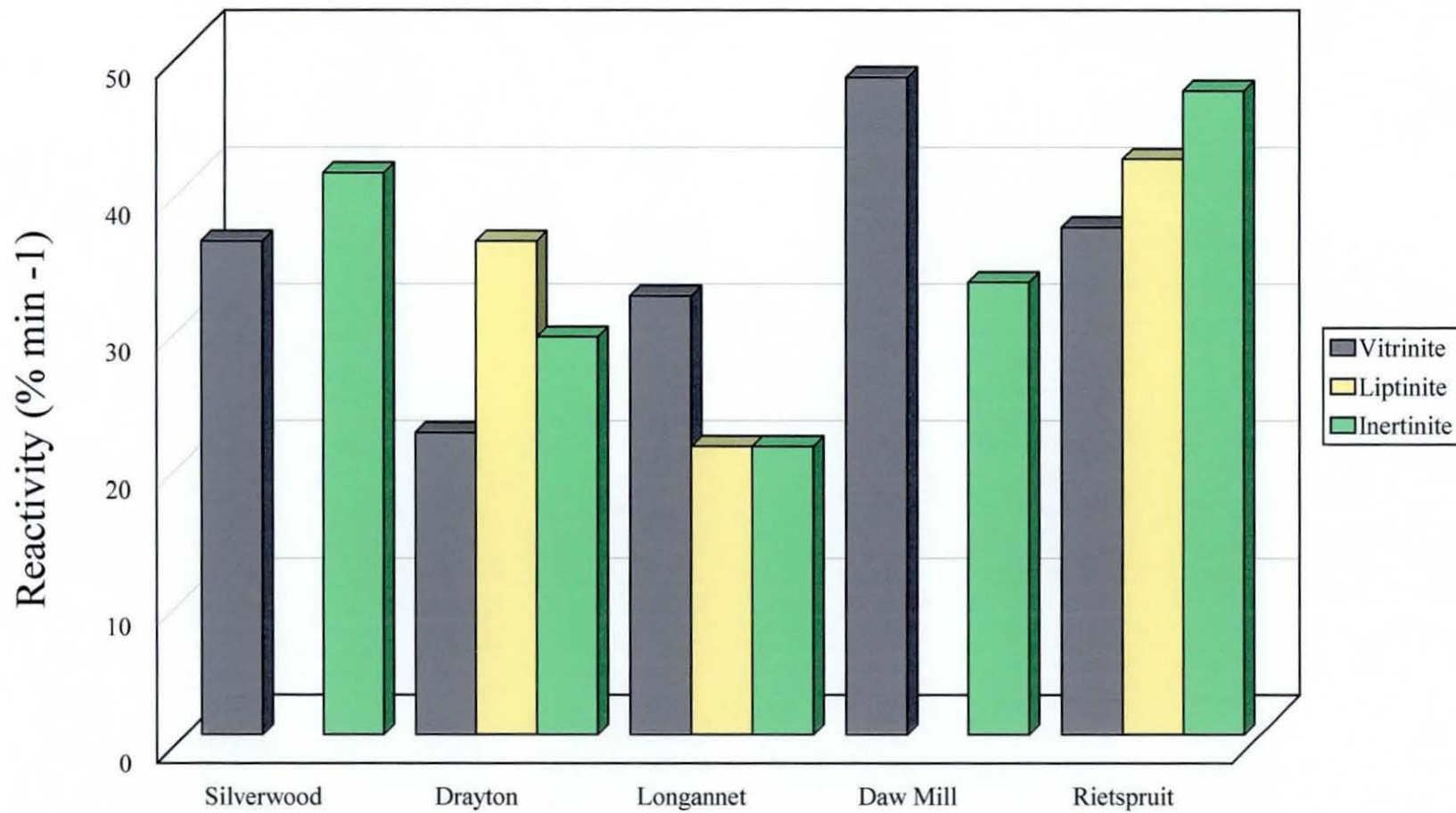


Figure 4.45: Variation of Reactivity with Maceral Type
Char in Steam at 950°C and 2.5 MPa

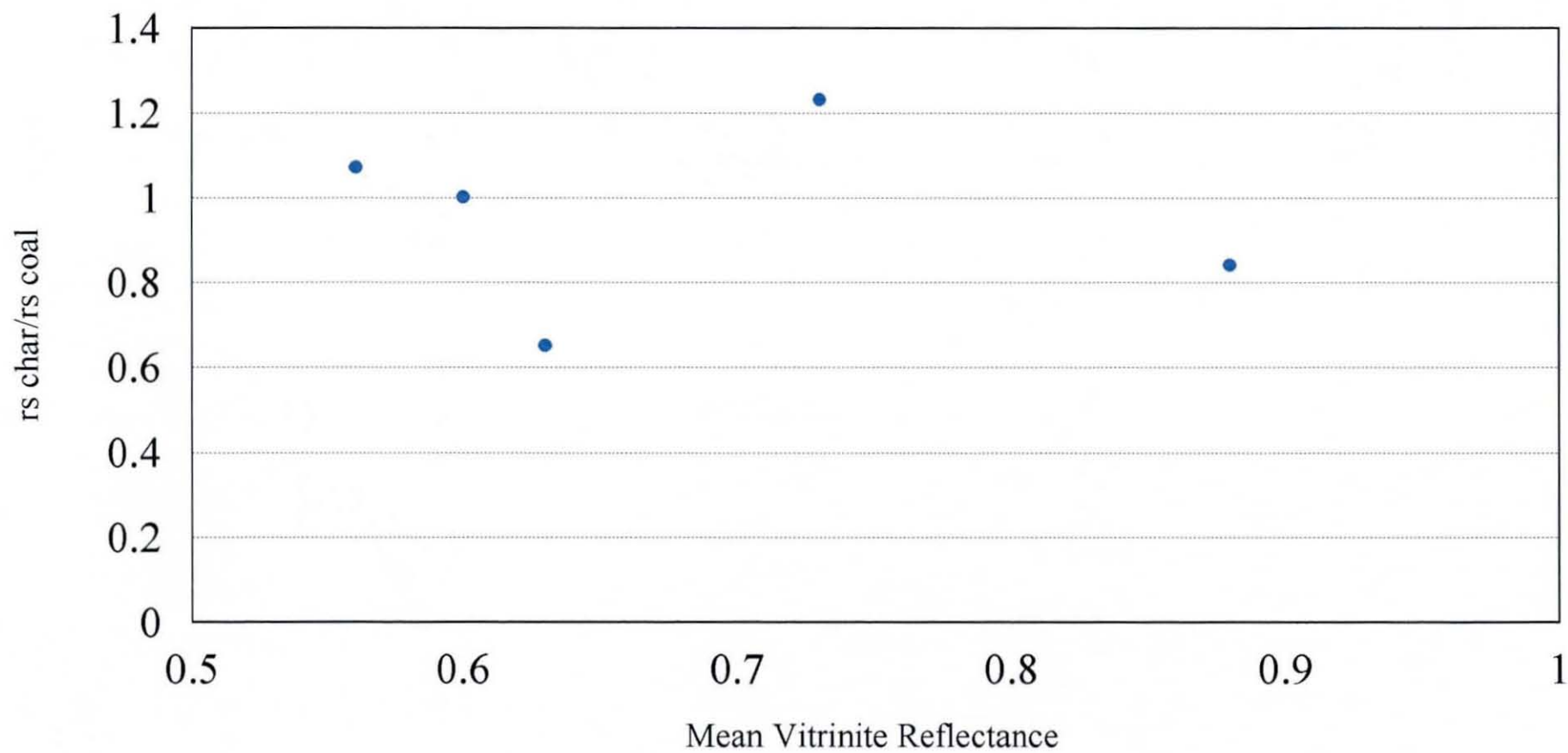


Figure 4.46: Ratio of Vitrinite Reactivity Before and After Pyrolysis in the FBR vs Mean Vitrinite Reflectance

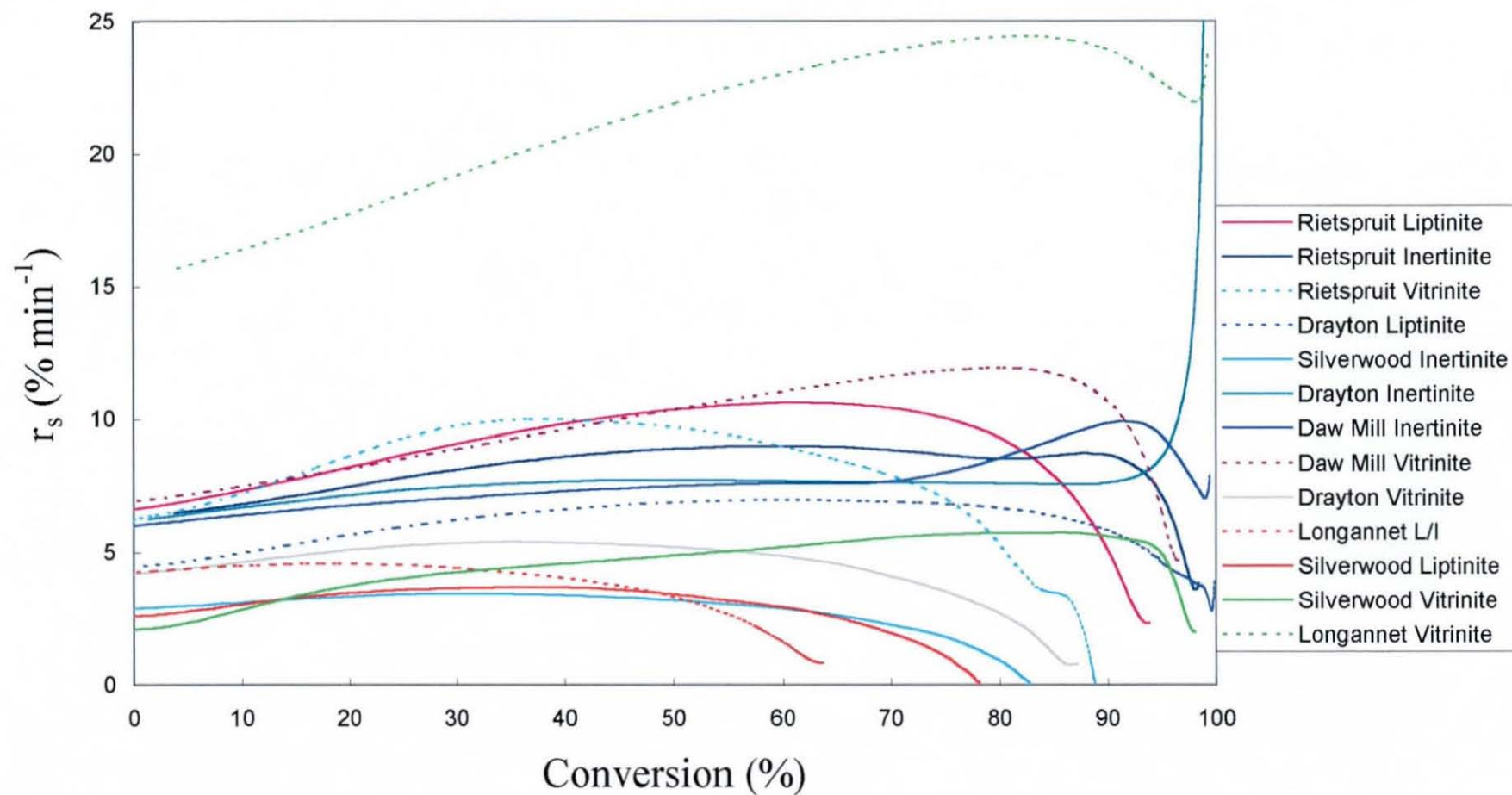


Figure 4.47: Reactivity of Maceral Chars to CO₂ at 950°C and 2.5 MPa

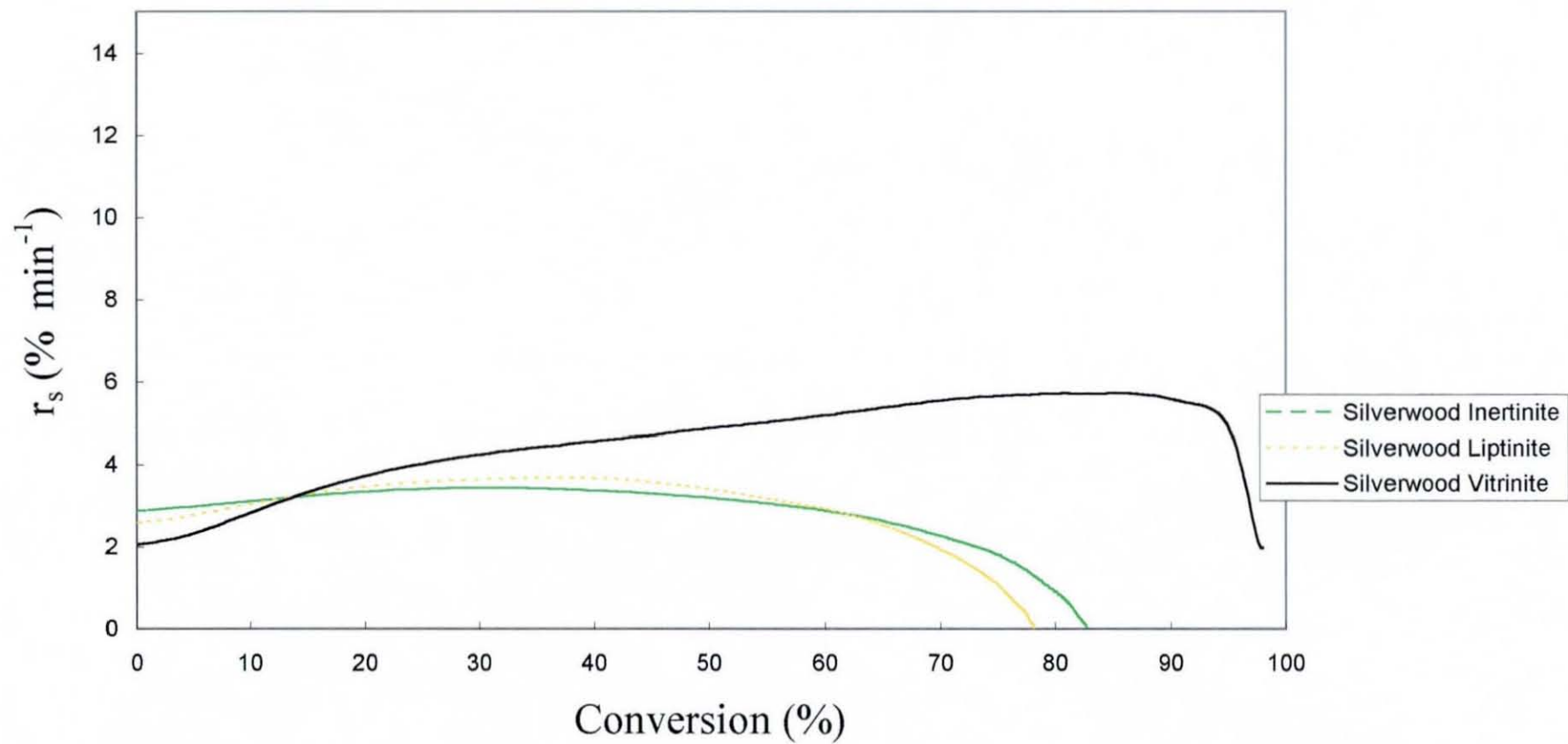


Figure 4.48: Reactivity of Silverwood Char Samples to CO_2 at 950°C and 25 Bar

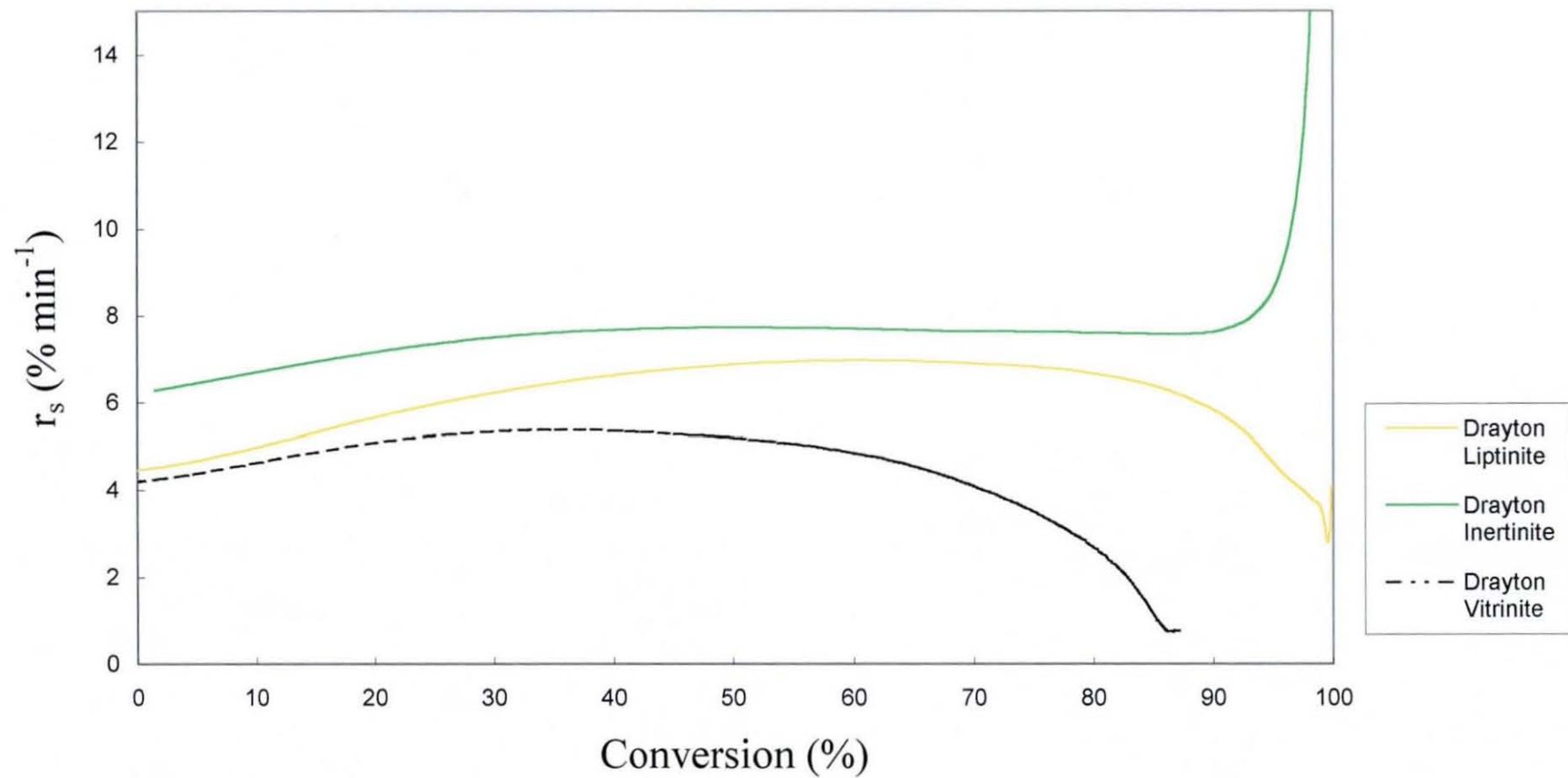


Figure 4.49: Reactivity of Drayton Char Samples to CO₂ at 950°C and 2.5 MPa

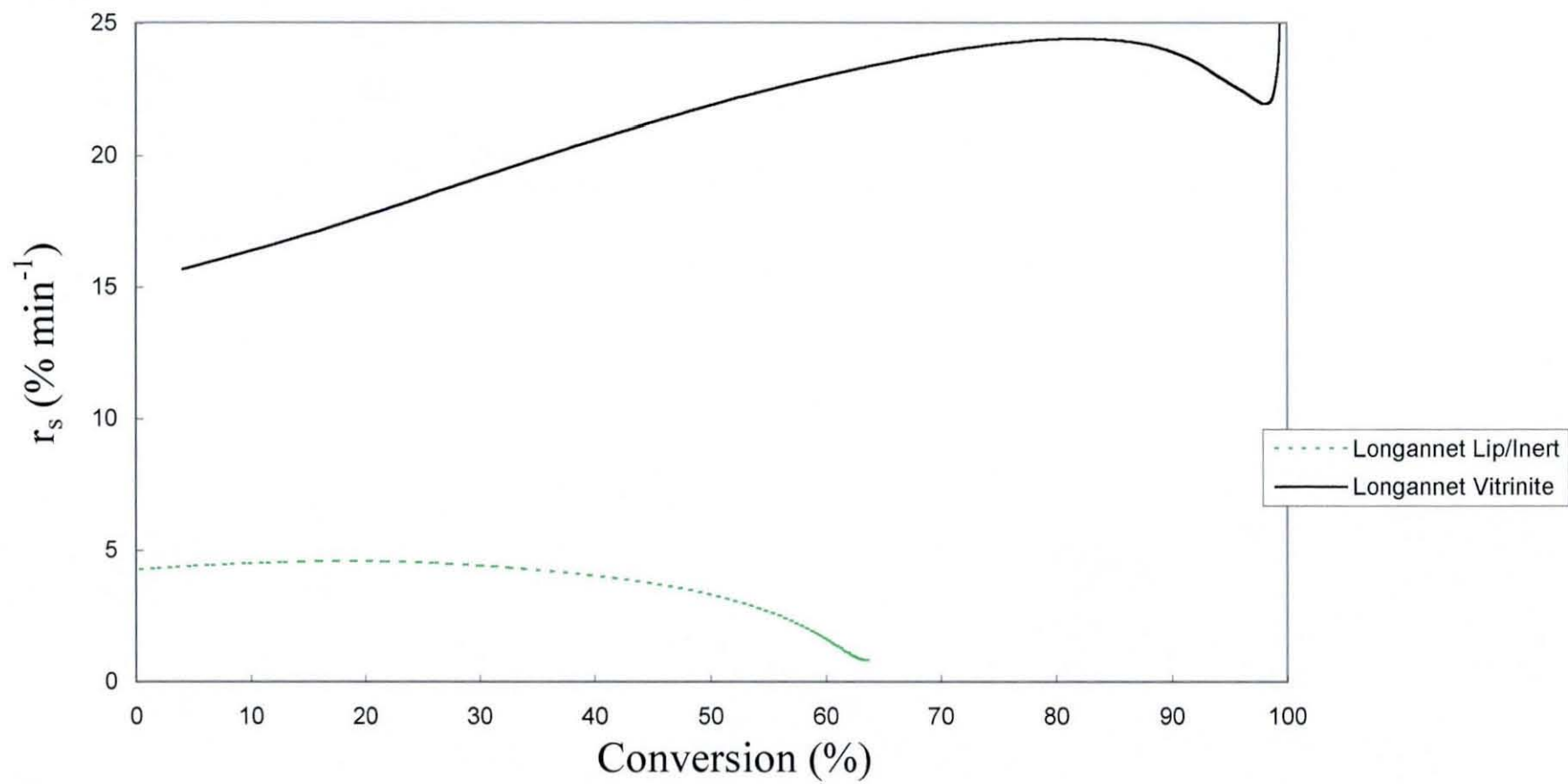


Figure 4.50: Reactivity of Longannet Char Samples to CO_2 at 950°C and 2.5 MPa

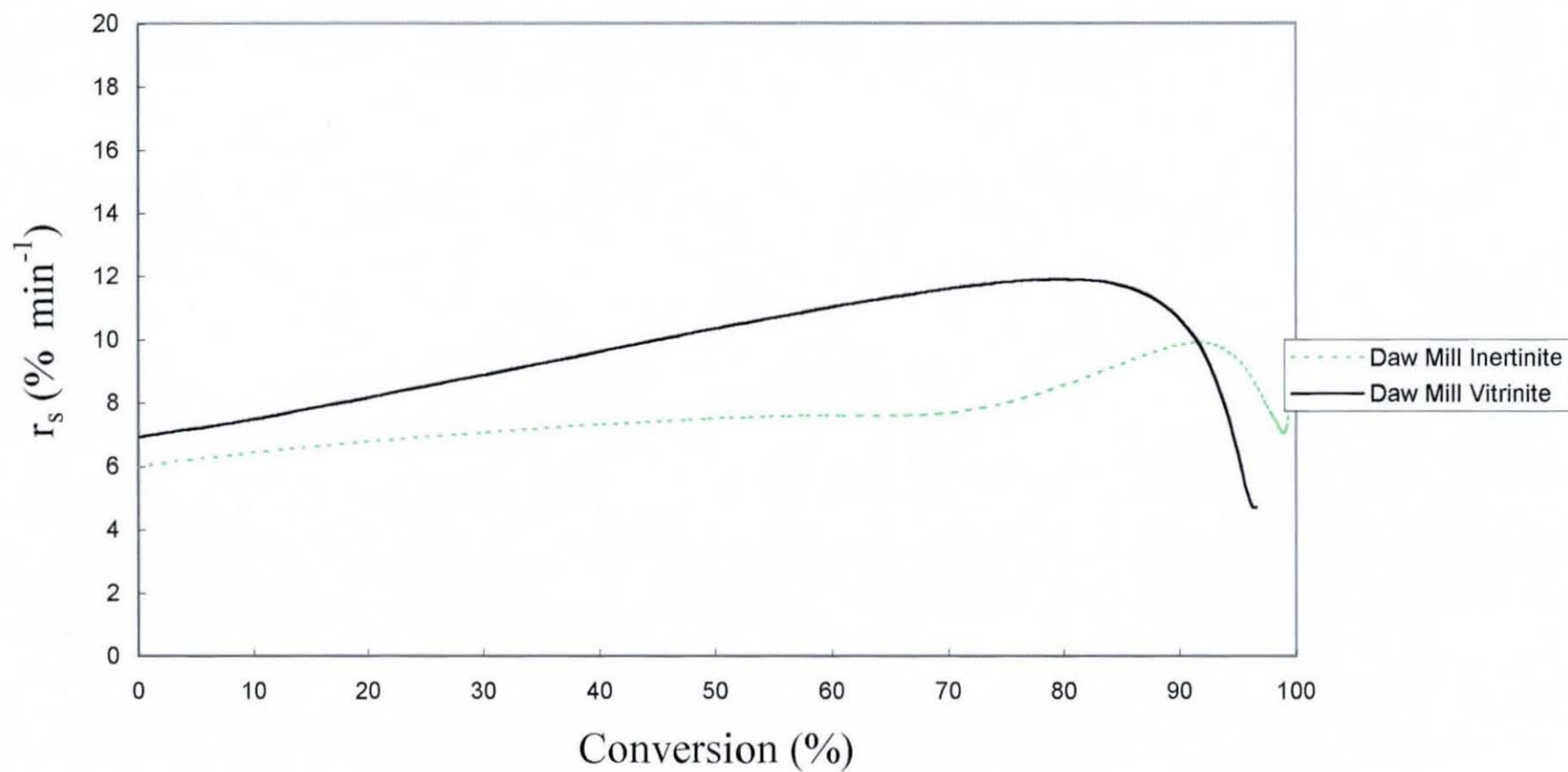


Figure 4.51: Reactivity of Daw Mill Char Samples to CO_2 at 950°C and 2.5 MPa

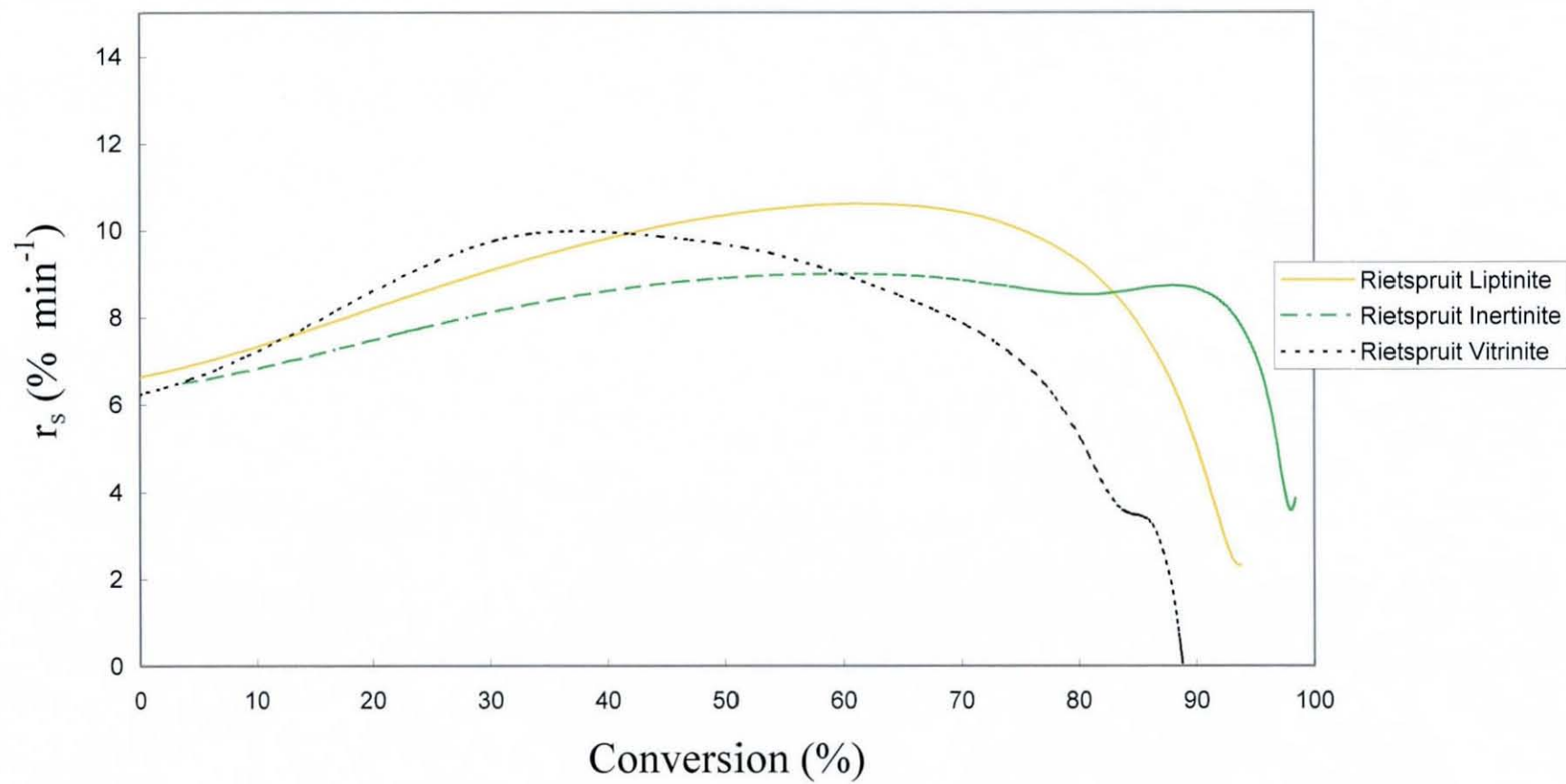


Figure 4.52: Reactivity of Rietspruit Char Samples to CO_2 at 950°C and 2.5 MPa

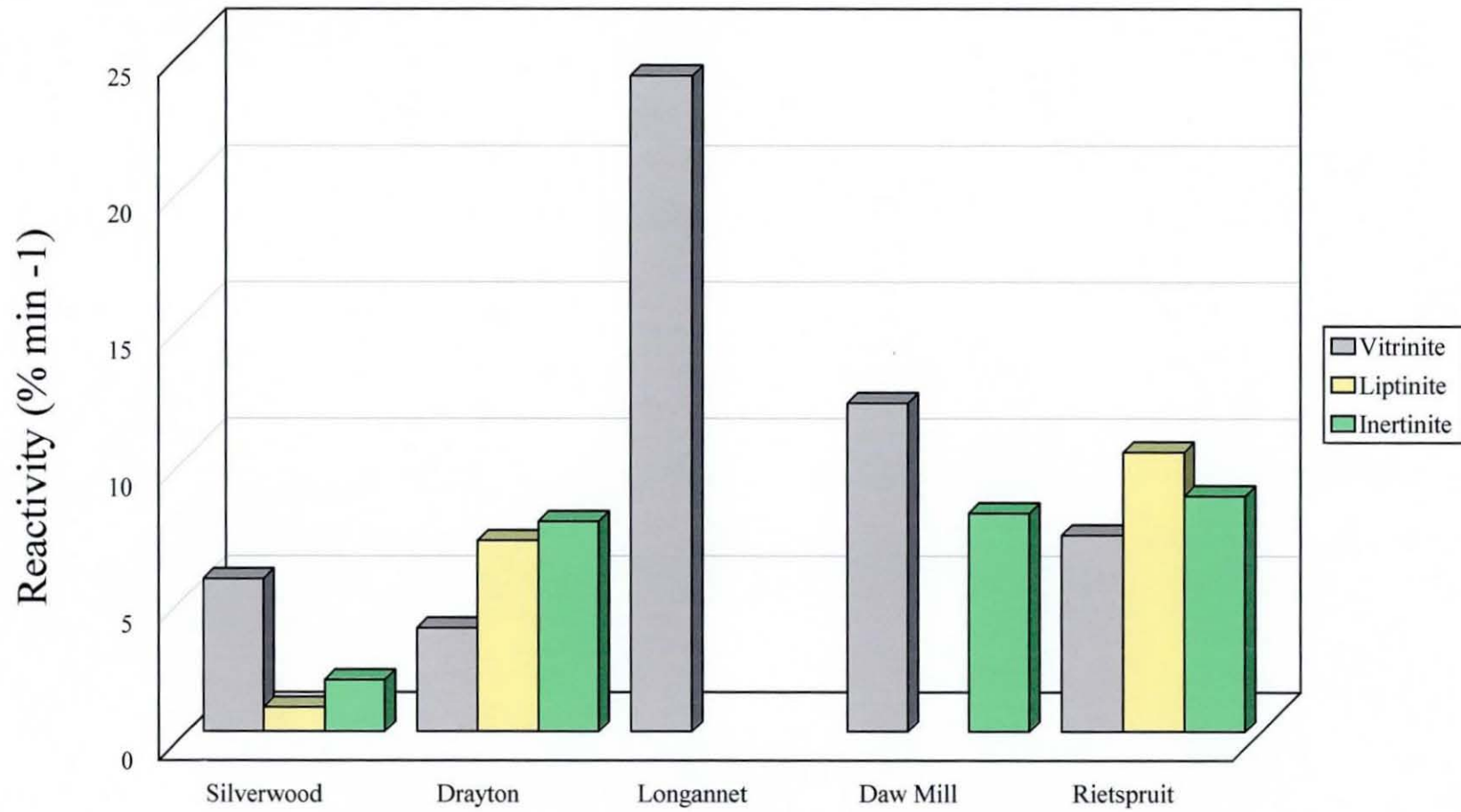


Figure 4.53: Variation of Reactivity with Maceral Type
Char in CO₂ at 950°C and 2.5 MPa

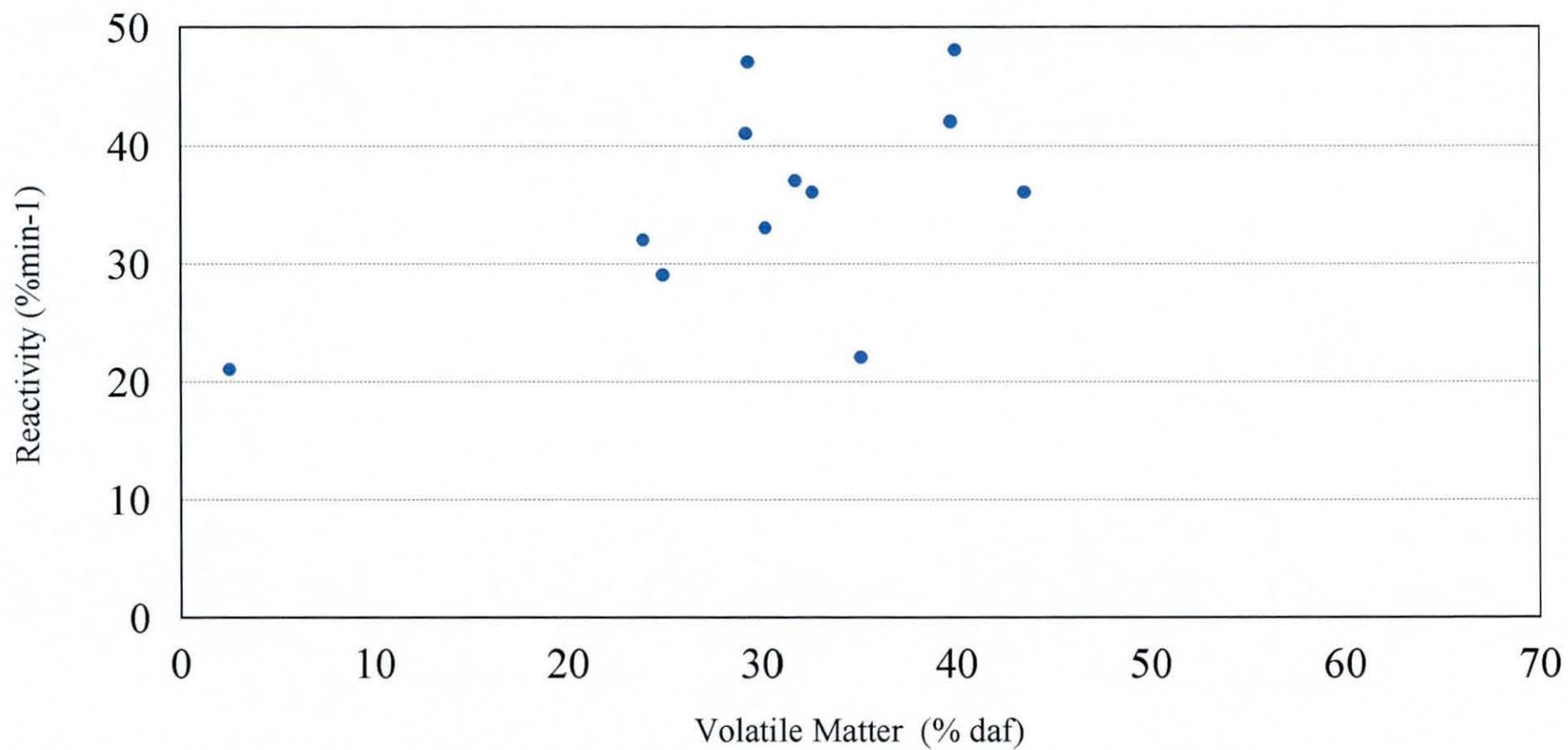


Figure 4.54: Reactivity of Char to Steam vs Volatile Matter in Coal for Maceral Concentrates

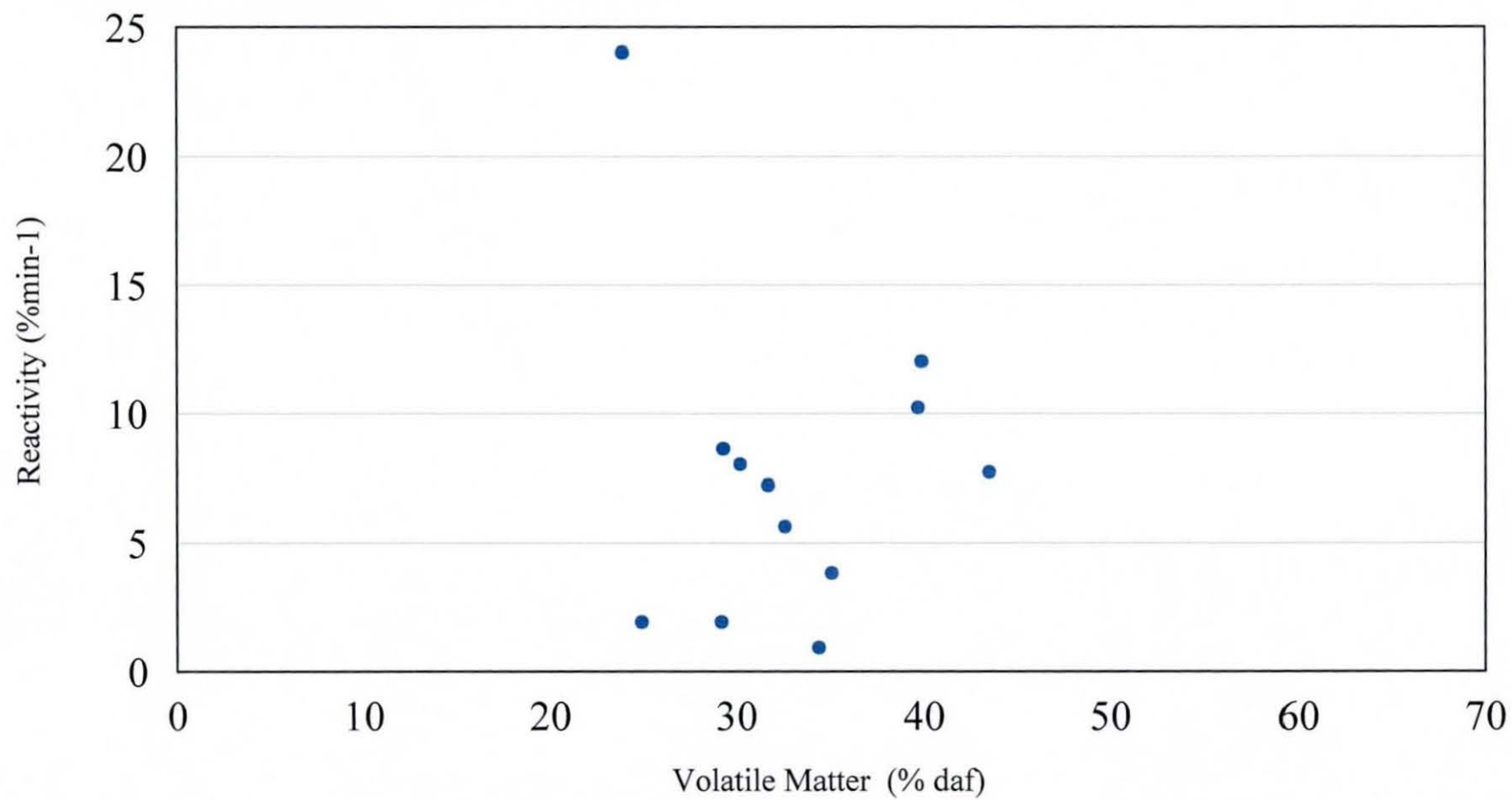


Figure 4.55: Reactivity of Char to CO₂ vs Volatile Matter in Coal for Maceral Concentrates

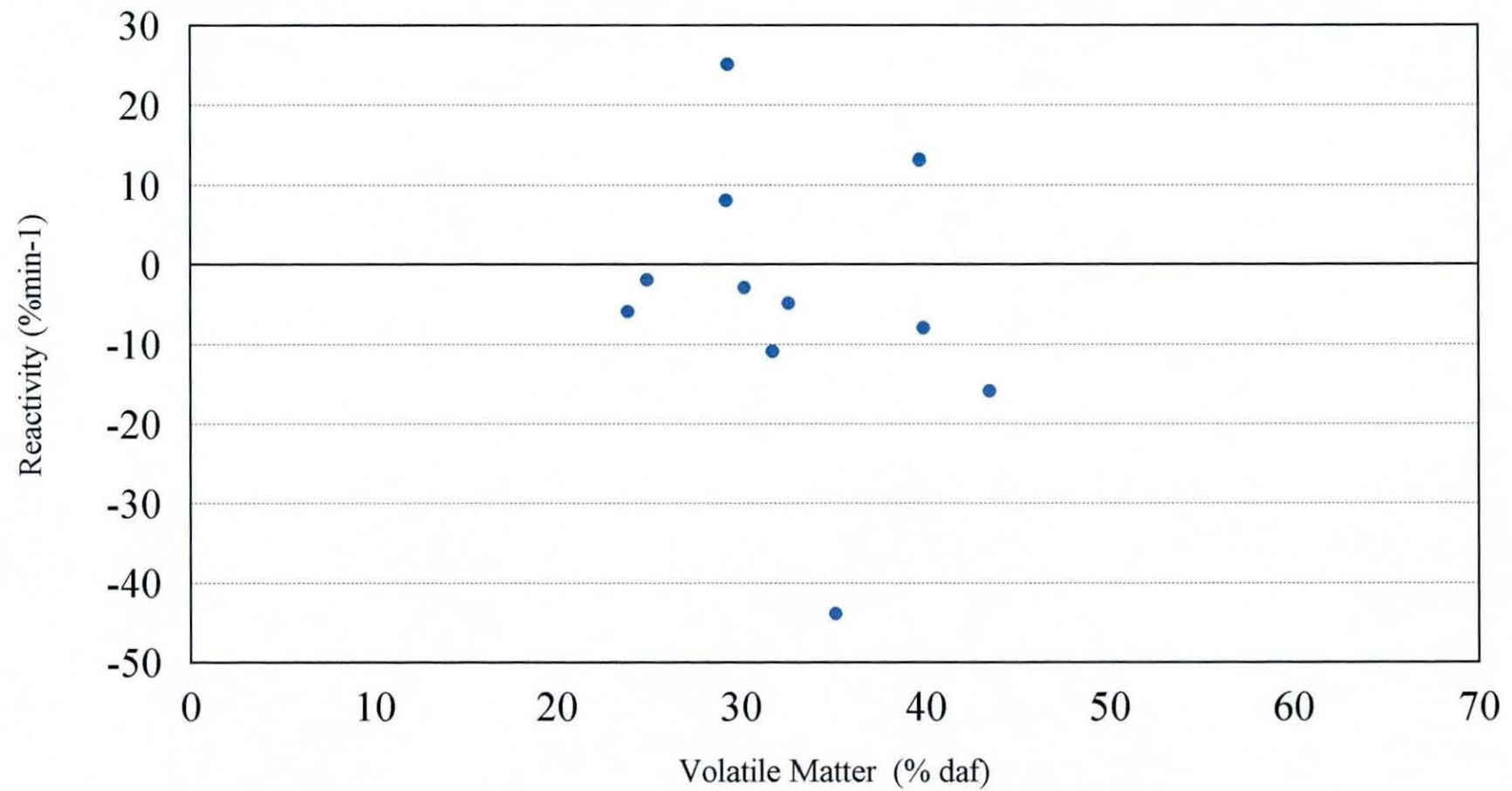


Figure 4.56: Difference in Reactivity between Coals and Chars for Maceral Concentrates vs Volatile Matter in Coal

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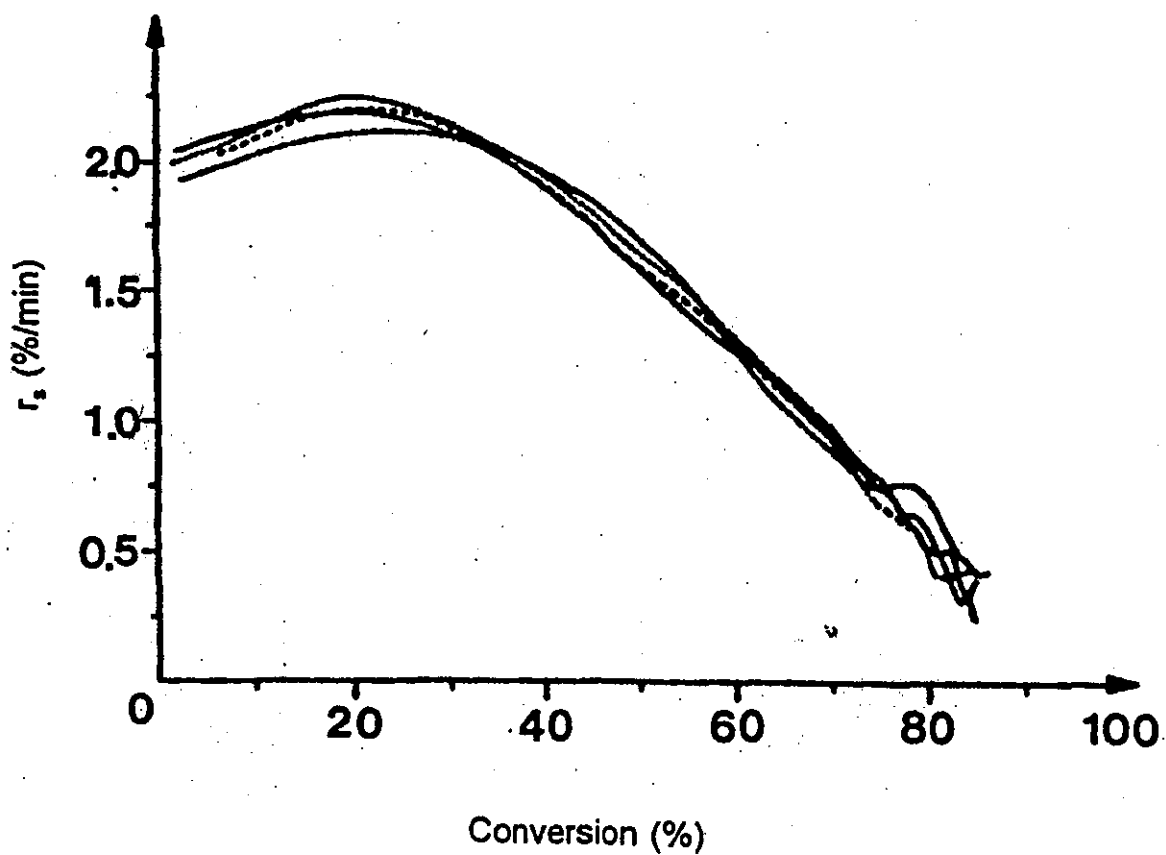
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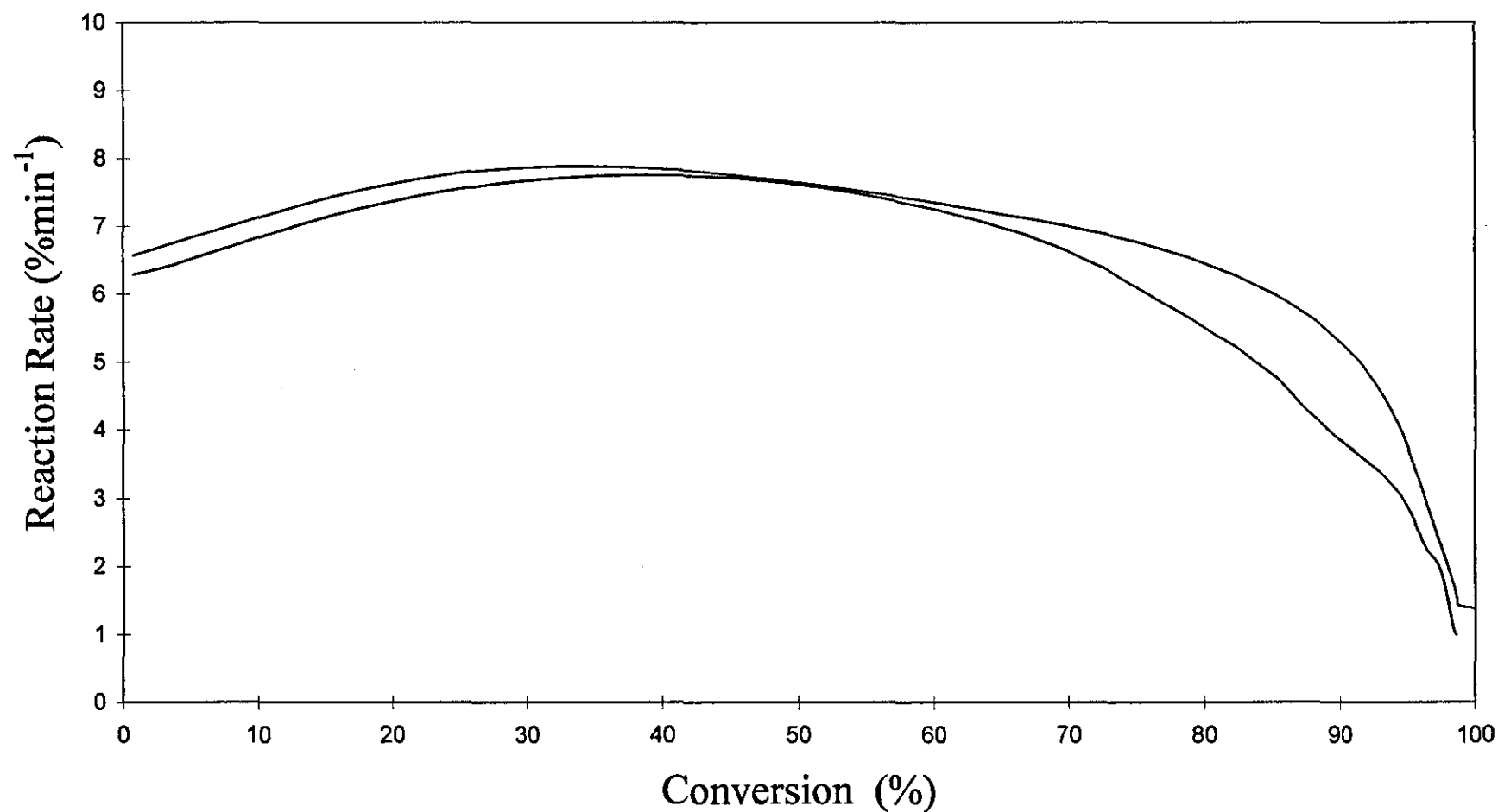
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Appendix 1: Illustration of Reproducibility of PTGA Tests (From Sowa⁽²⁰⁾)

Four Tests on Steam Gasification of a Char Sample at 850°C, 2.5 MPa Pressure

H₂O/H₂ = 96%/4%



Appendix 1a Reproducibility of PTGA Tests
Repeat Tests on Daw Mill Coal at 0.8MPa and 850°C

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1
R Square	1
Adjusted	65535
Standard	0
Observati	4

ANOVA					
	df	SS	MS	F	ignificance F
Regressio	3	380.75	126.9167	0	#NUM!
Residual	0	7.84E-26	65535		
Total	3	380.75			

	Coefficient	andard Err	t Stat	P-value	ower 95%	pper 95%	ower 95.0	pper 95.0
Intercept	-119.1167	0	65535	#NUM!	-119.1167	-119.1167	-119.1167	-119.1167
X Variable	1.688153	0	65535	#NUM!	1.688153	1.688153	1.688153	1.688153
X Variable	0.402439	0	65535	#NUM!	0.402439	0.402439	0.402439	0.402439
X Variable	1.480836	0	65535	#NUM!	1.480836	1.480836	1.480836	1.480836

Appendix 2a: Results of Multiple Linear Regression for
Data On Rietspruit Coal Macerals

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1
R Square	1
Adjusted	65535
Standard	0
Observati	4

ANOVA					
	df	SS	MS	F	ignificance F
Regressio	3	858.75	286.25	0	#NUM!
Residual	0	4.05E-24	65535		
Total	3	858.75			

	Coefficient	andard Err	t Stat	P-value	ower 95%	pper 95%	ower 95.0	pper 95.0
Intercept	-745.3379	0	65535	#NUM!	-745.3379	-745.3379	-745.3379	-745.3379
X Variable	8.371385	0	65535	#NUM!	8.371385	8.371385	8.371385	8.371385
X Variable	3.914764	0	65535	#NUM!	3.914764	3.914764	3.914764	3.914764
X Variable	8.415525	0	65535	#NUM!	8.415525	8.415525	8.415525	8.415525

Appendix 2b: Results of Multiple Linear Regression Analysis for
Data on Drayton Coal Macerals

SUMMARY OUTPUT

Regression Statistics	
Multiple R	1
R Square	1
Adjusted	65535
Standard	0
Observati	4

ANOVA					
	df	SS	MS	F	ignificance F
Regressio	3	118.75	39.58333	0	#NUM!
Residual	0	3.08E-25	65535		
Total	3	118.75			

	Coefficient	andard Err	t Stat	P-value	ower 95%	pper 95%	ower 95.0	pper 95.0
Intercept	256.4443	0	65535	#NUM!	256.4443	256.4443	256.4443	256.4443
X Variable	-1.747519	0	65535	#NUM!	-1.747519	-1.747519	-1.747519	-1.747519
X Variable	-4.329658	0	65535	#NUM!	-4.329658	-4.329658	-4.329658	-4.329658
X Variable	-3.492834	0	65535	#NUM!	-3.492834	-3.492834	-3.492834	-3.492834

Appendix 2c Results of Multiple Linear Regression for
Data on Silverwood Coal Macerals

