GASIFICATION OF SOUTH AUSTRALIAN LIGNITE

A thesis submitted for the degree of
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SUMMARY

South Australia has large reserves of low rank coals. Most of these coals contain substantial amounts of moisture and inorganic impurities as Na, Ca, Cl and S. Such impurities will result fouling and slagging in the pulverized-fuel conventional combustor. Gasification provides an attractive method for the future utilization of these coals.

This study is concerned with obtaining a detailed understanding of kinetics of gasification of South Australian Bowmans coal, which is a typical S.A. lignite. Experimental investigations were carried out in a vertical quartz-tube reactor which can simulate behaviour in fluid-bed gasifier. The major factors which affect reactivity were examined, with emphasis given to the role of inherent inorganic minerals. Experiments consisted of two major parts: steam gasification and carbon-dioxide gasification. To eliminate the influence of external diffusion and intra-particle diffusion, all experiments were conducted in the chemical-reaction-control region. The variables examined were:

- coal treatment (raw, demineralized and catalysed)
- reaction temperature (710, 765, 806, 856 and 892°C);
- coal particle size (0.8~1.6, 1.6~2.4 and 2.4~4.1 mm);
- gas stream (CO_2, Steam, N_2);
- additives (Na, Ca, K and Ni; acetate, carbonate, chloride, hydroxide and sulphate)

Studies conducted were aimed at investigating the kinetics and mechanism of gasification of low-rank coal. Experimentally obtained results were compared with those of other investigators.

The present results show that gasification rate of Bowmans coal is sensitive to temperature and independent (approximately) of coal particle size. Reactivities of Bowmans coal with CO_2 and H_2O were high compared with other coals, the high reactivity being attributed to the high concentrations of inherent alkalis. Acid treatment greatly reduces the reactivity of raw coal, while water leaching only has slight effect. By taking typical data from the literature, the reactivities of Bowmans coal toward H_2O and CO_2 were compared with a wide-range of coals in the world to indicate whether correlations between reactivity and coal properties were suitable for Bowmans coal. Reactivity can generally be correlated by rank; high-rank coal has low reactivity; low-rank coal has a high reactivity but with spread values.

Gasification kinetics were studied by using experimentally obtained data to fit different models. It was found that models with assumption of chemical-reaction-rate control (e.g. Homogeneous model and Shrinking-Core model) reasonably describe CO_2 and H_2O gasification. Obtained kinetic parameters were compared with other results. Reasonable agreement was found between the present results and literature reported values. Gasification mechanism of reaction are discussed. The active site theory which assumes that gasification mainly occurs at active sites and that the reaction rate is determined by the concentration of such active sites seemed provide a satisfactory explanation for gasification behaviour.

Catalysed gasification studies were also conducted by adding various salts to demineralized coal by cation-exchange. A.A.S. was employed to examine the amounts of catalyst adsorbed by coal. Results show that the amount of cation loading is proportional to the concentration of impregnation solution. The catalytic activities of alkali and alkaline-earth metals were examined at different levels. Gasification of Bowmans coal with CO_2 and steam was found to be strongly catalysed by alkali metals Na, K and Ca. Transition metal Ni is also shown to be catalytically active, although less so than Na, K and Ca. Alkali salts of weak acids exhibited the strongest catalytic effect. Reactivities increased linearly with the amounts of catalysts added. Metals physically adsorbed on coal show less catalytic effect. The order of catalytic activity was found to be $NaAc \sim Ca(Ac)2 > Ni(Ac)_2 > CaCl_2 > NaCl > KCl > NiCl_2$ for CO_2 gasification and $NaAc \sim Na_2CO_3 \sim NaOH \sim Ca(Ac)_2 \sim KAc > Na_2SO_4 > Ni(Ac)_2 > NaCl$ for H_2O gasification.

Thermally treated coal was found to be insensitive to catalyst loading. This indicates that oxygen-containing groups play an important role in catalysis. Further study showed that cations are not active unless they associate with carboxyl groups to form 'active sites'.

The reactivity of Yallourn coal was also examined for comparison with Bowmans coal, results indicating that reactivity of lignite is dominated by the catalytic effect of inorganic impurities. Other properties, such as carbon content, pore structure, concentration of oxygen-containing function groups and total ash content are found to be less important.

Table of Contents

APPENDICES

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STATEMENT

This thesis contains no material which has been accepted for the award of any other degree or diploma in any University and the thesis contains no material previously published or written by other persons, except where reference is made in the text of the thesis.

The author consents to the thesis being made available for photocopying and loan if applicable for the award of the degree.

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LIST OF TABLES

LIST OF FIGURES

Chapter 1

INTRODUCTION

1.1 COAL IN SOUTH AUSTRALIA

Low-rank coal is the most abundant fossil fuel available in South Australia (A.I.E. Energy 83 1988). The use of these low rank coal deposits can help to satisfy the local energy needs. "The future development of South Australia's electrical power generation capacity will depend on the satisfactory utilization of these coals" (Agnew 1986). The Bowmans deposit, which is located 80 km north of Adelaide, is the largest lignite deposit in South Australia with reserves of 2000 million tonnes and 359 million tonnes inferred. The large deposit and attractive geology make this coal an ideal choice for being considered as a feedstock for power generation. However, low-rank S.A. coals contain high concentrations of moisture and inorganic impurities such as Na, Cl and S. ***Table 1-1*** gives the analysis of the major South Australian coal deposits.

A common feature of S.A. low rank coals is their high alkali content. For example, Bowmans coal contains 1.6% (d.b.) sodium in raw coal. These minerals and inorganics, especially sodium, directly affect the utilization potential of these fuels. The combustion of these coals in conventional pulverized fuel combustors will result in potential operational problems of fouling, slagging, high temperature corrosion and atmospheric emission. Fluidized bed gasification with steam and oxygen offers an attractive means of converting

Table 1.1 Analysis of major South Australian lignites (Readett et al.1986)

	Proximate analysis (% d.b.)				Ultimate analysis (% d.a.f.)			Na	Cl	S
	Mois.	Vol.	F.C.	Ash	C	H	N	(d.b.)	(d.b.)	(d.b.)
Bowmans	53	48	40	12	57	4.5	0.4	1.6	1.42	5.30
Lochiel	48	48	38	13	44	3.5	0.3	1.43	0.66	3.55
Leigh Creek	24	31	48	21	67	3.9	1.5	0.77	0.40	0.55
Sedan	49	46	33	21	54	4.2	0.4	0.31	0.12	4.10
Kingston	36	45	41	13	60	4.2	0.6	1.10	1.0	3.07

Note: F.C. is fixed carbon, Vol. is volatile matter.

these low-rank coals to clean fuel gas which can be utilized for power generation. Integration of coal gasification with combined-cycle (CGCC) power generation provides an efficient and environmentally acceptable way of generating electricity from these coals. This process can significantly increase the thermal efficiency and will markedly reduce emissions of CO_2 and other pollution gases. According to the present level of technology, overall thermal efficiency of 45% can be expected for such (CGCC) power generation compared with an efficiency of 35% in a conventional pulverised-fuel combustion process. In integrated gasification combined-cycle power generation, clean combustible gas can be obtained by treating the raw product gases to remove sulphur oxides, hydrogen sulphide and nitrogen oxides.

1.2 COAL GASIFICATION

Coal gasification is a process in which coal reacts with gasifying agents to produce a fuel-rich gas, which is typically a mixture of carbon monoxide, carbon dioxide, hydrogen, steam, nitrogen and hydrocarbons depending upon operating conditions and quality of coal feed. Coal gasification has been widely practised on an industrial scale for more than one hundred years. Recently, more and more attention has been given to this process because the modern technology of coal gasification provides the possibility of using any type of coal with high thermal efficiency and with minimal environmental impact.

When coal is introduced into a gasifier, it undergoes the following physical and chemical processes:

1. drying and devolatilization, releasing volatile matter (mainly CO_2, NO_2, CH_4, light hydrocarbon gases and tars).
2. combustion/gasification of char with reactant (O_2, H_2, H_2O and CO_2) to give product gases such as CO, H_2, and CH_4.

The reaction rate and composition of product gases may vary widely depending on the quality of feed coal and operating conditions. The product gas can be used as:

. synthesis gas for chemical production,

. substitute natural gas,

. fuel gas for electrical power generation,

. fuel gas for industrial steam and heating, and civil utilization.

There are several continuous coal gasification processes under development in the world. Commercial gasifiers may be classified by different categories such as state of ash, state of coal feed and state of coal particle movement. The Usual classification is by coal particle movement using: moving-bed (Lurgi), fluidized-bed (Winkler) and entrained-flow (Koppers-Totzek) processes (***Table 1-2***). In a moving-bed gasifier, the coal can be introduced at the top and moves downward through gravitational force; steam and oxygen are fed into gasifier from the bottom and rise against the coal flow. Relatively long residence time of coal will be required to achieve high carbon conversion. In a fluid-bed gasifier, the coal can be introduced at different points in the gasifier and particles are suspended in a fluidized state by the up-flowing gas. The fluid-bed gasifier has the advantages of uniform temperature, relatively high efficiency of solids mixing and high mass and heat transfer rates. In an entrained flow gasifier, feed coal fines are injected into the bottom or top of the gasifier with high velocity gas and are rapidly gasified at high reaction temperature, as they flow through the reactor.

The first generation of gasifiers (e.g. moving-bed Lurgi process) no longer meets present economic and environmental requirements. A second generation of gasifiers which can gasify almost all type of coal with high thermal efficiency has been developed. Among them the High Temperature Winkler (HTW) process is widely recognized as an effective method for gasifying non-agglomerating low-rank coal like South Australian lignite (Manzoori et al. 1988). The Electricity Trust of South Australia cooperated with South Australian

Table 1-2 Classification of Some Major Industrial Gasifiers (Cooper & Ellingson, 1985)

	Ash State			Feed Coal			Pressure		
Gasifiers:	Dry	Aggl.	Slag.	Lump	Fine	Slurry	Low	Medium	High
Moving bed									
Lurgi	Yes			Yes				Yes	
Wellman	Yes			Yes			Yes		
BGC-Lurgi			Yes	Yes				Yes	
Lurgi Ruhr 100	Yes			Yes				Yes	Yes
Fluidized-bed									
Winkler	Yes				Yes		Yes		
Winkler(HT)	Yes				Yes			Yes	
COGAS	Yes				Yes		Yes		
HYGAS	Yes				Yes		Yes	Yes	
U-GAS		Yes			Yes			Yes	
Entrained-flow									
Koppers-Totzek			Yes		Yes		Yes		
Otto-Rummel			Yes		Yes		Yes		
Texaco			Yes			Yes			
Shell-Koppers			Yes		Yes			Yes	Yes

Note: Aggl. Agglomerating; Slag. Slagging.

Department of Mines and Energy and the South Australian Gas Company to conduct a preliminary investigation on the gasification of South Australian Bowmans coal in an HTW gasifier in Germany. The preliminary results showed that Bowmans coal could be successfully gasified using this method. The major problem remaining in the HTW gasification of Bowmans coal was the influence of inorganics, which caused ash agglomeration and defluidization.

1.3 COAL RESEARCH AT ADELAIDE UNIVERSITY

This work is part of the coal research program which is being carried out in The Department of Chemical Engineering, Adelaide University. Knowledge of the behaviour of low-rank coals in gasifiers and combustors is important in planning the utilization of these coals. Studies on various aspects of low-rank coal investigations include:

- thermal dewatering and upgrading of low-grade low-rank coal, (Dunne 1986)
- drying and devolatilization, (Wildegger-Gaissmaier 1988)
- transformation of inorganics of coal in fluid-bed combustion (Manzoori 1990)
- temperature measurement and ratio of CO/CO_2 in fluid bed combustion (Linjewile 1992)
- mathematical modelling of fluid-bed gasifiers (Gururajan 1992)
- kinetic study of gasification and catalytic gasification (present work)

An experimental study of the thermal upgrading of S.A. Bowmans coal by high-temperature, high-pressure treatment has been conducted using microautoclaves to examine the removal of moisture, sodium and sulphur (Dunne and Agnew 1987). The kinetics of devolatilization was modelled using time-temperature equivalence and distributed-activation-energy kinetic models. The moisture removal was modelled using a correlation between the water removed from coal and devolatilization kinetics. It was found that up to 80% moisture, 60% of both sodium and chlorine, and 40% organic sulphur were removed by treating the coal at temperatures up to 350°C.

A bench-scale Single-Particle Furnace (SPF) was designed, constructed and operated to investigate the behaviour of drying and devolatilization of South Australian Bowmans coal (Wildegger-Gaissmaier, et al. 1988). A mathematical model for drying and devolatilization has been developed, assuming that heat transfer to and through the coal particle and the chemical reaction are the rate-limiting steps for coupled drying and devolatilization.

Transformation of inorganics in South Australian lignites was investigated by Manzoori et al. (1990). Experimental investigations were carried out to examine the role of the inorganic matter in agglomeration and defluidisation during fluid-bed combustion. The mechanism of agglomeration and transformation of inorganics was examined.

Mathematical modelling of bubbling fluid-bed gasification had been conducted by Gururajan (1990). A steady-state isothermal model, based on Davidson and Harrison's two-phase theory, was developed. The model prediction is in good agreement with experimental data reported in literature.

Recently, Adelaide University has been involved in a Commonwealth Government funded Cooperative Research Centre (CRC) program on new technology for power generation from low-rank coal. Research will continue on fundamental studies of gasification kinetics, ash agglomeration and other aspects which relate to the utilization of low-rank coals.

1.4 OBJECTIVES

Although coal gasification studies have been widely carried out on many coals, no major study has been made of the gasification kinetics of S.A lignites. The aim of present study is to obtain detailed information on the gasification kinetics of Bowmans coal with steam and carbon dioxide. Many factors may influence the gasification process, e.g: coal rank, physical and chemical structure of coal, quantity and quality of impurities, reaction temperature, pressure, reactant agents, charring process and pretreatment. The scope of this study is limited to:

- the gasification behaviour of Bowmans coal with steam and CO_2 under simulated fluidized-bed gasification conditions.
- the kinetics and mechanism of gasification of Bowmans coal with steam and carbon dioxide.
- the role of impurities of coal in gasification.
- the role of oxygen-containing functional groups in gasification.
- the catalytic effects of additives on the gasification rate.

The work embodied in this thesis is presented in the following chapters:

Chapter 2 gives a review of the previous work on gasification kinetics.

Chapter 3 gives a detailed description of the reaction system, experimental method and operation procedure for this study.

Chapter 4 gives results and discussion.

An evaluation of the present investigation and the major significance of the results is given in **Chapter 5**. Finally, **Chapter 6** summarizes the general conclusions drawn from this work and makes recommendation for further research.

Chapter 2

LITERATURE REVIEW

2.1 INTRODUCTION

Studies of coal gasification have been conducted for more than one hundred years. Gasification kinetics and mechanisms have been the subjects of investigation for a long period. Most investigations examined the relationship between gasification behaviour and the properties of coal such as: coal rank, chemical composition, functional groups and physical structure. Few investigations have been carried out on the effect of pre-treatment (for example, water leaching) on the gasification rate. Gasification rates differ widely with the type of coal. Low rank coals have reactivities, in some cases, as much as 200 times higher than those of high rank coals (Tomita et al. 1986). Hence, the literature reviewed in this chapter does not give much attention to the gasification behaviour of high rank coals. Instead, it mainly deals with the characteristics of gasification of low rank coals which are similar to South Australian lignites. South Australian lignites contain high concentrations of alkali impurities which could have a significant catalytic effect on gasification. Hence, this review gives more attention to the catalytic effect of inorganic matter and the role of active sites on the coal surface.

This chapter covers a number of topics selected to introduce and to provide a theoretical description of coal gasification research and technology. Aspects of stoichiometry, kinetics, reaction mechanism and intrinsic reactivity, as well as the function of coal gasification, are reviewed. This review is particularly concerned with the role of inherent inorganics, pre-treatment and the additives in gasification.

2.2 CHEMISTRY OF COAL GASIFICATION

Processing in gasification is fundamentally based upon the chemical reactions between carbon and gasifying agents such as steam, oxygen and carbon dioxide. In general, when coal is introduced into a gasifier, it undergoes two major steps:

(1) devolatilization of the coal to release volatile matter (H_2, H_2O, CO_2, CO, CH_4 and other hydrocarbon gases) and subsequent reaction of the volatile matter with gases;

(2) combustion/gasification of the residual char with reactants to give product gases.

Step 1 is fast. The rates of drying, devolatilization and the volatile matter combustion are orders of magnitude higher than the rate of char gasification. The rates of carbon-gas reactions are much lower and differ widely depending upon the coal rank. Therefore, knowledge of the nature of coal, such as chemical composition and structure, is important in understanding the behaviour of coal gasification.

2.2.1 Nature and Classification of Coal

Coal is the end product of a sequence of biological and geological processes called "coalification". It is formed from the accumulation and decomposition of plant substances. During the long period of coalification, the plant material underwent chemical, biochemical and geological change under elevated temperature and pressure. The extent of coalification determines the degree to which the original plant material approaches the structure of pure carbon. Coal varies widely in chemical and physical properties from source to source due to the complexity of the coal forming materials, geological circumstances, climatic conditions and the process of coalification. From the point of view of composition, coal is a highly complex heterogeneous mixture containing: non-crystalline, high molecular weight organic substances, consisting of carbon, hydrogen, oxygen and smaller amounts of nitrogen, sulphur, chlorine and trace elements; inorganics (minerals); and moisture.

There exist several different methods to classify coal. The most commonly used classification system was developed by the American Society for Testing Materials (ASTM). This method is based on the amounts of volatile matter and fixed carbon, and the heating value. According to this method, carbon content and heating value increase with increasing coal rank. The volatile matter, hydrogen and oxygen decrease with increase in rank. Low rank coals contain high concentrations of oxygen-containing functional groups such as -COOH, -OH and =CO. The oxygen-containing groups play an important role in coal gasification. Considerable amounts of plant materials such as wood and pollen, can often be found in South Australian lignites.

2.2.2 Devolatilization

Generally, coal conversion reactions fall into two classes: devolatilization and gasification-/combustion. These reactions occur in different parts of a gasifier and at different stages of the overall process. Under heat treatment, the coal firstly undergoes thermal decomposition, which is also named devolatilization:

$$\textit{coal} \rightarrow \textit{char (solid)} + \textit{volatile matter (liquid: tar; gas: } H_2, CO, CH_4\textit{...)} \qquad (2.2.1)$$

Devolatilization involves chemical bond breaking. It is a rapid reaction process. Volatile matter contains hydrogen, water, methane and heavy hydrocarbons, tar, hydrogen sulphide, phenols, naphtha and ammonia. The quality of char and amount and composition of the volatile matter are functions of the final temperature. They also depend on the coal type, pressure, residence time and heating rate. About 30-50 wt % (dry coal basis) of low rank coal is volatile. High rank coal yields less volatile matter (about 10-20 wt %). Devolatilization of coal occurs mainly in the temperature region of 400-900°C. Most oxygen-containing groups decompose at temperatures below 600°C.

The importance of devolatilization in coal gasification is that during devolatilization active and labile carbons are produced. Such active carbons are the basis for char gasification (Tsai 1982). For the charring process, the heating rate, maximum temperature and time for charring significantly influence the reactivity of the resulting char. Tsai (1982) reported that the char produced from low temperature pyrolysis is about as reactive as the parent coal and that char reactivity decreases with increasing final temperature of charring. The pore structure of char obtained from low temperature carbonization is also different from that obtained in high-temperature charring.

It is well known that, in a gasifier, volatile matter is more reactive than the char. Hence, during the gasification process, the volatile matter produced may firstly react with species such as O_2, H_2O and CO_2 to form product gases. Not many results have been published on the reaction between volatile and reactant gases because of the short residence time of the volatile matter in the gasifier. The major reactions involving the volatile matter are:

(1) decomposition of volatiles

$$4C_xH_y \rightarrow yCH_4 + (4x-y)C \qquad (2.2.2)$$

(2) hydrogenation of volatiles to methane and other hydrocarbons

$$oC_xH_y + pH_2 \rightarrow qCH_4 + rC_mH_n \qquad (2.2.3)$$

2.2.3 Heterogeneous and Homogeneous Reactions

Char gasification is considered as a typical solid-gas reaction (Levenspiel, 1979). It includes char-gas reactions and secondary homogeneous gas-gas reactions. A full examination of these reactions is beyond the scope of the present study. This section presents only a brief discussion of the basic heterogeneous reactions, their reaction rates, and the basic physical phenomena involved in the gasification of carbon with steam and carbon dioxide.

The principal chemical reactions involved in gasification are:

(i) Heterogeneous Reactions

(1) oxidation

$$C + O_2 = CO_2 \tag{2.2.4}$$

$$C + \frac{1}{2}O_2 = CO \tag{2.2.5}$$

(2) reduction

$$C + CO_2 = 2CO \tag{2.2.6}$$

(3) primary water-gas reaction

$$C + H_2O = CO + H_2 \tag{2.2.7}$$

(4) secondary water-gas reaction

$$C + 2H_2O = CO_2 + 2H_2 \tag{2.2.8}$$

(5) methanation reaction

$$C + 2H_2 = CH_4 \tag{2.2.9}$$

(ii) Homogeneous Reactions

(6) Water-gas shift reaction

$$CO + H_2O = CO_2 + H_2 \tag{2.2.10}$$

(7) water formation reaction

$$2H_2 + O_2 = 2H_2O \tag{2.2.11}$$

(8) oxidation of CO

$$CO + O_2 = 2CO_2 \tag{2.2.12}$$

The oxidation reactions (1) and (7) occur rapidly to completion at normal gasification conditions. The gasification reactions, carbon-steam and carbon-carbon dioxide, may take a long time to achieve significant carbon conversion. Generally, the carbon-steam reaction is faster than the carbon-carbon dioxide reaction at the same temperature conditions. The rates of reactions and composition of gases vary depending on the experimental conditions used. The individual gasification reactions are usually studied under isothermal conditions, and in different atmospheres of constant gas composition. Experimental investigations on the chemistry of gasification have often been carried out in three reaction systems:

1. The char - hydrogen - methane environment, which is relevant to reaction (5).
2. The char - carbon dioxide - carbon monoxide environment, which is relevant to the reactions (2) and (8).
3. The char - steam - hydrogen system, which is relevant to reactions (3), (4) and (5).

The present investigations have only been carried out for C-CO_2 and C-H_2O reactions. Hence, in this literature review special attention is given to the carbon-carbon dioxide and carbon-steam reactions.

2.3 KINETICS AND MECHANISMS OF GASIFICATION

2.3.1 Concepts of Active Site and Surface Reaction Theory

The reactions of coal with carbon dioxide and steam have been widely studied due to their importance in the combustion and gasification of coal. It is well known that not all the carbon atoms are considered reactive for the gasification reaction. Only certain carbon atoms, which are called active sites, are considered reactive. The active sites of coal can be attributed to: (1) inorganic impurities, (2) oxygen-containing functional groups and (3) carbon located at an edge or dislocation. The concentration of active sites on the coal surface varies with the type of coal.

Numerous mechanisms have been proposed to explain the reactions between carbon and gaseous reactant. Most of these mechanisms are based on the concept of active site and surface reaction theory. According to the surface reaction theory, for a carbon-gas reaction, at each site, the following processes would occur in series:

1 adsorption of reactant onto the surface of the coal (chemisorption)
2 chemical reaction between the carbon and the adsorbed reactant
3 release of the product (desorption)

The rate of one of these steps may be orders of magnitude lower than the other steps. The overall rate is controlled by the slowest step.

2.3.2 C-CO_2 Reaction

Most investigators agree that carbon-carbon dioxide reaction follows a two-step oxygen-transfer mechanism (Laurendeau 1978, Johnson 1981 and Tsai 1982). It can be expressed as:

$$C_f + CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C(O) + CO \qquad (2.3.1)$$

$$C(O) \xrightarrow{k_3} C_f + CO \qquad (2.3.2)$$

where C_f represents the active site and *C(O)* represents the intermediate. k_1, k_2 and k_3 are reaction rate constants. The overall reaction includes two physical processes: adsorption of CO_2 on the active carbon site and the desorption of CO from the surface.

Assume that the second stage, the desorption of CO from the coal surface, is the rate-determining stage. For the overall reaction process, the change in the number of vacant sites is zero. The rate of desorption is presumed proportional to the fraction of the surface covered, and it may be expressed by a Langmuir-type equation (Laurendeau 1978, Johnson 1981 and Tsai 1982):

$$R_d = \frac{1}{(1-X)}\frac{dX}{dt} = \frac{k_1 \cdot P_{CO_2}}{1 + a \cdot P_{CO_2} + b \cdot P_{CO}} \tag{2.3.3}$$

where X is the fractional conversion of carbon, k_1 is reaction rate constant which depends on the temperature: a and b are kinetic parameters. $a = k_1/k_2$ and $b = k_2/k_3$. The rate is first-order with respect to CO_2 partial pressure if $aP_{CO2} << 1$ and $bP_{CO} << 1$. This process can also be explained as an oxygen-exchange mechanism. It suggests that the concentration of product, CO, inhibits the reaction. It should be noted that, due to the uncertainties involved in the extrapolating Langmuir-form constants to other temperatures, this formula can only be used within a certain range of temperature (Smoot and Pratt 1979).

The above rate equation is based on the assumption that the second stage, the release of CO from the carbon surface, is the rate-controlling stage. If the first step, the adsorption of CO_2 is the rate-controlling stage, the global reaction rate can be expressed as:

$$R_d = \frac{k_1 \cdot P_{CO_2}}{a' \cdot P_{CO_2} + b' \cdot P_{CO}} \tag{2.3.4}$$

where a' and b' are kinetic parameters. a' is k_1/k_3 and b' is k_2/k_3.

Other investigators have postulated reaction steps in addition to, or in place of, the above two oxygen transfer steps to simulate the C-CO_2 reaction process. For example, Blackwood and Ingeme (1978) proposed a 5 step sequence, and the rate equation obtained from their mechanism well describes the reaction process at elevated pressure.

2.3.3 C-H_2O Reaction

The mechanism of carbon-steam reaction has been extensively studied by many investigators (Ergun et al. 1956, Long and Sikhs 1974 and Johnson 1979). The kinetics of the carbon-steam reaction are in many respects analogous to those of carbon-carbon dioxide reaction. The postulated reaction mechanism is (Laurendeau 1978):

step 1
$$H_2O + C_f \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2 + C(O) \tag{2.3.5}$$

step 2
$$C(O) \xrightarrow{k_3} CO + C_f \tag{2.3.6}$$

where C_f represents the active site and $C(O)$ represents the intermediate, and k_1, k_2 and k_3 are reaction constants.

Surface reaction theory is also used to analyse the above mechanism. If step 2, the release of CO from char surface, is the rate controlling step, the overall rate equation can be expressed as:

$$R_d = \frac{1}{(1-X)}\frac{dX}{dt} = \frac{k_1 \cdot P_{H_2O}}{1 + a \cdot P_{H_2O} + b \cdot P_{H_2}} \tag{2.3.7}$$

where R_d is reaction rate index, X is fractional conversion, a and b are kinetic parameters.

If step 1, the chemisorption of H_2O onto the coal surface, is the rate controlling step, the overall rate equation can be expressed as:

$$R_d = \frac{k_1 \cdot P_{H_2O}}{a' \cdot P_{H_2O} + b' \cdot P_{H2}} \tag{2.3.8}$$

where a' and b' are kinetic parameters: a' is k_1/k_3 and b' is k_2/k_3.

Other researchers have proposed other mechanisms to describe the carbon-steam reaction. Most of these mechanisms consist of more than two steps (Benford and Eyring 1956 and Ergun 1956). Blackwood and McGrory (1976) also investigated carbon-steam reaction behaviour at high pressures (1-50 atm.) and found that methane production appears to be considerable. Another factor which influences the C-H_2O reaction is the water-gas shift reaction, which is expressed as:

$$H_2O + CO \rightleftharpoons CO_2 + H_2 \tag{2.3.9}$$

In most cases, the equilibrium of the water-gas shift reaction is not achieved.

Other reactions such as the carbon-hydrogen reaction may occur in a gasifier. The rate of C-H_2 reaction is much lower than the C-CO_2 and C-H_2O reactions under normal gasification conditions (Cooper & Ellingson, 1983).

2.4 FACTORS INFLUENCING THE GASIFICATION RATE

2.4.1 Introduction

The overall process of char gasification consists of two parts: intrinsic chemical reactions between carbon and gases, and the physical transfer of reactant and product gases to and from reaction sites. Therefore, the overall rate of gasification can be obtained by correcting the intrinsic reaction rate for intraparticle diffusion and film diffusion (Levenspiel 1972). The rates of various gasification reactions differ widely. For example, the rate of the C-H_2 reaction is several orders of magnitude lower than that of steam gasification. The reactivity of anthracite may be hundreds of times smaller than that of lignites (Miura et al. 1989). The gasification rate depends on the following factors (Laurendeau 1978, Johnson 1981, Takarada et al. 1985 and Tomita et al. 1985):

(a) the concentration of active sites which depends on the chemical and physical properties of the parent coal;

(b) the amount and dispersion of active inorganics in coal;

(c) the surface area, pore structure and its variation during gasification;

(d) the amount of oxygen-containing functional groups in coal.

The above properties make different contributions to the gasification rate. The discussion is focused on the effects of each property of coal on the coal reactivity.

The following questions arise: how may coal reactivity be defined, and how can the number of active sites in a coal be determined?

2.4.2 Determination of Active Sites and Index of Reactivity

Extensive investigations have been carried out to determine the concentration of active sites in coal. The chemisorbed oxygen and carbon dioxide content provide a satisfactory index of the reactivity of coal (Radovic and Walker 1984). The number of active sites can be determined from the amount of chemisorbed oxygen measured at about 100°C. Hashimoto et al. (1986) correlated the reactivities of 19 coals with oxygen uptake and found that the rate of gasification of coal with steam increased with increasing oxygen uptake. Suzuki et al. (1988) studied the relationship between reactivity of carbon-carbon dioxide reaction and the amount of chemisorbed oxygen for 14 coals and found that the rates of gasification with carbon dioxide are correlated well with the amounts of chemisorbed oxygen measured by TPD (Temperature Programmed Desorption). Kyotani et al. (1988) examined the oxygen complex on the coal surface during gasification using the TPD method. They reported a good correlation between the reactivity of steam gasification and the sum of CO and CO_2 released which was determined in the TPD experiment. They further pointed out that the desorption of CO and CO_2 could be attributed to catalytically active minerals. Similar results on the correlation between coal reactivity and the amount of chemisorbed gases (oxygen, carbon dioxide and nitrogen) were reported by Ahmed et al. (1985), Causton and McEnanay (1985), Khan (1987) and (1985) Muehlen et al. (1987). The above discussion suggests that chemisorbed gases (oxygen, carbon dioxide and nitrogen) provide an index for the reactivity of coal.

2.4.3 Intrinsic Reactivity of Coal

The intrinsic reactivity of coal/char with reactants (carbon dioxide and steam) has been widely investigated (Smith 1978). Intrinsic reactivity of a coal/char particle is defined as chemical reaction rate (rate per unit mass, $g/g \cdot s$) with insignificant intraparticle diffusion and film diffusion. Takarada et al. (1985) measured the reactivities of coal with steam using 34 coals with carbon contents ranging from 65 to 94% (daf) from different countries. Their results showed that: generally, reactivity of coal decreases with increasing coal rank; the reaction rates of high-rank coals (C > 78% daf) were low; the reaction rates of low-rank coals were high but did not show a clear correlation with carbon content of their parent coals. The reactivities of coals were found to have a good correlation with the amount of the exchangeable alkali and alkaline-earth metals such as Na, K and Ca. The sum of the exchangeable cations showed a good correlation with the amount of CO and CO_2 released during devolatilization. They further concluded that the gasification rate of lower-rank coals was dominated by the number of active sites and the catalytic effect of inherent active inorganics. Pore structure (size and distribution) was found to be of minor importance to reactivity of low-rank coals.

Miura et al. (1989) gave an excellent review of the reactivities of coals with various gases such as oxygen, carbon dioxide and steam. Based on numerous experimental data taken from the literature, they concluded that coal properties such as carbon content, surface area and pore structure do not indicate reactivity. They also found that the gasification rates of higher-rank coals (C > 80% daf) are low and tend to decrease with increasing coal rank; the reactivities of lower-rank coals (C < 80%) vary greatly. For low-rank coals, they indicated that the reactivity is dominated by catalytic effect of inherent inorganics. Highly dispersed metals such as Na, K and Ca act as catalysts for gasification. In contrast, the reactivity of high-rank coal depends on the structure of the char. Active sites, which are formed by the carbon atoms bonded to heteroatoms, nascent sites or edge carbon atoms, have a great influence on the reactivity of high rank coals. The number of active sites can be estimated from the amount of chemisorbed oxygen.

van Heek et al. (1985) also studied the effect of coal properties on gasification reactivity. The main factors influencing coal reactivity were inferred by taking typical data from the literature. They concluded that the correlation between coal properties and reactivity can only be established for special gasification processes. Factors which are important for coal reactivity are: the inherent minerals which act as a catalyst for the reaction (particularly important for low rank coals); and pyrolysis conditions (heating rate, final charring temperature and the residence time) which are responsible for the internal surface area of the char and the number of active sites. No general correlation could be established between the magnitude of the internal surface area of a char and its reactivity. They further pointed out that the intrinsic reactivity was important only at temperatures lower than 800°C. Other investigators (Knight et al. 1982, Kwon et al. 1988, and Hashimoto et al. 1988) also reported similar results. The relationship between coal reactivity and carbon content of coal are shown in ***Figures 2-1*** and ***2-2***.

2.4.4 Effect of Coal Rank

The relationship between coal rank and the reactivity of coal with CO_2 and H_2O has been widely investigated under varied conditions (Fung and Kim 1983, Kasaoka et al. 1984, van Heek et al. 1985, Takarada et al. 1985, Suzuki et al. 1986,, Hashimoto et al. 1986 and Miura et al. 1989). As discussed in **Section 2.4.3**, coal rank has a significant influence on reactivity. Numerous results showed that low rank coal has high reactivity. A possible explanation is compared to high rank coal, low rank coal contains higher concentrations of oxygen-containing function groups, higher concentrations of transitional and macro pores and higher concentrations of dispersed active minerals (Linares-Solano et al. 1979).

However, the reactivity of low rank coal is not always higher than that of high rank coal. For some low-ash-content low-rank coals, their gasification can be considered as non-catalytic reaction and their gasification rate is found to be similar to that of high rank coal.

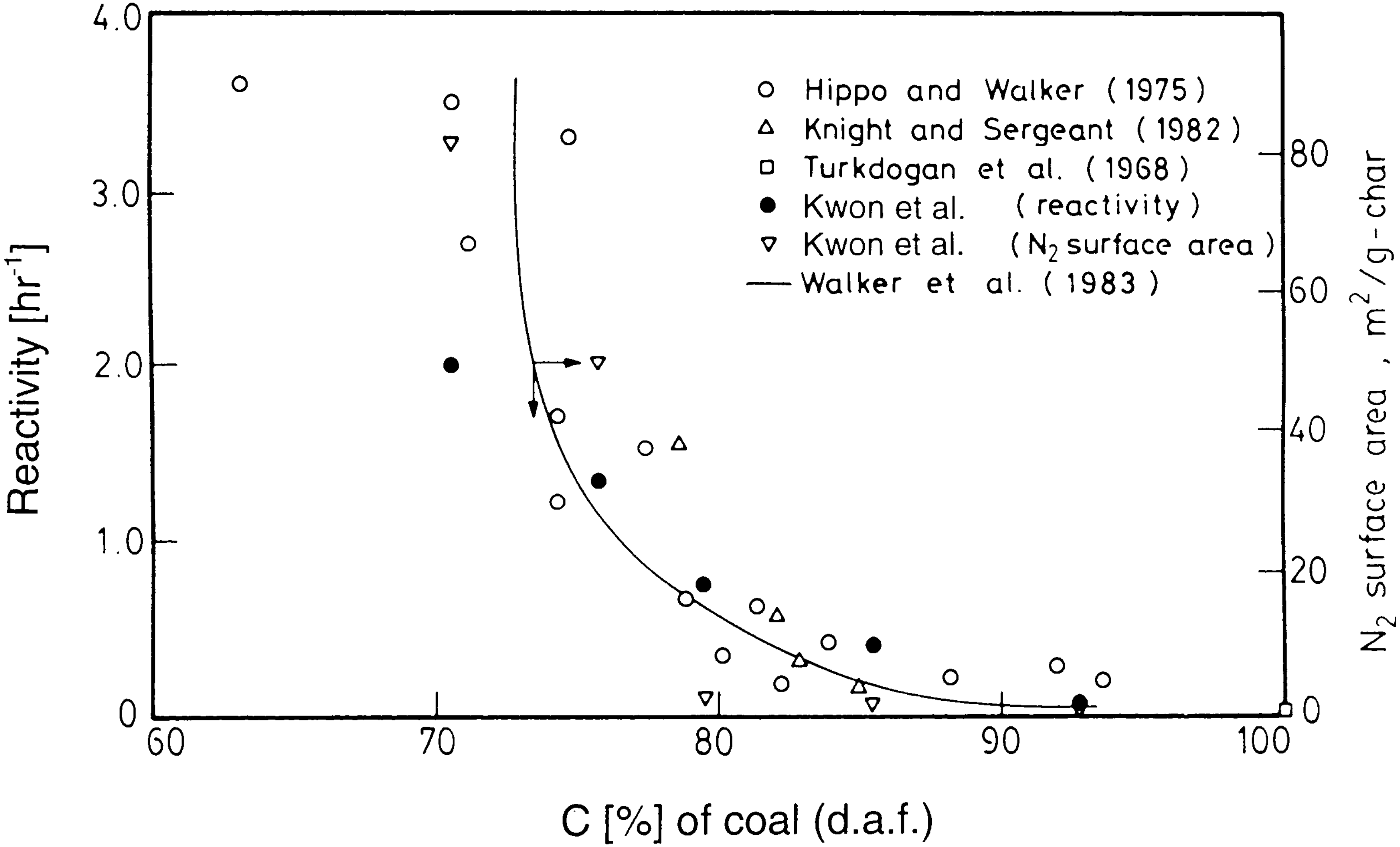


Figure 2-1 Relationship between CO_2 gasification rate and carbon content of coal at 900°C. (Kwon et al. 1988)

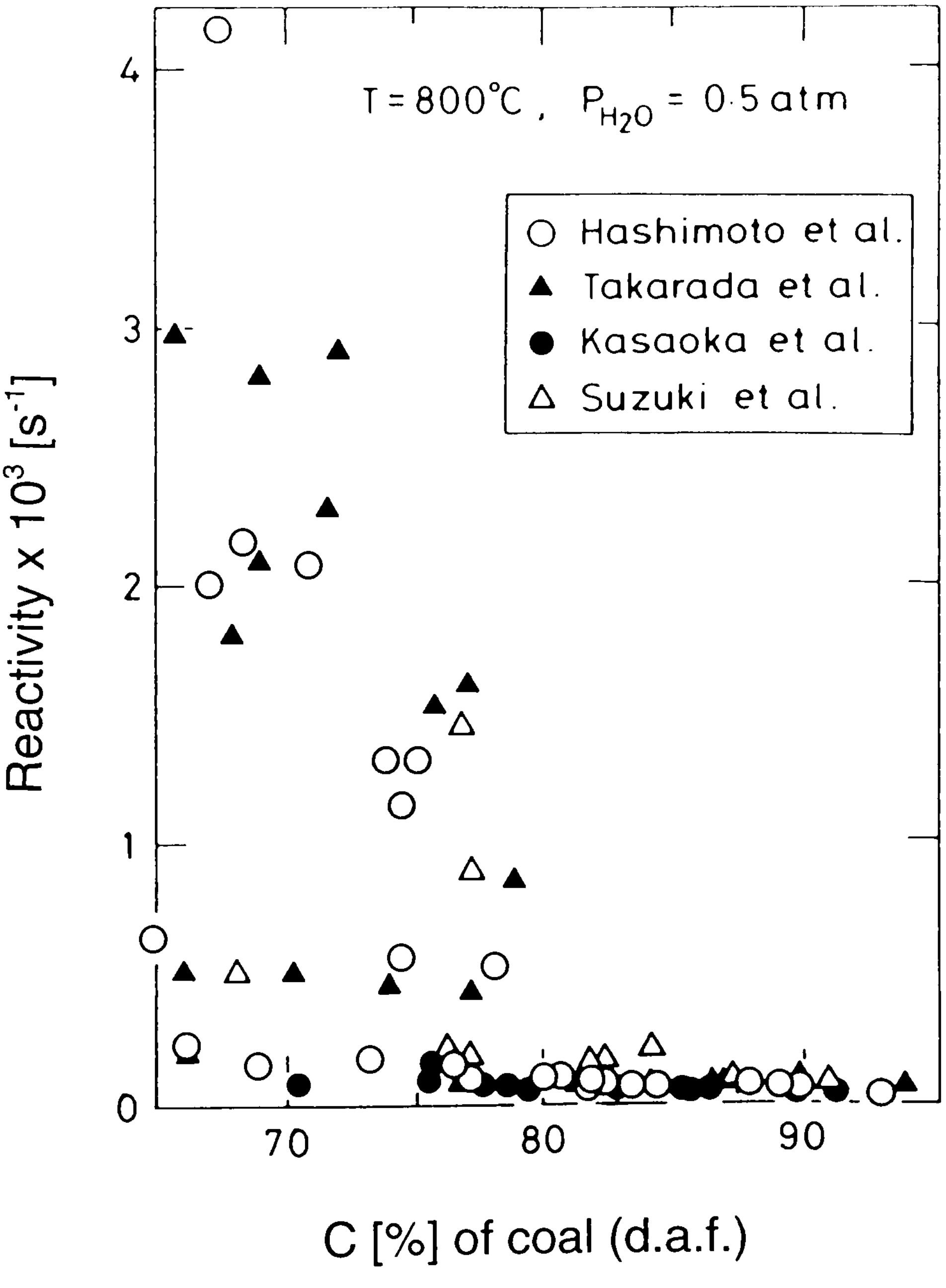


Figure 2-2 Relationship between H_2O gasification rate and carbon content of coal at 800°C. (Miura et al. 1989)

2.4.5 Effect of Pore Structure

The pore structure of coal is generally characterized by the internal surface area and pore size distribution. The effect of pore structure and its variation during gasification on coal reactivity has been studied by many investigators (Hashimoto et al. 1973, Gavalas 1980, Haynes 1982 and Furusawa 1987). Generally, pore structure is classified into three size ranges (Gan et al. 1972):

(1) micropores $\delta < 12\overset{o}{A}$

(2) transitional pores $12 < \delta < 300\overset{o}{A}$

(3) macropores $\delta > 300\overset{o}{A}$

The size of pores decreases with increasing coal rank. Laurendeau (1978) reported that low rank coal contains high concentration of macropores; transitional pores dominate for middle rank coals; and micropores dominate for high rank coal.

Different sizes of pores make different contributions to coal gasification. Macropores and transitional pores are considered as feeder pores which allow the transfer of reactants into the coal. Micropores do not contribute to the gasification (Miura et al. 1989). Fernandez-Morales et al. (1985) reported that char having a high concentration of feeder pores was highly reactive, because the reactant gases can easily diffuse into the internal surface. Sakawa et al. (1982) estimated the influence of pores on char gasification with CO_2 and found that the C-CO_2 gasification rate does not depend on the total volume of pores (ranging from 0.001 to 100 μm) in the char. Takarada et al. (1985) and Hashimoto et al. (1986) suggested that the factors controlling the gasification rate of char are not pore size and its distribution. Dutta et al. (1977) reported that only pores with $\delta > 30\overset{o}{A}$ are available for reaction. Johnson (1979) reported that most of solid-gas reaction occurs on surface for which $\delta \leq 50\overset{o}{A}$.

Pore size and surface area of high rank coal are more important than that of low rank coal. On other hand, the importance of pore structure on the gasification rate increases with the increasing reaction temperature. It is well known that in gasification, as in any solid-gas reaction, the overall process consists two parts: chemical reaction and diffusion (intraparticle and film processes). The overall rate of the process is controlled by the slowest step (Laurendeau 1978 and Levenspiel 1979). At low temperatures, the rate of the chemical reaction is low enough to allow the gasifying agent easy passage through the pores by diffusion. At high temperatures (T > 1200 °C), the chemical reaction rate becomes fast, and the intraparticle diffusion becomes the rate controlling step (van Heek et al. 1985). For high rank coals, and for some low rank coals for which gasification occurs at relatively high temperatures, the pore structure has a significant effect on the overall process. This is because the reactivity of high rank coal is controlled by the number of active sites.

2.4.6 Role of Minerals

It is well known that the gasification of coal with carbon dioxide and steam is catalysed by active minerals (Suzuki et al. 1989, Tomita et al. 1979, and Takarada et al. 1985). Alkali and alkaline-earth metals, such as Na, K, and Ca, inherent or artificially added to coal, are excellent catalysts for most gasification reactions. The catalytic effect of minerals is considered to be the controlling factor for the gasification of low rank coals. A detailed discussion on the catalytic effect of inorganics is given in **Section 2.7**.

2.4.7 Role of Oxygen-Containing Functional Groups

Oxygen-containing functional groups play an important role in coal gasification. These organic acid groups act as a bridge to connect carbons and inorganics for catalytic reaction. The concentration of carboxylic groups determines the efficiency of adding a catalyst for gasification. It is well known that cations, which are added to coal by ion-exchange, are more effective for low-rank coals than high rank coals because high rank coal contains fewer carboxyl groups to form carboxylates on the coal surface. Active metals such as K, Ca and Na have a low catalytic effect on gasification unless they are connected to carboxyl functional groups to form active sites (Ye and Agnew 1993a and 1993b). Mechanical addition of metals has a poor catalytic effect on gasification.

The amount and nature of oxygen-containing functional groups have a significant influence on the reactivity of coal. The measured amounts and features of oxygen-containing functional groups vary greatly with coal rank (Dryden 1963). The major oxygen-containing groups in coal are the hydroxyl, carboxyl and carbonyl structures. Lignites contain higher concentrations of carboxyl functional groups and other organic acid groups than higher rank coals. Under heat treatment, these oxygen-containing functional groups undergo thermal decomposition and release CO_2. The importance of oxygen-containing functional groups on the reactivity is that the organic acid groups, such as carboxylic acid groups, impart ion-exchange properties to low rank coals. In low rank coals, there are considerable amount of metals which are present as salts of these acids. Such carboxylates are commonly recognized as active sites which are available for the gasification reaction (van Heek et al. 1985 and Miura et al. 1989). Active metals such as Na and Ca associate with the carboxyl groups to form active sites on the surface of coal. Hippo et al. (1979) reported that the carboxylate salts of the inorganic constituents will dissociate and release CO_2 upon conversion of cation-exchanged lignite to char. Takarada et al. (1985)

pointed out that low rank coals have more oxygen-containing groups which act as exchanging sites, however, the total amount of exchangeable cations does not have any correlation with oxygen content of the coal.

2.4.8 Effect of Heat Treatment on Reactivity

The influence of heat treatment on the reactivity of coal has been reviewed by Laurendeau (1978). He concluded that, under heat treatment, the following changes occur: (*i*) loss of oxygen and hydrogen; (*ii*) change in inorganics-mineral matter converted to metal oxides (Murray 1972, 1973 and Given 1975); and (*iii*) change in the physical properties of coal such as porosity and surface area (Blake et al. 1967, van Krevelen 1961). Because coals consist mainly of aromatic and hydroaromatic structures, the functional groups and heteroatoms are crosslinked by ether oxygen and methylene bridges. Upon heating, the liberation of volatiles results in increasing the number and size of pores, thus enhancing char reactivity (Walker 1981). With increasing temperature, most cross links break, so that hydroaromatic groups are converted into aromatic structures; the char structure becomes more graphitic and the size of the carbon crystallites decrease, thus the reactivity of the coal is reduced.

The method of char preparation, particularly heat treatment, has a significant influence on reactivity. Walker (1981) reported that the gasification rate of char produced by rapid pyrolysis of lignites is higher than that of chars produced by a slow charring process. The reactivity of char is found to decrease with increasing residence time at the final pyrolysis temperature. He attributed this behaviour to the change in the physical properties of the coal particle during heat treatment. Orenbakh (1973) pointed out that, under rapid heating, the release of volatile matter is considerably rapid, while repolymerization is less favoured. Thus, rapid heating results in higher porosity of the char. Khan (1987) reported that the char prepared from a high-volatile bituminous coal at 500°C was more reactive than high-temperature chars, and the reactivity of the char prepared at low temperature was even higher than that of the raw coal. He attributed the high reactivity of low-temperature chars to the high concentration of hydrogen. It is believed that hydrogen-rich coals are preferentially oxidized, leaving behind highly reactive "nascent" carbon sites.

In general, it can be concluded that the reactivity of char is largely influenced by the charring process. High temperature thermal treatment causes a decrease in the number of active sites and internal surface area. Fast heating results in an increased reactivity.

2.5 KINETIC MODELS FOR COAL GASIFICATION

2.5.1 Introduction

Kinetic models of coal and char gasification have been investigated for a long time and several comprehensive studies have been performed in this area. Numerous mathematical models have been proposed to give kinetic descriptions of varying complexity for coal gasification. The intrinsic reaction rate is determined by correcting the overall rate for intraparticle diffusion. Investigations into kinetic models of coal gasification are mainly classified into three groups:

(a) models for intrinsic reaction;
(b) models for intraparticle heat and mass transport;
(c) models for evolution of pore structure.

Most gasification reactions occur under conditions (e.g. $T < 850^{\circ}C$ and $P < 10$ kPa) where the chemical reaction is the rate controlling factor (Kasaoka et al. 1986, Riley et al. 1987). At higher temperatures, intra-particle diffusion becomes the rate controlling step. Thus, the selection of models depends on the conditions of interest. The simplest models are the Homogeneous and the Shrinking-Core models. Both models have been widely used to describe coal gasification processes. Some models have been proposed to describe the pore structure of a coal (or char) particle and its variation during reaction (Petersen 1957, Simons and Finson 1979, Bhatta 1980 and Gavalas 1980). Other workers have proposed empirical kinetic correlations based on their own experimental results (Dutta et al. 1977, Agarwal et al. 1980, Johnson 1980 and Kasaoka et al. 1986).

In this section, typical coal gasification models are discussed.

2.5.2 Models Including Chemical Reaction Control

Models belonging to this group assume that the overall gasification rate is dominated by chemical reaction. The physical structure of the coal and transfer processes are of little importance. Typical models in this group are the "Shrinking-Core" and "Homogeneous" models. As ideal noncatalytic gas-solid reaction models, these two models are widely used to describe coal gasification (Wen et al. 1968, Jensen 1975, Schmal et al. 1982, Matsui et al. 1987 and Goyal et al. 1989). Both models assume that the reaction rate constant does not change during the reaction. They are illustrated in ***Figure 2-3***.

The Homogeneous model simply assumes that the solid-gas reactions occur throughout the whole particle uniformly. As the reaction progresses, the particle size remains relatively constant while density decreases. A mass balance for first-order reaction in a particle under this condition reduces to (Levenspiel 1978):

$$\frac{dX}{dt} = k \cdot (1 - X) \tag{2.5.1}$$

$$-\ln(1 - X) = k \cdot t \tag{2.5.2}$$

where X is the fractional conversion of solid reactant, t is the reaction time, and k is the first-order reaction rate constant. For coal gasification, this model assumes that the carbon-gas reactions occur at the active carbon sites and that these sites are uniformly distributed throughout the particle.

The Shrinking-Core model assumes that the gaseous reactants diffuse through a gas film surrounding the particle, penetrate and diffuse through the ash layer and react on the unreacted core surface. As the reaction progresses, the zone of reaction moves into the solid and the unreacted core size keeps "shrinking". At any time during the reaction, there exists an unreacted core of reactant material. Assuming first-order chemical reaction, the total reactant mass balance can be expressed as:

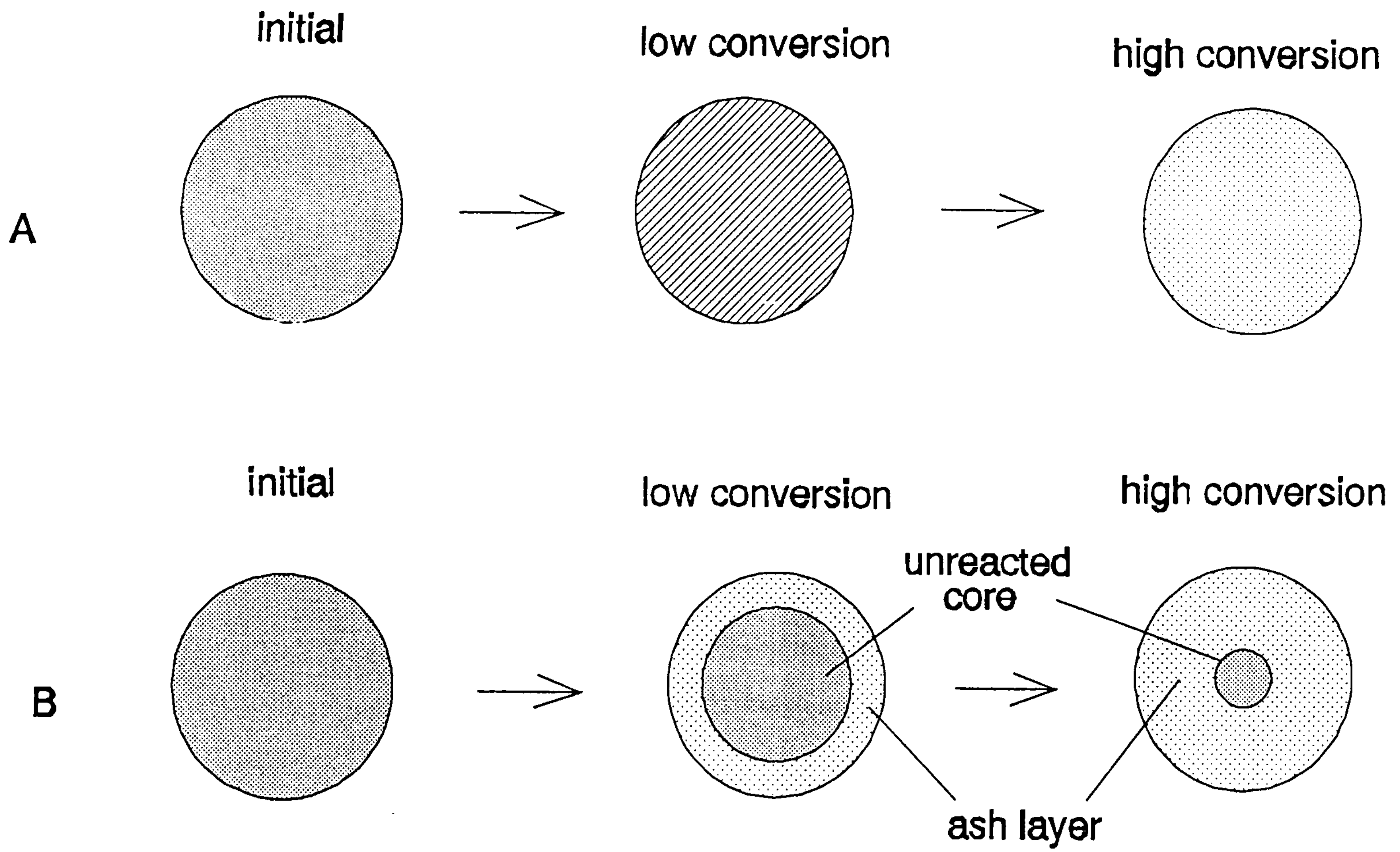


Figure 2-3 Model simulation of different gas - particle reactions
A: Homogeneous model, B: Shrinking-Core model

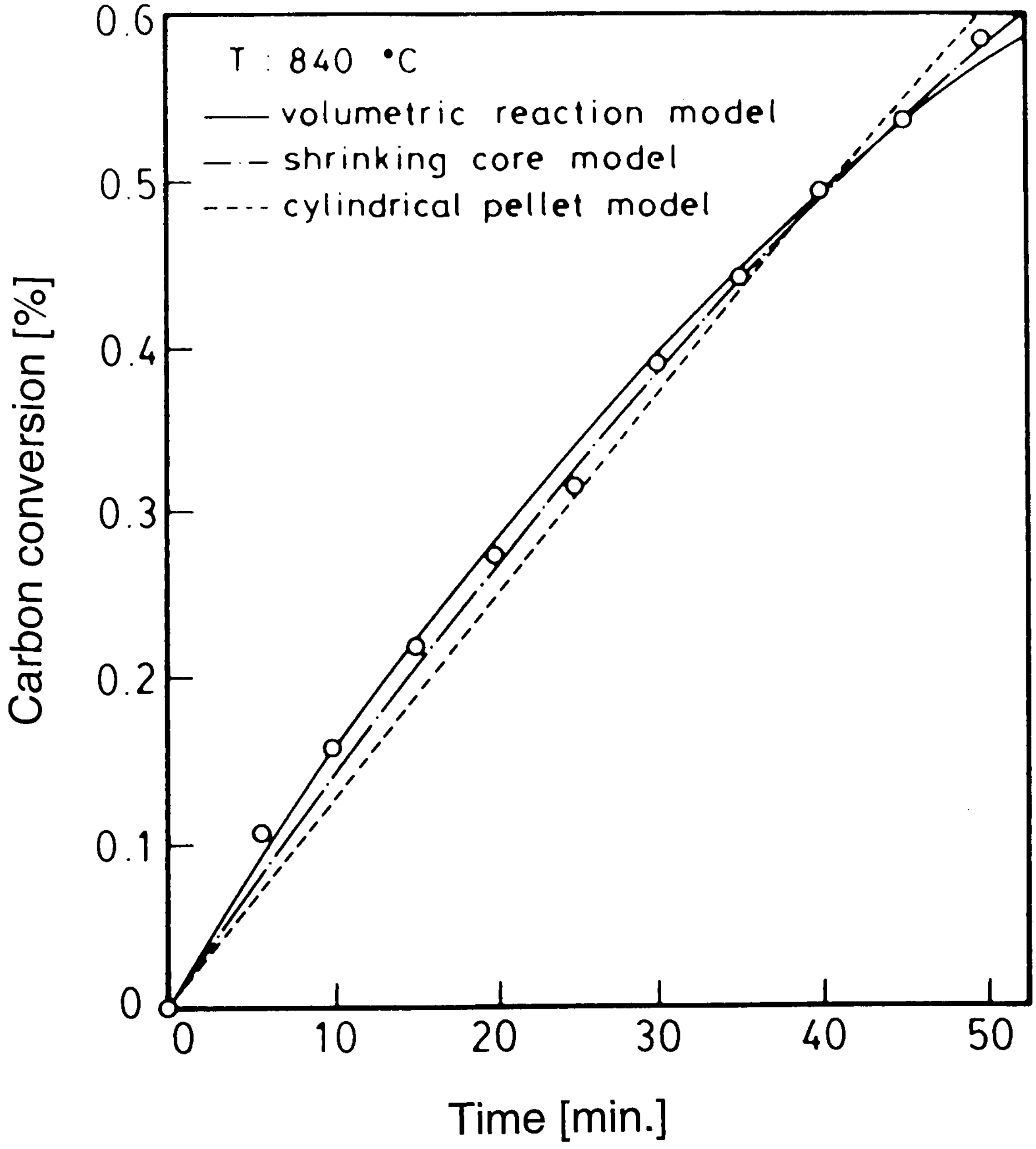


Figure 2-4 Comparison between CO_2 gasification experimental data and model prediction at 840°C. (Kwon et al. 1988)

for chemical reaction control

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3} \qquad (2.5.3)$$

$$\tau = \frac{\rho_p R_o}{b k_s P_g} \qquad (2.5.4)$$

for ash diffusion control

$$\frac{t}{\tau} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \qquad (2.5.5)$$

$$\tau = \frac{\rho_p \cdot R_o^2}{6bDP_g} \qquad (2.5.6)$$

for film diffusion control

$$\frac{t}{\tau} = X \qquad (2.5.7)$$

$$\tau = \frac{\rho_p \cdot R_o}{3bk_g P_g} \qquad (2.5.8)$$

where X is the fractional conversion of the solid particle, t is the reaction time, and τ is the reaction time for complete conversion. R_0 is the radius of the particle, ρ_p is the density of the solid, b is stoichiometric coefficient, P_g is the partial pressure of the reactant gas, k_s is the reaction rate constant, D is the diffusivity, k_g is the mass transfer coefficient between fluid and particle

Kwon et al. (1988) studied the gasification kinetics of lignites with carbon dioxide at different reaction temperatures (700-888°C) in a thermobalance reactor. Two models (homogeneous and shrinking-core) were used to correlate the gasification data for raw coals. As shown in ***Figure 2-4***, both models fitted the experimental data well. Kwon et al. (1989) also investigated the kinetics of steam gasification and found that both Homogeneous and Shrinking-Core models describe steam gasification well at the low temperature conditions (700°C). At higher temperatures and high carbon conversion, the values predicted by the homogeneous model exhibited larger deviations than those from the shrinking-core model (under the assumption that the chemical reaction is the rate controlling step). The reaction order was found to change with the loading of alkali catalyst. It was zero-order when the reaction was catalysed by K_2CO_3, Na_2CO_3, and mixtures of K_2CO_3 and Na_2CO_3. Other investigators (Fung and Kim 1983, Schmal et al. 1983, Adanez and de Diego 1990) also reported that both of these models describe the gasification process well. Schmal et al. (1985) pointed out that, in fluid-bed gasifiers, at a sufficiently high fluidizing gas velocity, film diffusion and the effect of mass transfer could be neglected and thus chemical reaction was the rate-controlling step for the gasification.

Goyal et al. (1989) developed a kinetic model to correlate the gasification rate of Western Kentucky bituminous coal with steam and synthesis gases under varied experimental conditions (925-1038°C, 4-28 atm.). The model is based on Johnson's (1980) correlation. By separating variables and integrating it gives:

$$M(X) = \int_0^X \frac{\exp(aX^2)}{(1-X)^{2/3}} dX = Kt \qquad (2.5.9)$$

Here, a is a kinetic parameter which is a function of temperature and gas composition. They found that, for steam gasification, a=0, the experimental data were well represented by plots of $3[1-(1-X)^{1/3}]$ versus reaction time. For the reaction with steam-hydrogen mixtures, a=1.0, the experimental data were well correlated by plotting $-ln(1-X)$ with time.

Kasaoka et al. (1985) proposed a modified "volumetric" (homogeneous) model to correlate the gasification of coal with steam and carbon dioxide. They found that their gasification data for all reactant gases (CO_2 and steam), at different temperatures and irrespective of the type of coal used can be correlated by a single curve:

$$X = 1 - \exp(-A\tau_{0.5}^{B}) \qquad (2.5.10)$$

where $\tau_{0.5}$ is the reaction time required to achieve X=0.5 conversion, and A and B are constants. They concluded that all the coals were gasified according to essentially the same reaction mechanism. They indicated that coal gasification is under chemical control at temperatures below 1000°C and the reaction rate constants varied as the reaction progressed. Other investigators (Yuh et al. 1984 and Fernandez-Morales et al. 1985) use the dimensionless reaction time, $t^*=t/\tau_{0.5}$, to correlate the gasification process. It is interesting to note that most of their experimental data fitted well onto a single curve at low temperatures.

In an experimental study, Johnson (1981) investigated the kinetics of coal gasification under varied conditions (e.g. $C\text{-}H_2O\text{-}H_2$, $C\text{-}CH_4\text{-}H_2$ and $H_2O\text{-}CO\text{-}CO_2\text{-}H_2$ mixtures, temperatures from 800 to 1100°C and pressures from 1 to 70 atm.). He developed an empirical kinetic model to describe the coal gasification process:

$$\frac{dX}{dt}=f_L \cdot k_T(1-X)^{2/3}e^{-aX^2} \tag{2.5.11}$$

where f_L is the reactivity factor which depends on the coal type, temperature and the partial pressure of individual gas. a and k_T are kinetic parameters. The term $(1-X)^{2/3}$ is proportional to the effective surface area for gasification. The term $exp(-aX^2)$ represents the relative reactivity of surface. Johnson's kinetic model has been widely used to describe gasification behaviour. Good agreement between the model predictions and experimental results has been reported in the literature (Purdy et al. 1981, Goyal et al. 1989, Gururajan et al. 1991). The main drawbacks of this model are the complexity of its rate equations and the large number of parameters which need to be determined by experiment. Johnson's correlation is applicable only to gasification with steam and hydrogen.

Prasad et al. (1990) investigated $C\text{-}CO_2$ kinetics using thermogravimetric analysis (TGA). They pointed out that, in a TGA system, the flow of a gas must be restricted to the laminar regime, because high flow rates can cause turbulence which may affect the accuracy of weight recording. Thus, kinetic data obtained by the TGA method include the effect of film or bulk diffusion. They presented a correlation which combined the effect of gas film diffusion, ash layer diffusion resistance, pore diffusion and the intrinsic reaction rate. The overall equation is:

$$r = \frac{(1-\varepsilon)\cdot(p-p^{*})}{\frac{d^{o}}{6k_f} + \frac{RTd^{o2}(1-X)^{-1/3}}{12D} + \frac{1}{\theta f(c_c)}} \tag{2.5.12}$$

where $(p - p^{*})$ is the overall thermodynamic driving force in partial pressure units, $d^{o}/6k_f$ is the film diffusion resistance, the second term in the denominator is the ash layer diffusion resistance. $f(c_c)$ is the intrinsic reactivity which depends on the concentration of active carbon sites. d^{o} is the particle diameter, ε is bed voidage, θ is effectiveness factor, D is the bulk diffusivity and k_f is the gas film mass transfer coefficient. They concluded that if the experiments are carried out with sufficiently small particle size, the effect of ash-layer diffusion and pore diffusion on the rate could be neglected.

2.5.3 Models for Pore Structure

During coal gasification, the pore structure of char changes due to the difference of the char particle and the product. Various models for noncatalytic gas-solid reactions have been proposed (Smith 1977, Georgakis et al. 1979 and Gavalas 1979) to describe the variation of the pore structure. An excellent review of these models, which is based on the different characterizations of the solid structure, has been given by Lindner and Simonsson (1980). In their discussion, structural models were classified into three categories: cylindrical pore models, network models and partially-sintered-sphere models. Detailed geometric explanations of these models have been given by Linder and Simonsson (1980).

Bhatia and Perlmutter (1980) proposed a random-pore model to describe the gasification of coal with steam. The model assumes that the coal surface area is formed by a randomly overlapping set of cylindrical surfaces of a given size distribution. The reaction rate is proportional to the steam partial pressure and the specific surface area of the pores. The relation between the specific surface area of the pore and the conversion of fixed carbon was expressed as:

$$\frac{dX}{dt} = k \cdot S_o \cdot p_{H_2O}(1-X)\sqrt{1-\phi\ln(1-X)} \tag{2.5.13}$$

where X is the fractional conversion of fixed carbon. k is the rate constant per unit surface area, and is a function of temperature and the concentration of active sites. S_0 is the initial specific surface area and φ is the pore structure parameter. Similar correlations have been proposed by other investigators (Gavalas 1980, Chin et al. 1983, and Belci et al. 1987) to simulate the variation of pore structure during gasification.

2.5.4 Models for Intraparticle Heat and Mass Transport

Many gasification models consider the influence of mass and heat transfer on the reaction rate. In some cases, particularly under high temperature conditions, the overall process is dominated by heat or mass transfer. As discussed in **Section 2.4.3**, for some well known gasification models, such as the shrinking-core model, heat and mass transfer become significant when temperature increases beyond a certain value. Hastaoglu et al. (1988) proposed a porous grain model to describe C-CO_2 gasification. The model considers the concentration, temperature, and pressure gradients for the reaction of a porous pellet. Various factors such as the structure parameter (which varies with time and location), film diffusion, and mass and heat transfer are taken into account. The principal assumptions regarding the model are: (i) the coal (pellet) consists of numerous uniformly spherical grains; (ii) reactions occur at sharp interfaces in the grains; (iii) mass and heat transfer can be calculated by transfer coefficients; and (iv) the shape of a grain is not influenced by the presence of any catalyst. The relevant formulation can be summarized as:

$$r_i = r_o - \int_0^t \frac{M_s}{\rho_s} b f(C_g, C_p) dt \qquad (2.5.14)$$

where r_0 is initial radius of grain, r_i is radius of reaction front into grain, M_s is the mass of carbon, ρ_s is the density of the solid reactant (carbon), and C_g and C_p are the concentrations of the reactant and product gases.

2.6 THE ROLE OF INHERENT INORGANICS IN GASIFICATION

2.6.1 Introduction

The reactions of coal gasification are very sensitive to cations of positive and negative catalysts. Investigations, both theoretical and experimental, have been carried out to clarify the role of minerals in gasification processes. Many researchers draw conclusions based on their own investigations (McKee et al. 1983, Kasaoka et al. 1986, van Heek et al. 1985 and Miura et al. 1989). Few detailed studies have been reported on the combined effects of the amount, state and dispersion of coal minerals, the interaction of the minerals with carbon and their variation during reaction. For low-rank coals like Bowmans lignite, the presence of high concentrations of alkali metals strongly influences the gasification characteristics. Hence, it is necessary to define the nature of inherent inorganic impurities and the role of such impurities in gasification.

In this section, the relationships between the gasification rate and the properties of inherent inorganic matter are reviewed. The catalytic activities of various active metals such as Na, Ca, K and Fe are discussed. Factors such as pretreatment, demineralization and cation-exchange which influence the catalytic gasification are examined.

2.6.2 Nature of Coal Minerals and Inorganics

Since coal contains many inorganic elements which may be present in different forms in coal, it is necessary to indicate which parts of the minerals have catalytic effects on gasification. Firstly, we need to give a clear definition of "coal mineral" and describe its nature. Based on detailed studies of the transformation of inorganic matter in South Australian brown coals, Manzoori(1990) pointed out that "inorganics" of coal include atomically dispersed inorganic elements such as Na, Ca, Mg, K, Fe, Si, Al, Cl, P, S, N and other trace elements. "Minerals" means quartz, clay, carbonates, pyrites and other mineral components.

The quantity and quality of inherent impurities vary widely with coal type. Si and Al are the dominant inorganic elements in high-rank coals. Low-rank coals contain considerable amounts of alkali and alkaline-earth metals (Takarada et al. 1985). Morgan et al. (1981) reported that lignites contain large amounts of exchangeable cations which are associated with organic acid groups. About 40-60% of the carboxyl groups are exchanged with cations. Readett et al. (1986) reported that inorganic substances were present in low-rank coals in two forms: dissolved ions present in the water in coal and cations connected with the oxygen-containing groups as salts of humic acids. This may explain why lower rank coals are more reactive than higher rank coals. Almost all the alkali and alkaline-earth elements can be removed by washing raw coal with acids. Minerals may change their chemical form by reacting with gases during gasification. The presence of inorganic impurities affects not only the reactivity of coal, but also the structural properties of the char.

2.6.3 Catalytic Effect of Inherent Inorganics

It is well known that minerals in low rank coals are important factors which influence or control the gasification rate of coal (Mahajan et al. 1978, Kasaoka et al. 1985, van Heek et al. 1985, Miura et al. 1989 and Adanez et al. 1990). Lignites and subbituminous contain large amounts of carboxylic acid groups which are associated with cations such as K^+, Ca^{++}, Na^+ Mg^{++} and Fe^{++} (or Fe^{+++}). The rate of gasification is proportional to the amount of alkali elements bonded to the oxygen-containing groups of coal matrix (Takarada et al. 1985). The catalytic effects of metal cations on gasification vary with different reaction atmospheres (Walker et al. 1979). For CO_2

gasification, potassium, sodium and calcium improve the reaction rate while iron and magnesium show poor catalytic effect. For H_2O gasification, K and Ca have higher catalytic activities than Na and Fe. Iron is found to have a strong catalytic effect in a hydrogen-steam atmosphere (Tsai 1982). van Heek (1985) reported that minerals in high-rank coal had little effect. Inherent minerals are found to be the controlling factor for the gasification of lignite. The catalytic effect of inherent inorganic impurities depends on the amount, quality and distribution of the inorganics in the coal.

Miura et al. (1989) reported that the gasification reaction consists of a non-catalytic process which is determined by the structure of the char and a catalytic process which is dominated by the catalytic effect of inherent minerals, so:

gasification rate = non-catalytic reaction rate + catalytic reaction rate

As the inherent minerals play an important role in coal gasification, the concentration and dispersion of active metals should be considered as a relevant parameter in gasification modelling. Radovic et al. (1986) suggested that the gasification of lignites should be considered as a catalytic gas-solid reaction. Therefore the normal gasification model should only be used for demineralized coal.

Morgan et al. (1981) investigated the inorganic constituents and the amount of carboxyl groups in American lignites by using ion-exchange techniques. Their results show that exchangeable cations such as Ca, Na, K, Mg, Sr and Ba and carboxyl groups exist in significant amounts in lignites from North Dakota, Texas and Montana. Ca and Mg were found to be the most abundant cations.

Various studies (Fernandez-Gonzalez et al. 1986 and Hashimoto et al. 1986) indicate that not all the minerals of coal have a catalytic effect; only some elements such as Na, Ca, K and Fe, intimately bound with carbon, exhibit catalytic activity. Si and Al are not active elements for coal reaction. Takarada et al. (1985) indicated that the total ash content shows a poor correlation with coal reactivity. The gasification rate of lower rank coal is proportional to the amount of exchangeable Ca and Na. By quantitatively studying the relation between ash and char reactivity, Sakawa et al. (1982) presented a useful parameter, the alkali index (*B*), for characterizing the catalytic effect of coal ash on gasification:

$$B = ash(wt\%) \cdot \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \tag{2.6.1}$$

Their experimental results show that as the alkali index increases, the rate of CO_2 gasification increases. ***Figure 2-5*** illustrates the relationship between alkali index (*B*) and reactivities of some coals (Sakawa et al. 1982).

The presence of large quantities of non-catalytic coal minerals can even inhibit the gasification process. Inactive inorganics (e.g. Si and Al compounds) may block the pores, reducing the ability of the reactant gas to diffuse to the internal surfaces of the micropores (Linares-Solano et al. 1986). These inactive compounds can react with alkaline matter to form non-catalytic alkali compounds like $KAlSiO_4$ and $KAl_2Si_3AlO_{10}(OH)_2$. The irreversible reaction of coal ash with alkaline matter reduces the amount of catalytic alkali present (Bruno et al. 1986, Formella et al. 1986, and Kim et al. 1989). For example, the mineral kaolinite reacts with potassium carbonate to form kaliophilite as follows:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + K_2CO_3 \rightarrow 2KAlSiO_4 + 2H_2O + CO_2 \tag{2.6.2}$$

This catalyst consumption effect becomes significant particularly for catalytic gasification or for reaction which occurs at high temperatures.

2.6.4 Effect of Demineralization on Gasification

2.6.4.1 Effect of Acid Washing

Demineralization is a process in which raw coals are treated by acids to remove inherent inorganic matter. In lignites, most cations are associated with carboxyl groups and can be removed by acid-washing. The overall process of demineralization is:

$$R-COOM+H^{+}\rightarrow R-COOH+M^{+} \qquad (2.6.3)$$

Extensive experimental work has been carried out on deashed coal to determine the effect of ash on reactivity by washing the coal or char with HCl or HF (Garcia et al. 1986, Fernandez-Morales et al. 1987, Adanez et al. 1990, and Kim et al 1989). The methods for the demineralization of coal have been well established. Most investigators agree that the reactivity of coal is decreased by treating raw coal with acid since this causes the loss of active cations (Knight and Sergeant 1982, Tomita et al. 1985, Miura et al. 1989, and Kopsel and Zabawski 1990.). ***Figure 2-6*** shows the effect of demineralization on coal reactivity (Miura et al. 1989). However, the demineralization of coal can not be considered as a simple deactivation process. In fact, acid-washing results in the change of the coal gasification behaviour, and it is difficult to ascertain whether this process will enhance or obstruct the gasification reaction. The problem is complex because the demineralization process couples the deactivation process and the variation of the coal's surface area (Fernandez-Gonzalez et al. 1986 and Fernandez-Morales 1985). A detailed discussion of the influence of demineralization on coal structure is given in **Section 2.6.3.3**. Garcia and Radovic (1986) indicated that the change of the organic structure is less important than the variation of the minerals in coal during the demineralization. Both Kasaoka (1985) and Garcia (1986) reported that, after demineralization, coals of different ranks seemed to have reactivities similar to those of higher rank coals.

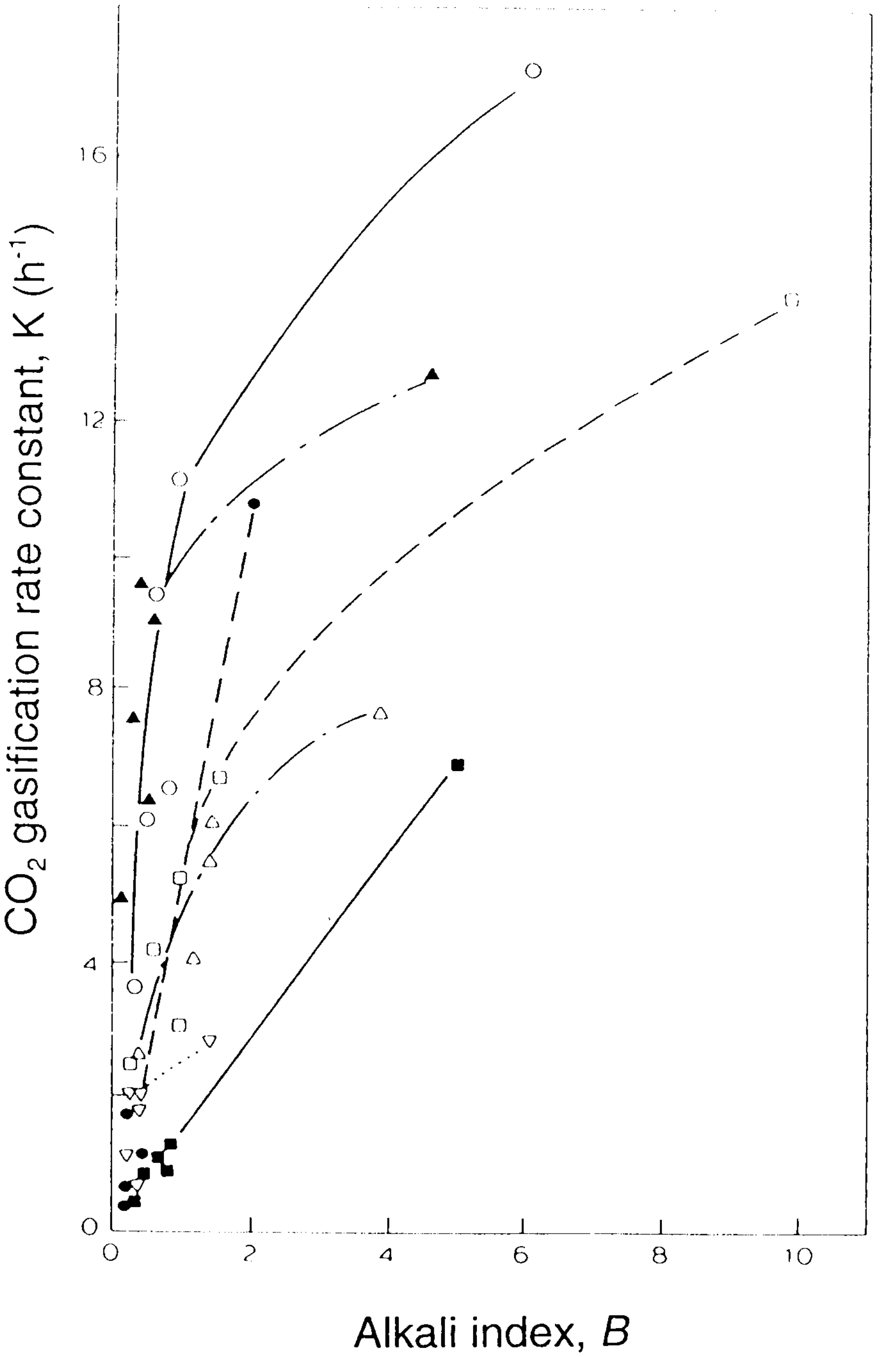


Figure 2-5 Relation between the B value and the rate of CO_2 gasification. ■ Smoky River coke; □ Liddell coke; ● Goonyella coke; o South Black coke; △ Itman coke; ▽ Balmer coke; ▲ Lemington coke. (Sakawa et al. 1982)

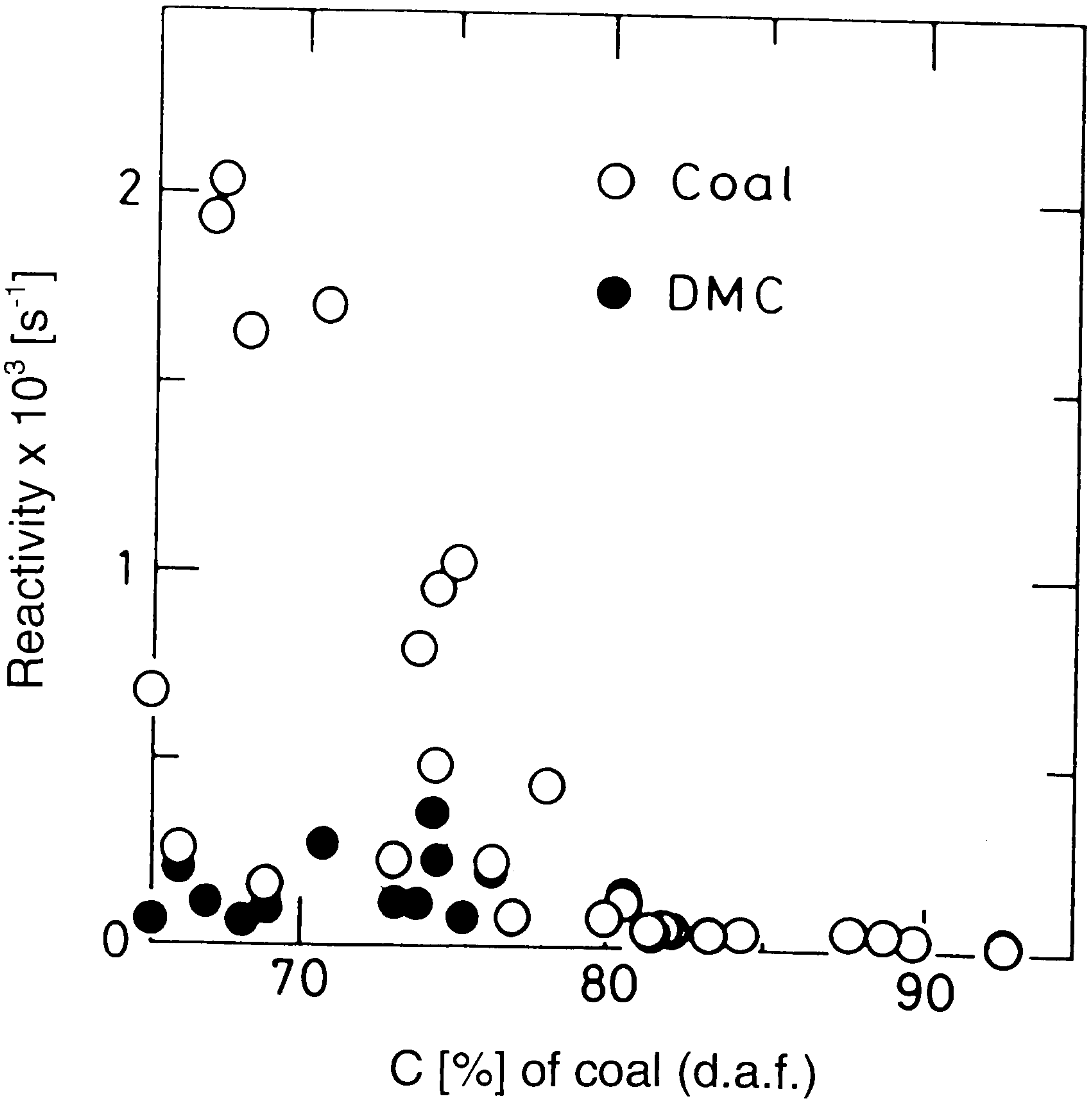


Figure 2-6 Relationship between H_2O gasification rate of raw coal (o) and demineralized coal (DMC), and carbon content of coal at 787°C , P_{H2O}=0.5. (Miura et al. 1989)

Adanez et al. (1990) have shown that the gasification rates of lignites can be significantly reduced by treating the coal sample with HCl or HF. Addition of coal ash to the acid-washed samples cause a slight increase in reactivity over the acid-washed samples, but this was still much lower than the reactivity of the raw coal. They attributed this to the poor dispersion of the ash in the char. Knight et al. (1988) studied the catalytic activities of inherent inorganics on the gasification of char derived from some Australian coals and found that the reactivities of chars tended to increase with increasing percentage of any inorganic component. After treating the coals with acids, the reaction rates were significantly changed. Fernandez-Morales et al. (1986) reported that the demineralization process generally increases the activation energy of coal gasification so that the reaction rate is lowered.

Kopsel and Zabawski (1990) found that the rates of CO_2 gasification of raw lignites were 30-50 times higher than those for acid-washed lignite. Experiments were also conducted on deashed lignite which was loaded with Ca, Na, K and Fe according to their original percentages in the raw coal. They found that none of the individual elements control the gasification reaction. The catalytic effect of inherent inorganics seems to be dominated by the combined catalytic effect of the different active elements. Experiments on steam gasification of the same lignite have been conducted separately (Kopsel and Zabawski 1990). The results showed that the steam gasification rate of raw coal is 19-35 times higher than that for deashed coal. Their results clearly indicated that coal minerals play an important role in the gasification and that the reactivity of lower rank coal is mainly controlled by the content and dispersion of the inorganic matter.

Demineralization does not always reduce the reactivity of raw coal. Some investigations (Fernandez-Gonzalez et al. 1986, Linares-Solano et al. 1986) showed that acid-treatment may have little influence on the gasification rate, and it can even increase the gasification rate. For example, Linares-Solano and coworkers (1986) studied the reactivities of two high-ash high rank Spanish coals and found that the reactivities of the coals markedly increased by treating the raw coals with HCl or HF. They also found that the reactivities of two low-ash coals were increased by acid-washing. This behaviour, they considered, was due to the combined effect of the removal of minerals and the variation of the chemical and physical nature of the char caused by acid-washing.

2.6.4.2 Effect of Water Washing

Water-washing (or water-leaching) is a process which results in partial removal of minerals from raw coal. A great deal of work has been conducted to investigate the beneficiation of South Australian low rank coals by water-leaching (Readett and Quast 1985, 1986, 1989, Dunne et al. 1988, and Manzoori 1990). Their results showed that most alkali elements such as sodium and potassium are present in a water-soluble form in coal and can be removed by water washing. Paulson et al. (1981) have shown that considerable amounts of cations can be exchanged from an aqueous solution with organically bound cations and that the sequence of replacement of cations from weak-acid exchange with lignites is: $Na^+ > K^+ > Mg^{2+} > Ca^{2+} > Al^{3+} > Fe^{3+} > H^+$. The above studies provided a satisfactory explanation of the transformation of inorganics during the process of water-treatment but none related this process to coal gasification.

It is reasonable to believe that the water-leaching process, which removes a considerable quantity of the active inorganics, will result in decreasing the number of active sites on the coal surface. Due to the lack of experimental data on the gasification of water-washed coal, it is difficult to be definite about the influence of water-leaching on the rate of gasification. This is a subject of the present investigation

2.6.4.3 Influence of Demineralization on Coal Structure

The demineralization process causes not only the removal of minerals from raw coal but also the change of the surface area and porosity (Hengel and Walker 1984). Mahajan and Walker

(1979) found that the removal of inorganic matter from coal by acid-treatment, in some cases, can increase the surface area. The change in the surface area of the char mainly depends upon whether the acid treatment is given to the coal precursor prior to charring, or to the char of the raw coal. Brooks and Sternhell (1957) reported that demineralization has a negligible effect on the amount of oxygen-containing functional groups of coal. Fung et al. (1988) found that acid treatment can smooth the pores and change the resulting char from predominantly microporous to macroporous. The changes in reactivity can be explained in terms of a balance of the opposite effects - a decrease in catalytic activity opposed by an increase in the internal surface area.

Fernandez-Gonzalez et al. (1986) studied the role of inorganics in the reactivity of coal by using some high-ash coals. They found that the macroporosity increased and the microporosity was unaffected by treating the coal with acids. The reactivity of the acid-washed high-ash content coal was found to be higher than that of the raw coal. Walker and Mahajan (1986) also reported that the removal of minerals from high-rank American coals increased the reactivities with CO_2, H_2O, H_2, and air. They suggested that, the loss of catalytic effect due to the removal of minerals is offset by the change in the porous structure of coal. Miura et al. (1989) pointed out that demineralization removes coal minerals without greatly affecting the pore structure of low-rank coal.

2.7 CATALYTIC GASIFICATION

Introduction

The above discussion is concerned with the role of inherent inorganics in gasification. In fact, most studies of cation activities of cations are conducted by artificially adding cations to coal, i.e. catalytic gasification. A detailed treatment of catalytic gasification is beyond the scope of this study. In this section, the catalytic activities of a wide range of salts are reviewed. Special attention is given to the influence of anions on the catalytic activities of alkali salts. The discussion is also concerned with the mechanism and kinetics of catalysed gasification.

2.7.1 Effect of Artificially-Added Cations

Various investigations into catalytic gasification have been conducted with the objective of finding ideal catalysts that enhance the reaction rate at low temperature (Otto et al. 1979, Lang 1986, Saber et al. 1986, Hashimoto et al. 1988, and Shimada et al. 1991). Much attention has been given to brown coal which seemed particularly appropriate for gasification. Alkali and alkaline-earth metals (e.g. K, Na and Ca) are commonly recognized as good catalysts for gasification. Transition metals like Fe, Ni, Cu, Au, Cr, Mo and Zn have also been found to have effective catalytic activity (Holsterin et al. 1983). The catalytic effect of additives on gasification differs greatly. Haynes et al. (1974) tested the catalytic effect of various additives on coal gasification. More than 40 different oxides and salts were used. They observed that alkali compounds promoted the coal gasification rate by 31-60%, while, 20 other metal compounds increased the rate from 20 to 30%. The catalytic activities of the same metals vary with changing gasifying agent. For example, Ca and K are good catalysts for C-CO_2, C-H_2O and C-O_2 reactions, but are poor catalysts for C-H_2 reaction (Walker et al. 1983); Fe can enhance the gasification of coal in a H_2O-H_2 environment, but is inactive in CO_2 and O_2 atmospheres (Walker et al. 1966).

The major factors which influence the rate of catalytic gasification are: the nature of the coal, the activation of the catalyst precursor, the deactivation of active species, and the method of catalyst loading.

2.7.2 Activities of Alkali and Alkaline Earth Salts

Walker et al. (1983) found that Na, K and Ca, added to low-rank coals by ion-exchange and high-rank coals by impregnation can greatly promote gasification in O_2, H_2O and CO_2. Hippo (1977) found that the reactivity of K^+-exchanged lignite was more than one order of magnitude greater than that for the demineralized lignite. He reported that the order of catalytic activity was K>Ca~Na. McKee et al. (1983) reported significant differences of catalytic activities for Li_2CO_3, Na_2CO_3 and K_2CO_3 in CO_2 gasification of Illinois No.6 bituminous coal. Hamilton et al. (1984) reported that the rate of K-catalysed CO_2 gasification is dominated by the concentration of catalyst. They pointed out that before the catalyst reaches saturation, the gasification rate is controlled by the K/C ratio. After surface saturation, the rate is determined by the total surface area available for the reaction.

Calcium compounds show strong catalytic activity in some gasification reactions. Hippo et al. (1975 and 1979), Radovic et al. (1982), regarded calcium as the most important *in-situ* catalyst for the gasification of coal. Linares-Solano et al. (1986) studied the activity of $Ca(Ac)_2$ in gasification of a Texas lignite in different atmospheres (steam, carbon dioxide and hydrogen). Ca was added to the coal in twelve different concentrations from 1.1 to 12.9 wt%. Gasification rates were found to increase linearly with increasing calcium loading. Their results indicated that, in lignite, the carboxyl groups are associated with Ca under ion-exchange. Under heat treatment, these carboxyl groups undergo decomposition, releasing CO_2, and leaving a quantity of well dispersed CaO in the lignite char. The uniformly distributed CaO species act as active sites which allow the chemisorption of the reactant gases in the gasification of the lignite.

2.7.3 Effect of Anions on the Catalytic Activities of Cations

Importantly, experimental results showed that the catalytic alkalis are active only when these elements are present in the form of certain salts (Plogman et al. 1983). Yuh and Wolf (1983) evaluated the catalytic effect of K_2CO_3, $KHCO_3$, KOH, KCl and K_2SO_4 on the gasification of coal with steam by the TGA method at 750°C. Their results showed that the activities of alkali salts increased with increasing pH of the solution of the salts. They found that the order of catalytic activity was $KOH \sim K_2CO_3 > KHCO_3 > K_2SO_4$. KCl had almost no catalytic effect. Similar results were reported by Huttinger and Minges (1986), who investigated the influence of anions on the potassium catalysed gasification of coal with steam. The sequence of catalytic activity was: $KOH \sim K_2CO_3 \sim KO_2CH \sim K_2C_2O_4 \sim KO_2C_2H_3 > KNO_3 > K_2SO_4 > KCl$. Hashimoto et al. (1986) examined the catalytic activities of various salts in steam gasification and found that the activities of alkali carbonates were much higher than others like sulphate and nitrate salts, while alkali chlorides were inactive. The order for the catalytic activity of the various catalysts was: $Na_2CO_3 \sim K_2CO_3 \sim KOH \sim NaOH > K_2SO_4 \sim KNO_3 > NaCl \sim KCl$.

The above phenomena can be explained by the interaction between cations and carboxyl groups. For low rank coal, carboxyl groups (-COOH) provide a basis for cation exchange on the coal surface. Impregnating the coal with a solution of a strong acid salts, like chloride, only results in the physical adsorption of the cation onto the coal surface. Impregnating coal with solution of weak acid salts, such as carbonates and acetates, causes the cations to be associated with the carboxyl functional groups. The gasification rate of coal is proportional to the concentration of these chemisorbed cations.

2.7.4 Activities of Salts of Transition Metals (Fe and Ni)

The activity of transition metals is much lower than that of alkalis. Many investigations have been carried out to examine the catalytic activity of iron on coal gasification. Fe is found to exhibit a significant catalytic effect on steam gasification. It is generally accepted that, for H_2O and CO_2 gasification, iron only has a catalytic effect in the reduced form and is inactive in oxidised form (McKee 1974, Kasaoka et al. 1981, Hermann and Huttinger 1986, and Ohtsuka et al. 1986). Walker et al. (1988) have shown that a metallic iron surface is a good catalyst for the dissociation of molecular oxygen-containing species. Iron is a good catalyst for the methanation reaction and is also an excellent catalyst for dissociating chemisorbed H_2.

Nickel can greatly enhance gasification at low temperatures (McKee 1974, Tomita et al. 1981, and Nishiyama 1983). Yamada et al. (1983) found that nickel exhibits high activity in low temperature gasification of coal with carbon dioxide. The reaction rate was found to depend on the nickel loading in temperature region of 600-780°C. Colle et al. (1983) found that nickel showed high catalytic activity for steam gasification at low temperatures, but lost its activity rapidly at 30-50% carbon conversion. They attributed this to the strong nickel-carbon interaction. Opposite results have also been reported. For example, Spiro et al. (1983) found that $NiCO_3$ was totally inactive. In general, the catalytic activity of Ni is varied and easily influenced by environmental factors.

2.7.5 Mechanism and Kinetics of Catalytic Gasification

In the presence of active cations, gasification behaviour is significantly influenced by changing the reaction rate, mechanism and kinetics. Extensive studies have been carried out to examine the mechanism of catalytic gasification. Spiro et al. (1983) summarized the principal roles of catalysts: (i) catalysts act as adsorption sites for reactants; (ii) catalysts may dissociate reactants; (iii) catalysts may generate active carbon atoms by disrupting the carbon structure; (iv) catalysts may create active carbon atoms by dissolving carbon into a surface catalyst phase; (v) catalysts may create active carbon atoms by perturbing the electronic structure; (vi) catalysts may participate in a chemical step either by transferring atoms, electrons, or both between carbon and reagents.

A full understanding of catalytic gasification mechanism at a molecular level is not presently available. However, it is generally agreed that the presence of metal compounds may form active sites on the coal surface and promote gas-solid reactions (Linares-Solano et al. 1986, Kwon et al. 1988). Most investigators agree that the catalytic gasification of coal with CO_2 and H_2O follows one of the two mechanisms -*"oxygen transfer"* (McKee 1981, Walker et al. 1968) and *"electron transfer"* (Long et al. 1950, Hosltein et al. 1981). Both mechanisms assume that the role of the catalyst is to accelerate one or more steps of the uncatalysed reaction, rather than to create a new reaction. The *"electron transfer"* theory proposes that the catalyst accepts electrons from carbon, resulting in weak carbon-carbon bonds. It places less importance on the interaction between the catalyst and the gas. The *"oxygen transfer"* theory assumes that the catalyst accelerates the rate of oxygen adsorption on the carbon, the interaction between the catalyst and carbon is not important for the reaction.

Different mechanisms have been proposed by different investigators for the catalytic reaction process. Among them, the two-step oxygen-transfer mechanism is widely accepted:

$$C_f + CO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C(O) + CO \qquad (2.7.1)$$

$$C(O) \xrightarrow{k_3} CO + C_f \qquad (2.7.2)$$

Freund (1986) applied this two-step oxygen transfer mechanism to study Ca-catalysed CO_2 gasification. He found that k_1 was greatly increased by the addition of Ca, while k_2 was unaffected. Ca catalyses the reaction by increasing the number of active sites. The rate-determining step, the diffusion of CO molecules from the coal surface, is not affected by the addition of a catalyst. Similar results have been reported by Kapteijn et al. (1986), in which CO_2 gasification of carbon was strongly catalysed by Na, K, Rb and Cs. The alkali-catalysed reaction can be described by the above-mentioned two-step kinetic model. For step 2, the activation energy of catalysed reaction is lower than that of the uncatalysed reaction. They attributed this to the increase in the steady-state concentration of sites occupied by catalysts. They also concluded that the main role of a catalyst is to increase the number of active sites. The presence of active inorganics such as K, Na and Ca makes it possible to form in-situ active sites on the coal surface; such sites act as effective places for oxygen or electric transfer.

Other investigators (McKee 1983, Koening et al. 1986 and Hashimoto et al. 1986) have proposed other mechanisms to describe the catalysed gasification process. For all of the mechanisms they proposed, the role of catalyst is to form active sites on coal surface. Yuh et al. (1984) suggested that the addition of an alkali catalyst not only increases the number of active sites but also changes the gas-solid interaction.

2.7.6 Models for Catalytic Gasification

There are many models which have been proposed for coal gasification. Most of them do not consider the catalytic effect of coal minerals and added catalysts. Although some workers have presented correlations which include the influence of catalysts (Hamilton et al. 1984, Adanez et al. 1990), there is not yet a sound theoretical model suitable for general catalytic gasification processes. Adanez and de Diego (1990) proposed a modified homogeneous model, in which the catalytic effect of inherent minerals on the gasification was taken into account. It is expressed by the following equation:

$$\frac{dX}{dt} = k \cdot n(1-X) \cdot p_{CO_2} \qquad (2.7.3)$$

where X is the fixed carbon conversion, k is the first order reaction rate constant, p_{CO2} is the partial pressure of CO_2 and n is the activity constant of the inorganics. Their results indicated that the presence of minerals increases the concentration of active sites.

Miura et al. (1986) introduced the catalytic effect of inorganic matter into a general gasification model, as:

$$\frac{dX}{dt} = k \cdot (1-X)^n \qquad (2.7.4)$$

They found that the kinetic model of steam gasification varied depending on the nature of the added cations, so that, for an uncatalysed sample, n is 1. Equation 2.7.4 becomes:

$$\frac{dX}{dt} = k \cdot (1-X) \qquad (2.7.5)$$

For a sample with K or Na added, n is 0. Equation 2.7.4 then becomes:

$$\frac{dX}{dt} = k \tag{2.7.6}$$

For a sample with Ni added, n is 2/3. Equation 2.7.4 then becomes:

$$\frac{dX}{dt} = k \cdot (1 - X)^{2/3} \tag{2.7.7}$$

Other investigators (Ruan et al. 1987) found similar results. Kwon et al. (1989) indicated that gasification catalysed by alkali carbonates (Li_2CO_3, Na_2CO_3 and K_2CO_3) was of zero reaction order. The activation energy was found to decrease with increasing the catalyst loading. Ruan et al. (1987) studied the gasification kinetics of a Chinese bituminous coal (Datong coal) with CO_2 and found that the value of the activation energy, calculated from a first-order reaction rate, decreased from 59 to 38 kJ/mol in the presence of alkali catalysts. Kayembe and Pulsifer (1976) also found that the activation energy of the gasification of coal with steam decreased from 254 to 145 kJ/mol by adding 10% K_2CO_3 to the raw coal.

2.7.7 Other Factors Influencing Catalytic Gasification

Catalyst Loading Method

The method of catalyst loading has a significant influence on the catalytic activity (Liu and Zhu 1986 and Huttinger 1986). It is well known that impregnation or ion-exchange is more effective than the physical mixing of a catalyst with the coal. The catalytic activities depend on the state of the connection between the catalyst and the coal (Johnson 1981). Compared to physical mixing, catalyst added by the method of impregnation is well dispersed in the coal. Huhn et al. (1983) compared the interaction of an alkali catalyst with carbon using these two methods of loading. They found that in the case of impregnation, due to the good dispersion of the catalyst in the coal, the reduction of the alkali carbonate to the elementary metal and the reaction rate was a maximum at 720°C; while in the case of dry-mixing, the reaction rate reached maximum at 890°C, which is near the melting point of the alkali carbonate.

The dry-mixing of the catalyst with the coal has the advantage of being easy to control the amount of catalyst loading, while the ion-exchange or impregnation method results in good distribution of catalyst in the coal but it is difficult to determine the amount of catalyst loaded

Adsorption of Cations on Coal

The method of impregnation or ion-exchange has been widely used for catalyst loading but few studies have been performed to determine the adsorption of cations on coal by this method. Hippo et al. (1979) carried out acid-washing and ion-exchange treatment to load desired amounts of calcium onto a Texas lignite. Acid-washed coal samples were exposed to 10 levels of concentrations of calcium acetate solution, ranging from 0.04 to 2.0M, for 24 hours. The cation loadings thus obtained ranged between 0.10 and 2.14 mmol/g coal (daf). Demineralized coal samples were also exposed in 0.1 M solutions of other cations. The amount of added catalyst was approximately 0.3 mmol/g of coal (daf). The influence of concentration of the solution on cation loading was also investigated by Walker et al. (1983), in which a raw bituminous coal was treated with HCl and HF to remove the inherent inorganics, followed by loading several acetate catalysts. Three cations, Na, K and Ca, were tested. Their results showed that, for all cations, loading increased linearly with solution concentration increase from 0.1 to 1.0 M. The added cation concentration was found to vary from 0.2 to 0.58 mmol/g. For the three metals used, the order of adsorption on raw or demineralized coal was Ca > Na ~ K.

Temperature

Many publications (Juntgen 1983) have indicated that, for coal gasification, catalysts are effective only within the temperature region in which chemical reaction is the rate-controlling factor. For example, Ni was found to exhibit a strong catalytic effect on steam gasification at low temperature (500°C), but was less active at high temperature (800°C) (Hashimoto et al. 1986). The catalytic effects of additives decrease with increasing temperature. At high temperatures, the overall reaction rate is mostly like to be dominated by pore diffusion. The minerals can decompose and agglomerate at high temperatures, causing the inorganic catalyst to lose activity.

2.8 CONCLUSIONS

Based on the above discussion, the following conclusions can be drawn:

- The gasification reactivity of coal shows a general trend of decreasing with increasing coal rank. The reactivity of low-rank coal may be several orders of magnitude higher than that of high rank coal.
- The gasification rate of lower rank coals (C<80%) is controlled by the amount, state and dispersion of inherent coal minerals. The gasification rate of high-rank coal is dominated by the pore structure.
- Water-soluble alkali and alkaline earth metals such as Na, K, Ca and Mg act as catalysts for the reaction. Al and Si have no catalytic effect.
- Demineralization can greatly reduce the reactivity of lower rank coals, but has little influence on higher rank coals.
- The variation of the pore structure and surface area of coal due to demineralization is not significant, so that, in contrast to the removal of catalyst, the influence of changing organic structure on the reactivity can be neglected.

- Catalytic gasification seems likely to follow the two-step oxygen transfer mechanism. Addition of catalyst will accelerate one or two steps, but not change the general course of the non catalytic reaction.
- The importance of the catalytic effect of the coal minerals increases with decreasing reaction temperature. The effective catalysis of coal minerals becomes significant only if the reaction is under chemical control.
- Models proposed for non-catalytic gasification are not suitable for catalytic gasification. The gasification of lignite should be considered as a catalysed reaction. Higher rank coals gasify via a non-catalytic process.
- In general, the reactivity of coal increases with increasing catalyst loading, particularly for low catalyst concentrations. For most catalysts, there exists a saturation point, beyond which, further catalyst loading does not have any effect
- The specific methods and conditions used for catalyst loading can significantly affect the consequent gasification rate. Catalyst impregnation is more effective than physical mixing with coal.

Objectives of the present investigation

A knowledge of gasification kinetics is important for the simulation of gasifier behaviour. Although various studies have been carried out to investigate the characteristics of South Australia lignites, few studies have related the characteristics of these coals to their gasification kinetics. Most S.A. lignites are low rank and contain high concentrations of moisture, chlorine, sulphur and alkalis. Therefore, investigations of the gasification kinetics should be based on the role of these impurities in gasification. As mentioned in **Chapter 1**, fluid-bed gasification provides an attractive way to use this coal (Manzoori et al. 1989). The present work investigates the kinetics of gasification of S.A. low rank coal under fluid-bed conditions, with particular emphasis on determining the role of inherent alkalis on gasification rate.

Chapter 3

EXPERIMENTAL

3.1 INTRODUCTION

This chapter gives a detailed description of the experimental equipment, materials and operational procedures employed in the present study. The first section deals with the coals and other materials used. The second section describes the design and construction of the reaction system. The third section describes the sample preparation which includes sizing, washing, demineralization and catalyst addition. The fourth section deals with the reactor and operational procedures for the gasification experiments. The last section gives a detail description of analytical procedures used. A vertical quartz-tube reactor was constructed to carry out the gasification experiment. The feature of this technique is that it permits examination of gasification behaviour of single coal particles in a simulated fluid bed gasifier.

Experimental investigations have been carried out with the following objectives:

- to determine the rate of fixed carbon conversion under CO_2 or H_2O conditions to obtain the relation of reaction time and conversion for coal gasification under various conditions.

- to study the transformation of the inorganics of coal during demineralization to investigate the beneficiation of Bowmans coal by water and acid treatment.
- to determine the adsorption of various cations on the coal surface during cation-exchange.
- to determine the catalytic activities of various salts on the catalytic gasification of demineralized coal, and the factors which influence the catalytic effectiveness of added cations.
- to estimate the influence of particle size and temperature on the reaction rate so as to establish the mechanisms and kinetics of coal gasification

3.2 MATERIALS

3.2.1 Coal Samples

Bowmans coal:

The main coal used was South Australian Bowmans coal (proximate and ultimate analyses are given in ***Table 3.1***). 20kg of the raw coal supplied by the Osborne Power Station was used in the experiment. The coal sample had a moisture content of 57% (as received basis) and was stored in a plastic bag to prevent loss of moisture and further oxidation before it was used.

Yallourn coal:

Yallourn coal from Victoria was also used for some experiments so that comparison of reactivities between the S.A lignites and Victorian Brown coal could be made. The analysis of Yallourn coal is given in ***Table 3.2***. The Yallourn coal had a moisture content of 64% (as received basis) and was also stored in plastic bags for the same reason.

Table 3-1 Analysis of Bowmans Coal

Moisture (as received)	56
Ash (d.b.)	11.9
Volatile matter (d.b.)	49.3
Fixed carbon (d.b.)	38.8
Ultimate Analysis (mass% d.a.f.)	
C	69.4
H	4.6
O	20.9
N	0.5
S	4.6
Higher Heating value (MJ/kg d.b.)	23.9
Physical and Chemical Properties	
Oxygen-containing functional groups (meq/g)	2.93
Surface area (m^2/g)	196
Inorganics Analysis (wt% d.b.)	
Na	1.57
Ca	0.50
K	0.03
Mg	0.78
Fe	0.74
Si	2.10
Al	0.24

Table 3-2 Analysis of Yallourn Coal

Proximate Analysis (%wt)	
Moisture (as received)	64
Ash (d.b.)	1.3
Volatile matter (d.b.)	44.2
Fixed carbon (d.b.)	54.5
Ultimate Analysis (mass% d.a.f.)	
C	67.5
H	4.8
O	26.9
N	0.62
S	0.19
Higher Heating Value (MJ/kg d.b.)	26.2
Physical and Chemical Properties	
Oxygen-containing functional groups (meq/g)	6.42
Surface area (m^2/g)	268
Inorganics Analysis (wt% d.b.)	
Na	0.05
Ca	0.12
Mg	0.19

3.2.2 Chemicals Used

To investigate the role of inorganics in gasification and the factors which affect the gasification rate, a series of chemicals including acids and salts, were employed for sample preparation.

Reagent:

The hydrochloric acid used to wash the coal samples used was industrial reagent grade.

Catalytic Salts:

1 Sodium Chloride: $NaCl$. Analytical reagent.
2 Sodium Acetate: CH_3COONa. Analytical reagent.
3 Calcium Chloride: $CaCl_2$. Analytical reagent.
4 Calcium Acetate: $(CH_3COO)_2Ca.xH_2O$. Laboratory grade.
5 Potassium Chloride: KCl. Analytical reagent.
6 Potassium Acetate: CH_3COOK. Analytical reagent.
7 Nickel Chloride: $NiCl_2.6H_2O$. Analytical reagent.
8 Nickel Acetate: $(CH_3OO)_2Ni.4H_2O$. Analytical reagent.
9 Iron (II) Chloride, Ferrous Chloride: $FeCl_2.4H_2O$. Analytical reagent.
10 Iron (III) Chloride, Ferric Chloride: $FeCl_3$. Analytical reagent.
11 Magnesium Chloride: $MgCl_2.6H_2O$. Analytical reagent.
12 Sodium Carbonate: Na_2CO_3. Analytical reagent.
13 Sodium sulphate: Na_2SO_4. Analytical reagent.
14 Sodium Hydroxide: $NaOH$. Laboratory.

3.2.3 Gases

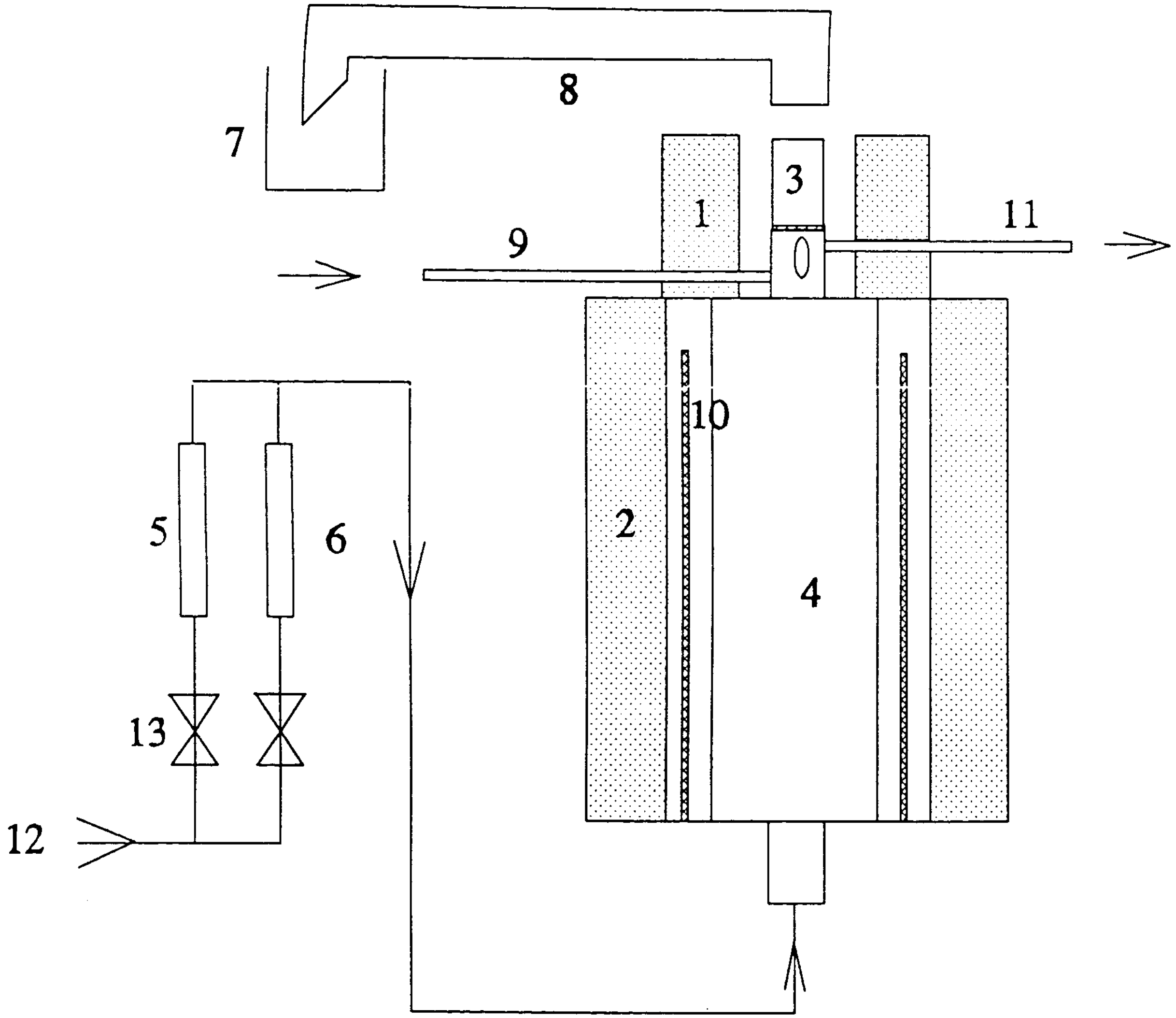
The gases used in the experiment were industrial nitrogen and dry carbon dioxide. Nitrous oxide and acetylene used for the Atomic Absorption Spectrophotometer were laboratory reagent grade. All gases were supplied by the Commonwealth Industrial Gases (C.I.G.). Steam was generated by a small boiler.

3.3 EXPERIMENTAL SYSTEM

3.3.1 Reactor

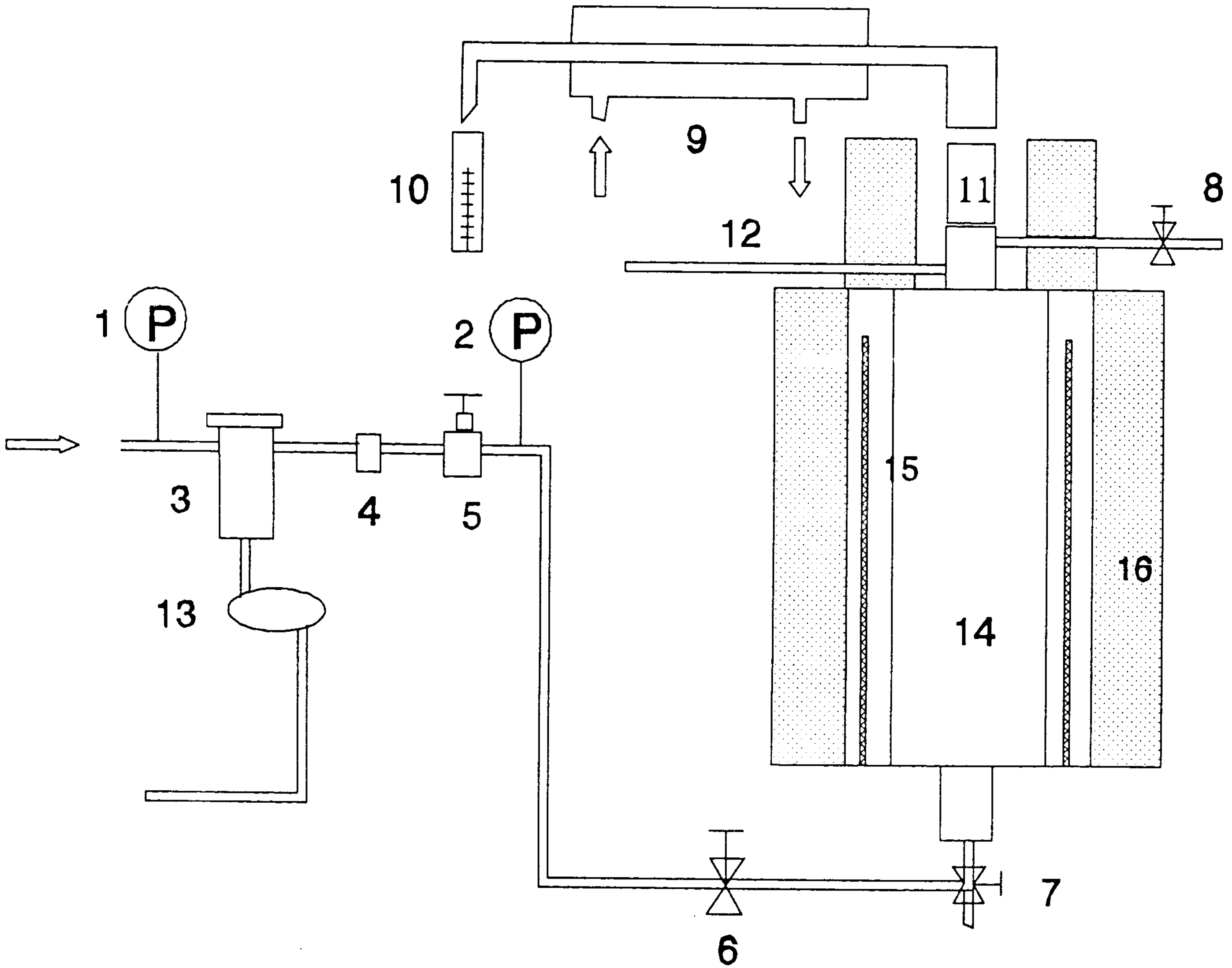
A vertical quartz-tube reactor, or Single Particle Furnace (SPF), was used for gasification experiments. This reactor was originally designed by Agarwal (1986) to study the drying and devolatilization of single coal particles. It was rebuilt and modified by the author to incorporate steam in the system (Ye et al. 1990); hence both CO_2 and H_2O gasifications can be conducted at atmospheric pressure.

A schematic diagram of the reaction system is shown in ***Figures 3-1*** and ***3-2***. The major parts of the reaction system are the stainless steel fluidised bed and vertical quartz-tube reactor. Four heating rods were used to heat the fluidized-bed. Each had a heat output of 2 kW. The stainless steel tube was filled with approximately 0.8 mm diameter sand as bed particles. The reactant gases entered the reactor from two channels: dry gases (N_2, CO_2) and air were introduced into the reaction system through channel 1; steam was introduced into the reactor through channel 2. Channel 1 consists of gas cylinders, rotameters and a preheater, while channel 2 consists of a steel pipe, a strainer, a pressure regulator, a condenser, a needle valve and a balance valve. For Channel 1, gas first enters a rotameter, then passes to the preheater, through a 750mm long, 80



1,2	Insulation
3	Quartz tube
4	Fluid bed
5,6	Flow meters
7	Dry ice container
8	Sample collector
9	N_2 tube
10	Heating rods
11	Exit tube
12	Reactant gases
13	Control valves

Figure 3-1. Reaction system for carbon dioxide gasification



1,2	Pressure meters
3	Separator
4	Strainer
5	Regulator
6	Control valve
7	Balance valve
8	Exit valve
9	Cooling water
10	Condensate collector
11	Quartz tube
12	N_2 tube
13	Steam trap
14	fluid bed
15	Heating rods
16	Insulation

Figure 3-2 Steam gasification system diagram

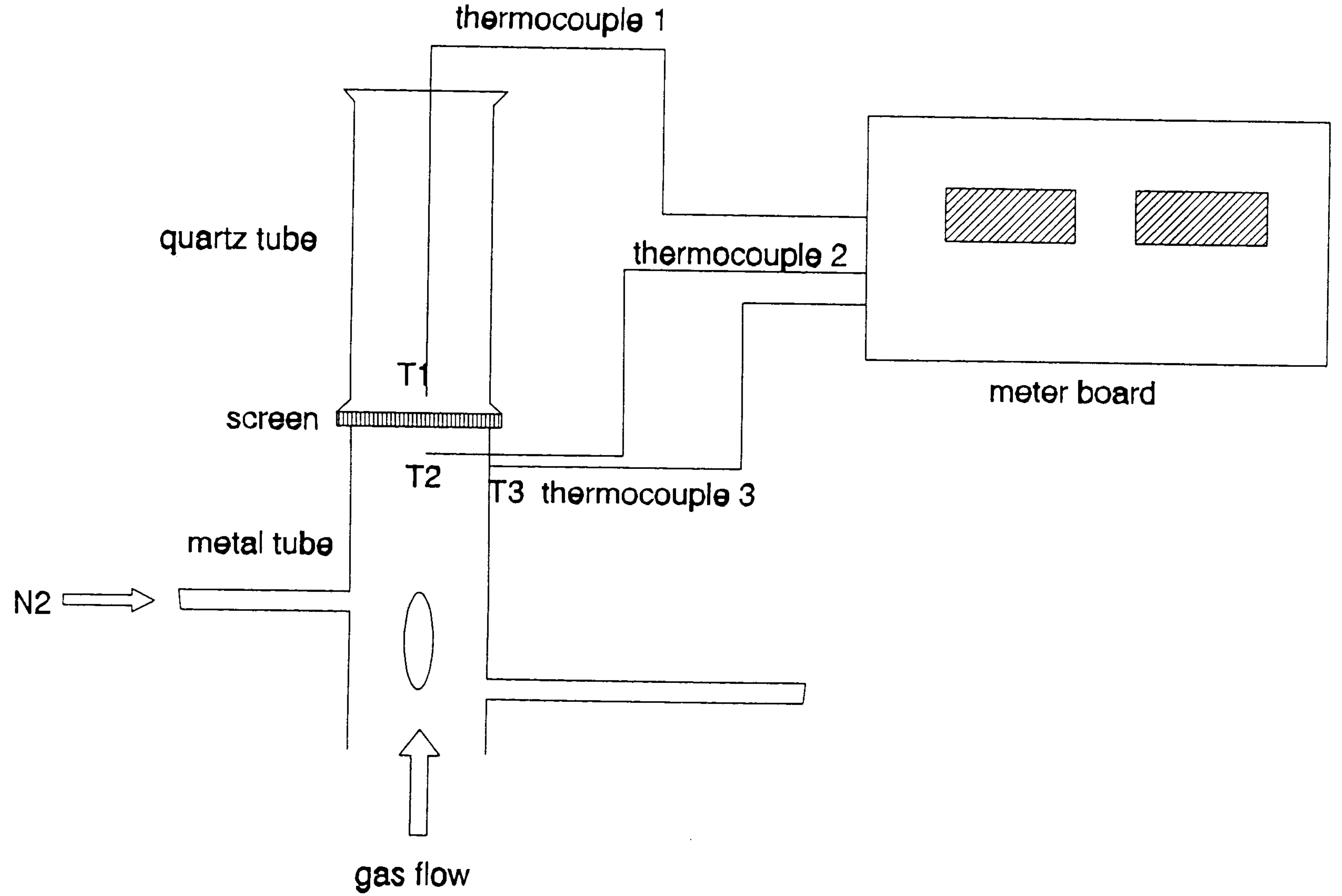


Figure 3-3 Temperature measurement for reaction system

mm diameter stainless steel fluidized bed. Finally, the heated gas entered the quartz-tube reactor. The reactant can be heated up to a maximum of 700°C by the preheater. Steam generated by the boiler was introduced into the fluidised bed after cleaning and reducing its pressure. To prevent damaging of the preheater by the wet steam, the preheater was not used to heat steam. The flow rate of steam was controlled by both the needle and balance valves. The heating rods that heated up the fluidised bed were automatically controlled by a temperature controller. The flow rates of dry gases such as nitrogen, air and carbon dioxide were measured by the rotameters. The flow rate of steam was measured by collecting water condensate from the quartz tube reactor.

A reducer on the top of the fluidised bed decreases the diameter of the steel tube to the diameter of the quartz tube reactor. Two metal screens were set on both the bottom and top of the quartz tube to prevent coal particles from falling into the fluidized bed or being blown out from the quartz tube reactor. Two holes in the reducer were opened: the upper one connected to the N_2 tube; the lower one connected to an exit balance tube. A butterfly valve was set at the centre of the reducer to adjust the flow rate of the gas. The velocity of the reactant gases was adjusted to ensure the suspension of coal particles in the quartz tube reactor. The whole reaction system was insulated to minimize heat loss. A gap in the heat shield, which was fitted around the quartz tube, made it possible to visualize the process reaction. Two different outlet pipes were used to connect the top of the quartz tube reactor. One outlet connecting the dry ice container was used to collect the reacted particles. The other one which was covered by a water cooling sheet was used to collect gas samples.

3.3.2 Temperature Measurement and Calibration

Three thermocouples were fitted at different levels of the reactor to measure the temperatures of gasification reaction. ***Figure 3-3*** gives a diagram of the temperature measurement of the reactor and fluid bed. One thermocouple was connected to the outside surface of the fluidised bed tube to measure the temperature of fluid bed heater. The second thermocouple was fitted at the reducer just below the quartz tube. A mobile thermocouple was placed inside the quartz tube, and it was placed above the screen and fitted at the bottom of quartz tube. Detailed discussion on the temperature calibration of the present reactor is given in **Appendix A**.

The gasification of Bowmans coal with steam was carried at temperatures of 714, 765 and 812°C. The gasification of Bowmans coal with carbon dioxide was conducted at temperatures of 765, 814, 845 and 892°C. The catalytic gasification was carried out at the constant temperature of 765°C. Yallourn coal was gasified at temperatures of 765, 790 and 805°C. A controller was used to control the reaction temperature. The reaction temperature was also influenced by both the heating controller and fluid flow rate.

3.4 COAL PREPARATION

The preparation of coal samples in the present investigation includes crushing of coal sample to a suitable size so that it can be used in a quartz-tube reactor, washing to remove the ash-forming mineral matter and cation-exchange to add a required amount of cation back to the demineralized coal.

3.4.1 Sizing

Chunks of Bowmans and Yallourn coals were crushed and sieved to less than 5mm in size. For Bowmans coal, the size fractions used in the present investigation were 0.8~1.6, 1.6~2.4 and 2.4~4.1mm in diameter. For Yallourn coal, the size fraction was 1.6~3.0mm in diameter. The coal samples were placed into plastic bags to prevent moisture loss or oxidation. The coal samples as received had a moisture contents of 57% (wet coal basis) and 62% for Bowmans and Yallourn coals, respectively. Devolatilization experiments were also conducted using large particles 5.6~8.5mm in diameter. The large coal particles were cut by knife to approximate sphere shape. The sized coal samples in a wet state were stored in a plastic bag to prevent oxidation.

3.4.2 Washing and Demineralization

Washing and demineralization of lignite are carried out to remove part or all of the discrete minerals like quartz, kaolinite and clay from coal; and convert carboxylic functional groups to the hydrogen form by ion-exchange. The basic methods which were used to remove the impurities in coal were physical and chemical. The physical cleaning only removes part of the impurities which are not associated with the carboxylic groups. The chemical cleaning consists of the use of acids or other chemical solutions to remove the inorganics which are highly dispersed in coal or associated with the organic functional groups by chemical bonds.

Water Washing

Water washing only removes part of the minerals from the coal. Approximately 50% of the total minerals of South Australian lignites is removed by water-leaching (Readett and Quast 1986). Some cations (e.g. Na) which are not associated with organic acids can be removed from coal by water washing

An 80 g coal sample was placed in a 800ml beaker. 400ml distilled water was added to the beaker. The beaker was stirred and the solution was boiled for 3 hours. The slurry was then cooled to room temperature and filtered. The coal sample was washed with distilled water several times and finally air-dried for about 5 hours. The water-washed coal samples were then ready for gasification. Some of the water-washed coal samples were analysed by A.A.S. After water leaching, the total ash content was reduced from 12% (d.b.) of raw coal to 6.2% (d.b.). About 85% of sodium was removed by water washing.

Acid Washing

Acid-washing can remove almost all of the inherent metal cations in coal. Therefore the influence of inorganics on gasification behaviour can be eliminated by treating raw coal with acids. Hydrochloric acid was used in the present study for acid-washing. Treating raw coal with HCl does not remove the quartz and clay in the coal. However, these compounds (e.g. of Al and Si) are catalytically inactive, and their presence does not affect gasification behaviour. The structure and surface characteristics of coal are also not influenced by acid-washing (Miura et al. 1989).

An 80 g of wet coal sample was placed in a 800 ml beaker. 200 ml distilled water was added to the beaker. 200 ml concentrated hydrochloric acid was then added. The beaker was heated and maintained at 85-90°C and stirred for 3 hours. The slurry was cooled and filtered. The filtered coal sample was put in 600ml distilled water and was stirred for 5 minutes and filtered again. The water-washing was conducted several times until no Cl^- was found in the slurry; this normally required 7 washings. Finally, the filtered coal sample was air-dried at room temperature for approximately 5 hours. The total inorganics content in the acid-washed sample was calculated on a dry coal basis. About 98% of the total Na, Ca, K, Fe and Mg was removed, only Si and Al components remaining in the acid-washed coal. The proximate analysis of the water-washed and acid-washed samples are given in ***Table 3-3***.

Tabe 3-3 Proximate Analysis of Different Bowmans Coals

	Raw	Water-washed	Acid-washed
Moisture (as received)	56	54	50
Ash (d.b.)	11.9	6.3	2.1
Volatile matter (d.b.)	49.3	49.2	48.8
Fixed carbon (d.b.)	38.8	44.5	49.1

3.4.3 Thermal Treatment

Under thermal treatment, low-rank coal undergoes a series of physical and chemical changes. As temperature is increased, thermal decomposition occurs with liberation of volatile matter. The degree of decomposition depends on the temperature; the reactive functional groups begin to decompose below 400°C and the decomposition is completed by 600°C (Murray 1973). The oxygen-containing functional groups are the controlling factor for gasification reactivity of low-rank coal. Cations associated with carboxylic functional groups form the active sites on the coal surface. The loss of carboxylic groups resulted in reducing active sites on coal surface. In other words, heat-treated lignite can not be cation-exchanged for catalyst loading.

In this work, the raw coal samples were first washed with acid to remove the inherent minerals. Therefore the catalytic effect of inherent alkalis on coal reactivity is negligible for acid-washed coal. The demineralized coal sample was then heat-treated to remove the oxygen-containing functional groups in coal.

De-ashed coal was prepared in a stainless steel container, heated in an oven at 600°C. To ensure that the time is long enough to destroy all the oxygen-containing groups, coal samples were kept in the oven for 15 min. The sample was then cooled to room temperature. Nitrogen was introduced into the oven throughout the process to avoid oxidation of the coal sample during heat treatment.

Desired amounts of catalysts were added to the heat-treated coal samples. The devolatilized coal samples were impregnated in the solutions of salts. Cations were added in the same amounts as that for other coal samples. Catalyst loading followed the same procedure which is given in the next section.

3.4.4 Cation Exchange

In the present investigation, the cations added to Bowmans coal were sodium, calcium, nickel, iron and potassium. Several alkali salts such as carbonates, acetates, chlorides, sulphates and hydrochlorides were used for cation-exchange. Since sodium and calcium are known to be important inherent catalysts of low-rank coals, particular attention was given to the salts of these two metals.

The appropriate mass of selected chemicals (e.g. $Ca(Ac)_2$, NaAc, Na_2CO_3) was dissolved in distilled water to form the solution of required concentration. The concentrations for cations loading were 0.2, 0.4, 0.6 and 1.0M. Approximately 10g of the acid-washed coal sample (or heat-treated deashed coal samples) and 50ml of solution of the required concentration were mixed in a 200ml volumetric flask and shaken for 24 hours. The slurry was then filtered in a Buchner funnel. Distilled water was added into the flask to wash the coal remaining in the flask. The filtered coal samples were dried in air at room temperature for approximately 4 hours. The air-dried coal sample was then stored for gasification experiment. The flask was carefully washed with distilled water to ensure that all cations have been recoved. The filtered solution was analysed by Atomic Absorption Spectrophotometry. Some filtered coal samples, which had been impregnated into the highly concentrated solution, were washed with distilled water three times to remove the salts which concentrated on the surface of the coal particle. The cation-exchanged coal samples were then dried in air at room temperature for 4 hours.

3.5 REACTOR OPERATION PROCEDURES

Experimental conditions for carbon and steam gasification are given in ***Tables 3-4 ~ 3-7***.

3.5.1 Carbon Dioxide Gasification

The reactor was heated to the required temperature before starting the experiment. Compressed air was introduced into the fluidized bed to warm the system. When the system reached the steady state the air flow was replaced by metered carbon dioxide from a cylinder. The velocity of CO_2 was adjusted to ensure that the coal particle was suspended in the quartz tube. Coal samples were introduced into the reactor from the top of the quartz tube. Time was counted from when particles were dropped into the reactor. At the end of the reaction time, the exit pipe was connected to the top of the quartz-tube reactor and the coal particles were blown out into a dry ice container using nitrogen. Five separate determinations were made for each reaction time to ensure reproducible results. The reacted coal samples were collected in a sealed container for further analysis. The average conversion was determined, after eliminating outlines

3.5.2 Steam Gasification

Steam generated from a boiler was fed into the reactor. The gate valve was turned off to prevent steam from entering the preheater during the experiment to prevent damage to the preheater. Steam was therefore introduced directly into the fluid bed heater.

Steam, from the boiler, passed through a regulator, in which its pressure was reduced to approximate 200 kPa. The steam flow rate was adjusted by needle and balance valves. The steam flow

Table 3-4 Experimental Conditions of CO_2 Gasification

Temp. (°C)	Particle Size (mm)	Gas Velocity (m/s)	Coal Samples raw coal	H_2O-wash	acid-wash
705	2.0	1.0	Yes		
764	2.0	1.4	Yes		
764	1.2	0.5	Yes		
764	3.3	1.8	Yes		
764	2.0	1.4		Yes	
764	2.0	1.6			Yes
806	2.0	1.6	Yes		
847	2.0	1.6	Yes		

Table 3-5 Experimental Conditions of H_2O Gasification

Temp. (°C)	Particle Size (mm)	Gas Velocity (m/s)	Coal Samples raw coal	H_2O-wash	acid-wash
705	2.0	1.0	Yes		
764	2.0	1.4	Yes		
764	3.3	1.8	Yes		
764	2.0	1.4		Yes	
764	2.0	1.4			Yes
806	2.0	1.4	Yes		
806	2.4	1.4			Yes

Table 3-6 Experimental Conditions of the Catalysed Carbon Dioxide Gasification (Temp. 764°C, Size: 3.0 mm, Gas velocity: 1.4 m/s).

Salts	Solution Concentration (M)
NaAc	0.04
NaAc	0.1
NaAc	0.3
NaAc	0.6
NaAc	1.0
NaCl	0.3
Na_2CO_3	0.3
Na_2SO_4	0.3
$Ca(Ac)_2$	0.3
$Ni(Ac)_2$	0.3
KAc	0.3

Table 3-7 Experimental Conditions of Steam Catalytic Gasification (Temp. 764°C, particle size: 3.0 mm, gas velocity: 0.4 m/s)

Catalyst	Solution Concentration (M)	Catalyst	Solution Concentration (M)
NaAc	0.04	$Ca(Cl)_2$	0.6
NaAc	0.1	$Ca(Cl)_2$	1.0
NaAc	0.3	$Ni(Ac)_2$	0.04
NaAc	0.6	$Ni(Ac)_2$	0.1
NaAc	1.0	$Ni(Ac)_2$	0.3
NaCl	0.1	$Ni(Ac)_2$	0.6
NaCl	0.3	$Ni(Cl)_2$	0.1
NaCl	0.6	$Ni(Cl)_2$	0.2
NaCl	1.0	$Ni(Cl)_2$	0.4
$Ca(Ac)_2$	0.1	$Ni(Cl)_2$	0.6
$Ca(Ac)_2$	0.3	KCl	0.1
$Ca(Ac)_2$	0.6	KCl	0.4
$Ca(Ac)_2$	1.0	KCl	0.6
$Ca(Cl)_2$	0.1	KCl	1.0
$Ca(Cl)_2$	0.25		

rate was measured by collecting condensate from the top of the quartz tube reactor. The balance valve was kept open during the entire experiment to allow the discharge of the water condensate from the bottom of the fluidised bed.

Coal samples were introduced into the quartz-tube reactor. The steam flow rate was adjusted to allow the coal particles to float in the quartz tube. The needle valve was used to adjust the reaction temperature. The time was recorded when the coal sample was introduced into the reactor. Gasification occurred in the quartz reactor. At the end of the reaction time, the balance valve was fully opened, while, the butterfly valve was closed. The exit pipe was connected onto the top of the quartz tube reactor. The reacted coal particles were blown out into a dry ice container by nitrogen. Five readings were taken each time to ensure repeatable results. The reacted coal sample was collected and sealed for further analysis.

3.5.3 Devolatilization

Devolatilization was also carried out for some coal samples to examine the loss of volatile matter under pyrolysis conditions. In these experiments, nitrogen was used in the reactor. All the operational parameters (e.g. reaction temperature, flow velocity) were the same as that for CO_2 gasification. Metered nitrogen, passed through the preheater, fluidised bed heater and finally the quartz tube reactor. The procedure for devolatilization experiments followed that for CO_2 gasification.

3.6 ANALYTICAL PROCEDURES

3.6.1 Proximate Analysis

Both raw and reacted coal samples obtained from the gasification experiments were analysed to determine carbon conversion. The moisture, volatile matter, fixed carbon and ash contents of all the coal samples were determined. The methods used in the proximate analysis generally followed the standard ASTM D 3173, ASTM D 3174 and ASTM D 3175. The methods used in the present work were slightly different from the ASTM standard methods due to the limitation of equipment available and the features of the South Australian lignites.

Moisture Content

The moisture content was determined by establishing the loss in the weight of the coal sample when heated at 105°C. After transferring approximately 1 g (± 0.5 mg) of selected coal sample into the crucible, the crucible was placed in a preheated drying oven at 105 to 110°C for 5 hours. The crucible was then taken out of the oven, cooled in a desiccator, and weighted until the crucible had reached room temperature. The crucible was then put back into the drying oven again for an hour. Cooling and weighing were repeated several times until the weight reached a constant. Only raw coals were measured for their moisture content. The moisture content of the reacted coal was not measured because reacted coal samples (from both devolatilization and gasification) were completely dry under current experimental conditions (Wildegger-Gaissmaier 1988).

Volatile Matter Content

The content of the volatile matter was determined by establishing the weight loss of sample heated at 900°C in nitrogen. The dry coal samples were put into a silica crucible and weighed.

The crucible was inserted directly into a preheated furnace and remained for 7 min. The temperature of the furnace chamber was kept at 900°C. The crucible was taken out from the furnace and cooled in air for 20 min. Then it was removed into a desiccator and cooled to room temperature. The lid was reseated on the top of the crucible to guard against the admission of air into the crucible during entire process. The temperature and time were carefully controlled during the volatile matter measurement.

Ash Content

The ash content was determined by weighing the residue remained after the burning of coal under certain temperature, time and atmosphere conditions. Bowmans coal contains high concentrations of sodium compounds are a low ash melting temperature (650°C). High temperature ashing caused the melted ash to stick on the crucible. To prevent this, coal samples were ashed under the melting point temperature. Therefore, low temperature (<600°C) ashing was used to determine the ash content of coal.

The devolatilized coal samples were put into a quartz crucible and weighed, and then placed in an oven heated at 650°C for at least 4 hours. In most cases, the samples were placed in the oven overnight to ensure complete combustion of carbon in the sample. Finally, the crucible was taken out from oven and cooled in air for 15 min, then removed into a desiccator. The crucible was weighed when it reached room temperature. During the ashing period, the oven door was held slightly open to provide sufficient air for combustion.

3.6.2 Atomic Absorption Analysis for Ash

The major metal elements in coal were measured by the Atomic Absorption method. The basic procedure to analyse the inorganics in coal is that the coal is firstly ashed, and the coal ash is fused with additives ($Li_2B_4O_7$) followed by a dissolution of the melt in hydrochloric acid to form a standard solution. Finally, the major elements of the solution are analysed using Atomic Absorption Spectrophotometer (A.A.S). It should be noted that the chemical composition of the coal ash does not represent the exact composition of the minerals present in raw coal. The amount of metals determined by the ashing method may be slightly lower than the values in raw coal, because some of the metals (e.g. Na) may be vaporized during ashing (Agarwal 1991 and White 1992). In the present study, it was assumed that the loss of metals during the ashing was negligible because of the ashing temperature employed.

Ash analysis was only conducted for Bowmans coal. The composition of ash was not determined for Yallourn coal because of its low ash content. The inherent mineral matter of Yallourn coal has less importance in gasification.

A.A.S. Operation Procedure

Ash Fusion and Solution:

0.1 ± 0.0002g of coal ash was weighed and put into a platinum crucible and mixed with 0.5 g of $Li_2B_4O_7$. Then 0.5 g of $Li_2B_4O_7$ was added into the crucible to cover the mixture. The crucible was placed in a muffle oven and maintained at 1000°C for 15 min until the mixture was completely fused. The crucible was then removed and cooled in air to room temperature. The platinum crucible was carefully cleaned and placed in a 400 ml beaker with 150 ml of HCl (5+95) added. The beaker was then heated and stirred for approximately 30 min until the melt was completely dissolved. After cooling, the solution was quantitatively transferred to a 250 ml volumetric flask; the beaker was washed several times with standard HCl solution to ensure that all metal cations were totally transferred into the flask. The flask then was filled up with the standard HCl solution. The concentration of the solution was 400 ppm with respect to the total sample. Certain amounts of the solution was piped into series of volumetric flasks and diluted with standard HCl to form a series solution with different concentration.

Atomic Absorption:

The composition of coal ash and the amount of catalyst loading were measured by Atomic Absorption Analysis. The sample solutions were tested for Na, Ca, K, Mg, Fe, Si and Al contents. A single beam Varian Atomic Absorption Spectrophotometer, model AA-1275, was used. An air-acetylene flame was used to measure sodium, calcium, iron, potassium and magnesium, while nitrous oxide-acetylene flame was used for the silicon and aluminium. Care was taken in order for the overall A.A.S. operating process to achieve maximum precision. To minimize interference, the blank solution which only contains the desired $Li_2B_4O_7$ concentration was used. Some other additives (e.g. lanthanum) were added into the solution as a release agent in some tests.

Standard solutions which contained the required concentrations of cations were made. The concentrations of the standard solutions varied from 0.5 to 400 ppm for certain cations depending on the particular test cations. A hollow-cathode lamp was used and other instrument parameters were adjusted to obtain optimum results. The reading of absorbency values was taken for the blank, standard and sample solutions. Readings obtained from the standard solutions were plotted to obtain a standard absorbency-concentration relationship curve. The concentration of the cations in the sample solution was determined from the standard curve.

Most of the experiments such as reactor construction, coal preparation, gasification and analysis were conducted at various laboratories in The Department of Chemical Engineering, The University fo Adelaide. Experiments on coal demineralization such as water leaching and acid washing were conducted at The Department of Physical and Inorganic Chemistry, The University of Adelaide. The experimental results obtained from the present investigation are presented in the following chapter.

Chapter 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

Experimental results are presented in this chapter. Gasification experiments were initially carried out on raw coal to determine the kinetics. More comprehensive studies on acid-washed, water-washed and cation-exchanged coal samples were then carried out to determine the catalytic effects of constituent and added cations. Results are compared with those previously published from other investigations. Experimental data obtained from this study are also compared with model predictions. Theoretical studies were aimed at obtaining information on the mechanisms and kinetics of gasification. Results are discussed in two parts: carbon dioxide gasification and steam gasification under various conditions. Most of the experiments were performed on S.A. Bowmans coal, while some experiments were undertaken to study the gasification characteristics of Victorian Yallourn coal.

4.2 CARBON DIOXIDE GASIFICATION

4.2.1 Heating Coal Sample in CO_2 and N_2

When a coal particle is introduced into a gasifier it firstly undergoes thermal decomposition and volatile matter is released to form char. In the present investigation, the fixed carbon conversion of coal during gasification is calculated by analyzing the "gasified char"; therefore the volatile matter content of the reacted coal may significantly influence the calculation of the fixed-carbon conversion. Information on the evolution of volatile matter under gasification conditions is required to determine the gasification behaviour of coal particles. It is necessary to know whether the evolution of volatiles is affected by the surrounding gas atmosphere. For example, if the volatile matter content of the heat-treated coal sample under pyrolysis condition is less than that under gasification condition, the difference, which is called "gasified" volatile matter must be taken into account to determine the degree of coal gasification. An investigation on the evolution of volatile matter during gasification and devolatilization was therefore conducted.

Coal samples of approximately 4 g (size 1.6~2.4 mm) were heated at 700°C in nitrogen or carbon dioxide for times ranging from 2 to 15 min. Reacted coal samples were analysed to determine the fixed carbon and volatile matter content remaining. Volatile matter content obtained under pyrolysis condition (in N_2) was compared with that obtained from gasification conditions (in CO_2). ***Figure 4-1*** shows the results. It is seen that there is little difference in the volatile matter remaining under these conditions. It indicates that gas environment has little influence on the release of volatile matter. ***Figure 4-2*** shows the relationship between carbon conversion X and volatile matter remaining in "gasified char". The results show that the volatile matter content (V.M. % d.a.f) in gasified coal slightly increased with increasing degree of

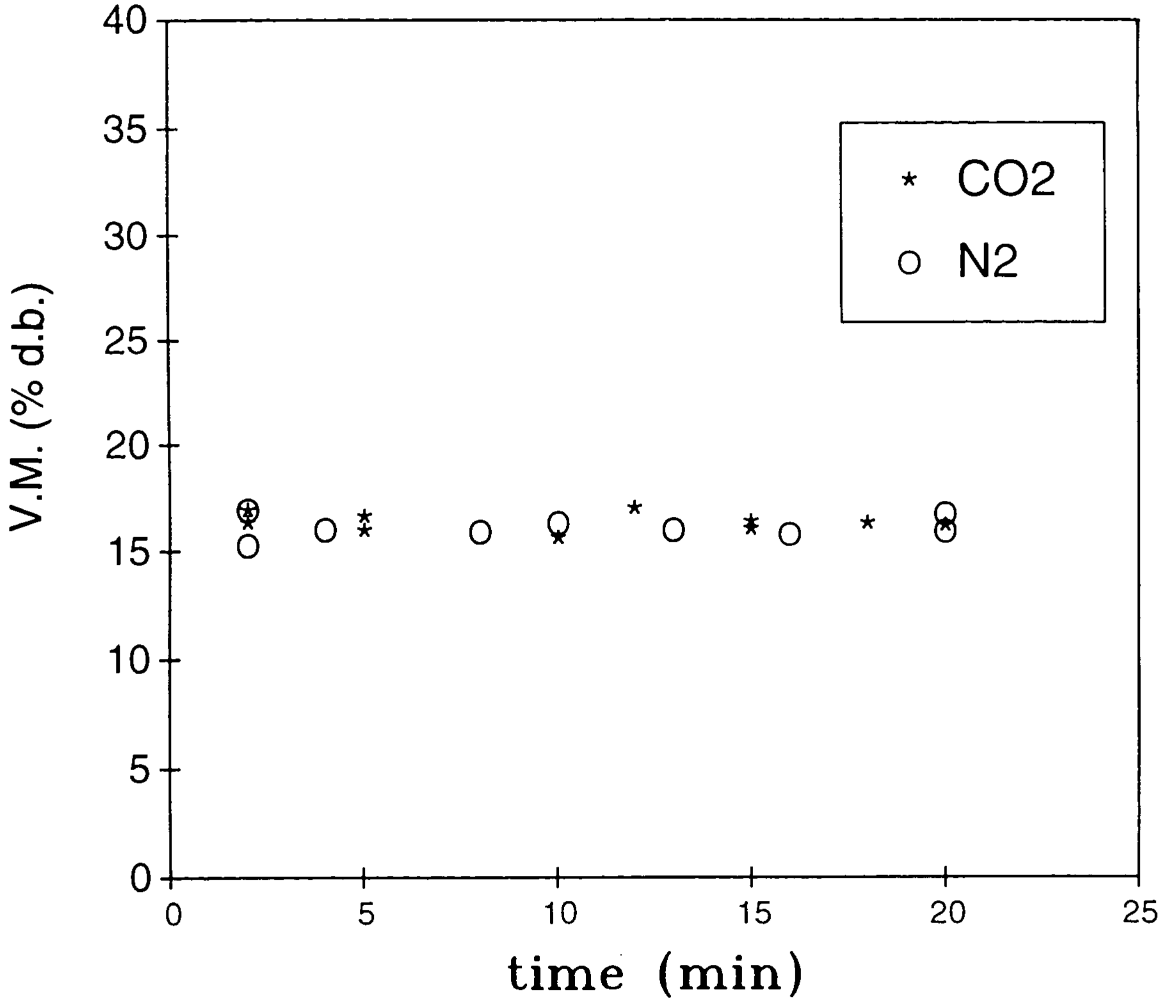


Figure 4-1 Volatile matter content remaining in gasified or devolatilized Bowmans coal samples at 700°C (Heating in CO_2 or N_2)

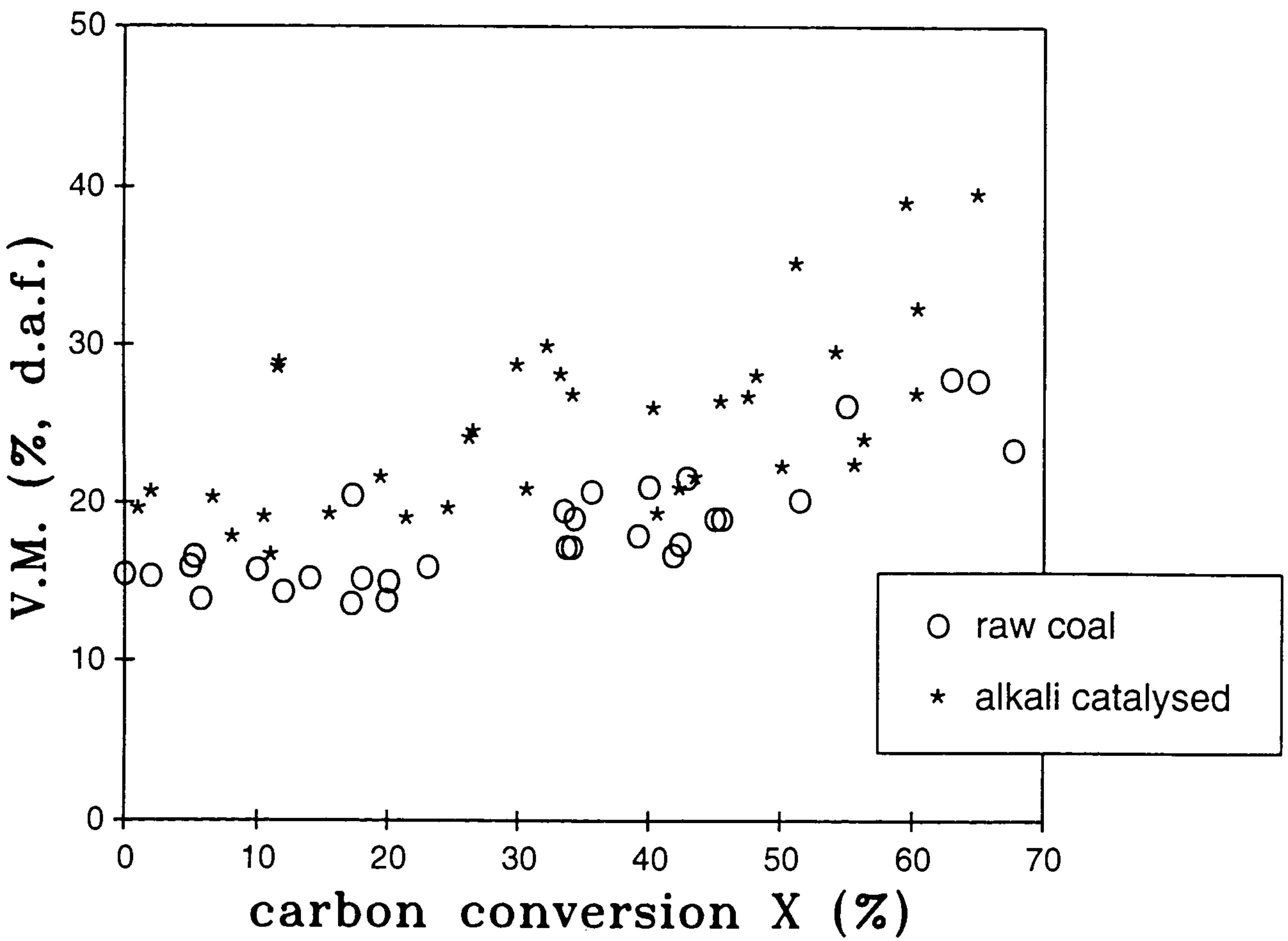


Figure 4-2 Relationship between volatile matter content remaining in coal and the carbon conversion during gasification of Bowmans coal with carbon dioxide at 765℃ (size 1.6~2.4mm)

gasification/carbon conversion. The volatile matter content of reacted coal at high carbon conversion is virtually equal to that at low carbon conversion on a dry basis.

Although numerous studies have been conducted to understand the behaviour of char during gasification, little attention has been given to the variation of volatile matter content during gasification. ***Figure 4-2*** shows that the volatile matter content of the gasified coal is affected by the addition of catalyst. Coal samples were impregnated in solutions of various alkali and alkaline-earth salts (e.g. NaCl, NaAc, $Ca(Ac)_2$, and KCl). For the catalysed (cation-exchanged) coal, the volatile matter remaining was found to be significantly higher than that for the non-catalysed coal. This indicates that the presence of active cations in coal strongly influences the decomposition of organic functional groups. The addition of cations decreased the decomposition of functional groups.

The influence of impurities on coal pyrolysis has been investigated by Schafer (1979 and 1980) who reported that the presence of cations was found to alter the yield of CO_2, CO and H_2O but not to affect the overall weight loss. Tyler and Schafer (1980) found that the addition of calcium ions to demineralized coal led to decreased tar and total volatile matter. They suggested that cations might supress tar evolution either by restricting the micropore structure or by catalysing the recombination of metaplast molecules.

In the present investigation, metals added by impregnating coal in the solution of chloride salts were found to have little influence on devolatilization. Metals, undergoing cation-exchange and associating with carboxyl groups, were found to significantly affect the volatile matter remaining in the gasified coal. Cation-exchange converts carboxylic acid groups to carboxylates which are more stable than the acid form. Therefore, the author believes that the main reason for the observed phenomenon is that the presence of cations increases the stability of carboxyl groups.

4.2.2 Gasification Rate and Reactivity

We are concerned with the gasification of char, as measured by the "fixed-carbon" content of the coal. "Char", or devolatilized coal, contains mineral matter and residual volatiles.

Consider a char particle undergoing gasification reaction. The carbon content is C g/m^3 at any time t. At t = 0, $C = C_0$. Assume that the volume the particle, V m^3, remains constant during the course of the reaction. The gasification rate is the rate of reaction of fixed carbon per unit volume of particle ($g/time \cdot m^3$).

Assuming that the gasification reaction is first-order in carbon, the reaction rate is expressed as

$$-r = k \cdot C \tag{4.2.1}$$

where k is the reaction rate constant (units of time^{-1}). A mass balance for carbon gives:

$$V\frac{dC}{dt} = -(-r) \cdot V \tag{4.2.2}$$

$$\frac{dC}{dt} = -k \cdot C \tag{4.2.4}$$

$$C = C_o(1 - X) \tag{4.2.4}$$

where X is the fractional conversion of carbon. Equation 4.2.3 becomes:

$$-C_o\frac{dX}{dt} = -kC_o(1 - X) \tag{4.2.5}$$

$$k = \frac{1}{(1 - X)} \cdot \frac{dX}{dt} \tag{4.2.6}$$

Here the first-order rate constant k can be determined from measured fractional conversion versus time data. The right-hand side of ***Equation 4.2.6*** is termed the "reactivity" (R_m) by Laurendeau (1978). The value of k can also be taken as a measure of "reactivity".

Expressing k in Arrhenius form:

$$k = k_o \exp(-E_a/RT) \quad (4.2.7)$$

where E_a is the activation energy.

4.2.3 Reactivity of Bowmans Coal Compared with Other Australian Coals

Gasification reactivity of Bowmans coal with carbon dioxide was estimated at temperatures in the range 765 to 891°C. An Arrhenius plot was used to compare the kinetic data. ***Figure 4-3*** shows the comparison of Bowmans coal with other Australian coals. It is seen that the reactivity varied widely for different coals. The sequence of the reactivities for the coals listed is Bowmans > Yallourn > Millmerran > Liddell > Merriown > Lithgow. Bowmans coal is the most active among Australia coals listed. This can be attributed to the presence of the high concentrations of inherent alkali metals (***Table 3-1***). ***Tables 4-1*** and ***4-2*** illustrate the analyses of these coals. Bowmans and Yallourn coals are lignites, others are higher rank sub-bituminous coals. For low-rank coal, its reactivity is dominated by catalytic effect of active mineral. For high-rank coal, the reactivity is controlled by physical and chemical properties. The relatively low reactivities of other coals can be attributed to various factors as higher rank, low oxygen-containing functional groups and low surface area. Although Millmerran and Lithgow have high mineral content, the inherent inorganics do not associate with carboxylic functional groups due to low oxygen contents. Detailed discussion on the catalytic effect of inherent minerals and the role of oxygen-containing functional groups are given in **Section 4.2.8**. The low reactivity of Millmerran coal can also be explained by the opposing balance of catalytic effect of inorganics and internal surface area. Millmerran coal has extremely low internal surface area. Knight and Sergeant (1982) reported, for some coals, the catalytic minerals are the dominating factor; for some coals, the internal surface area is more important.

It should be noted that the difference of experimental conditions between the present work and other investigations may influence the measured reactivity. For example, the result for

Table 4-1 Proximate Analysis of Coal Chars

Chars	M	Ash	V.M.	F.C.
Millmerran	1.9	28.5	8.1	61.5
Liddell	2.7	10.7	9.0	77.6
Merriown	2.3	4.1	8.7	84.9
Lithgow	2.5	14.7	6.6	76.2
Yallourn	2.4	2.8	3.3	92.5
Bowmans	0.8	23.3	8.2	67.7

Table 4-2 Surface Areas of Char/Coal

Chars/Coals	CO_2 Surface Area (m^2/g)
Millmerran coal char	36
Lithgow coal char	429
Yallourn coal	268
Bowmans coal	196

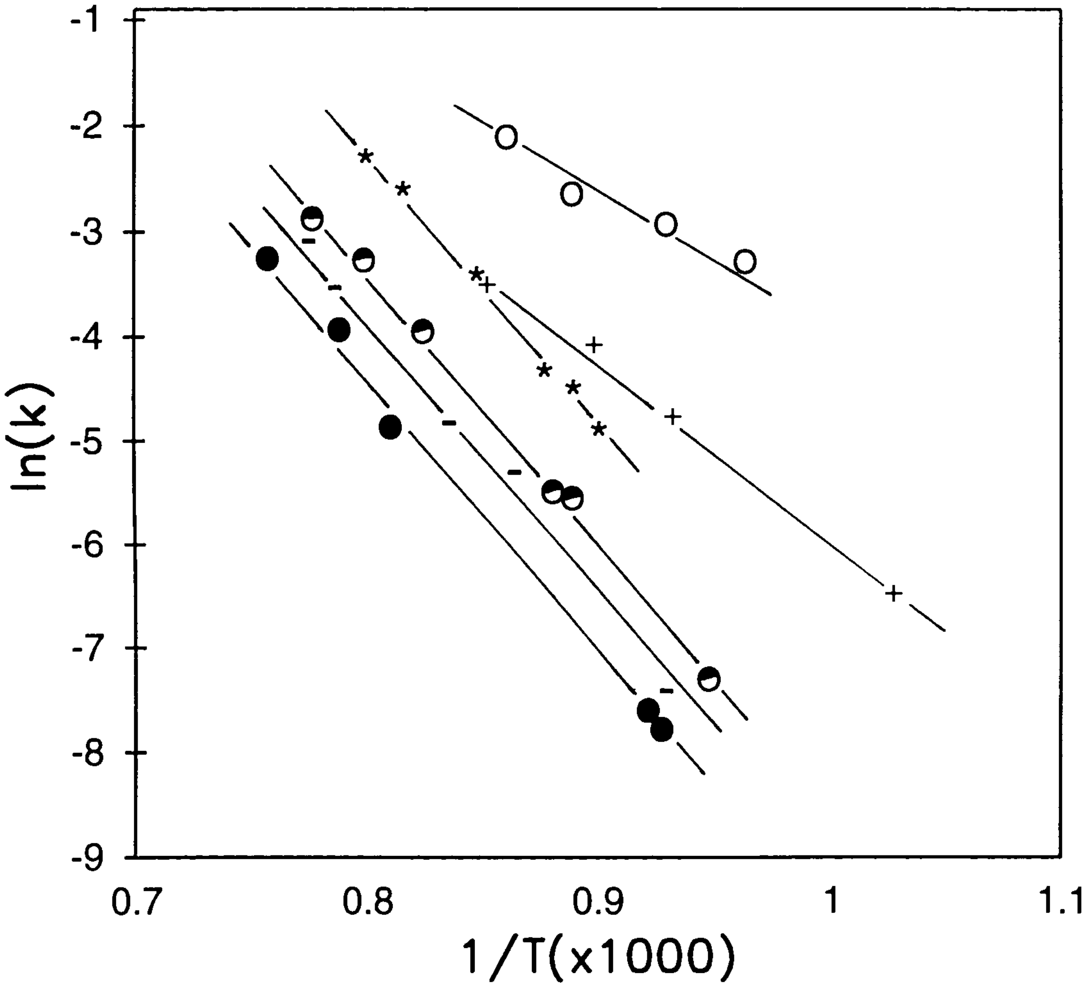


Figure 4-3 Comparison of carbon dioxide gasification reactivity of Bowmans (o) with reported values of other coals, +:Yallourn, *:Millmerran, ◐:Liddell, -:Merriown, ●:Lithgow (Knight et al. 1982)

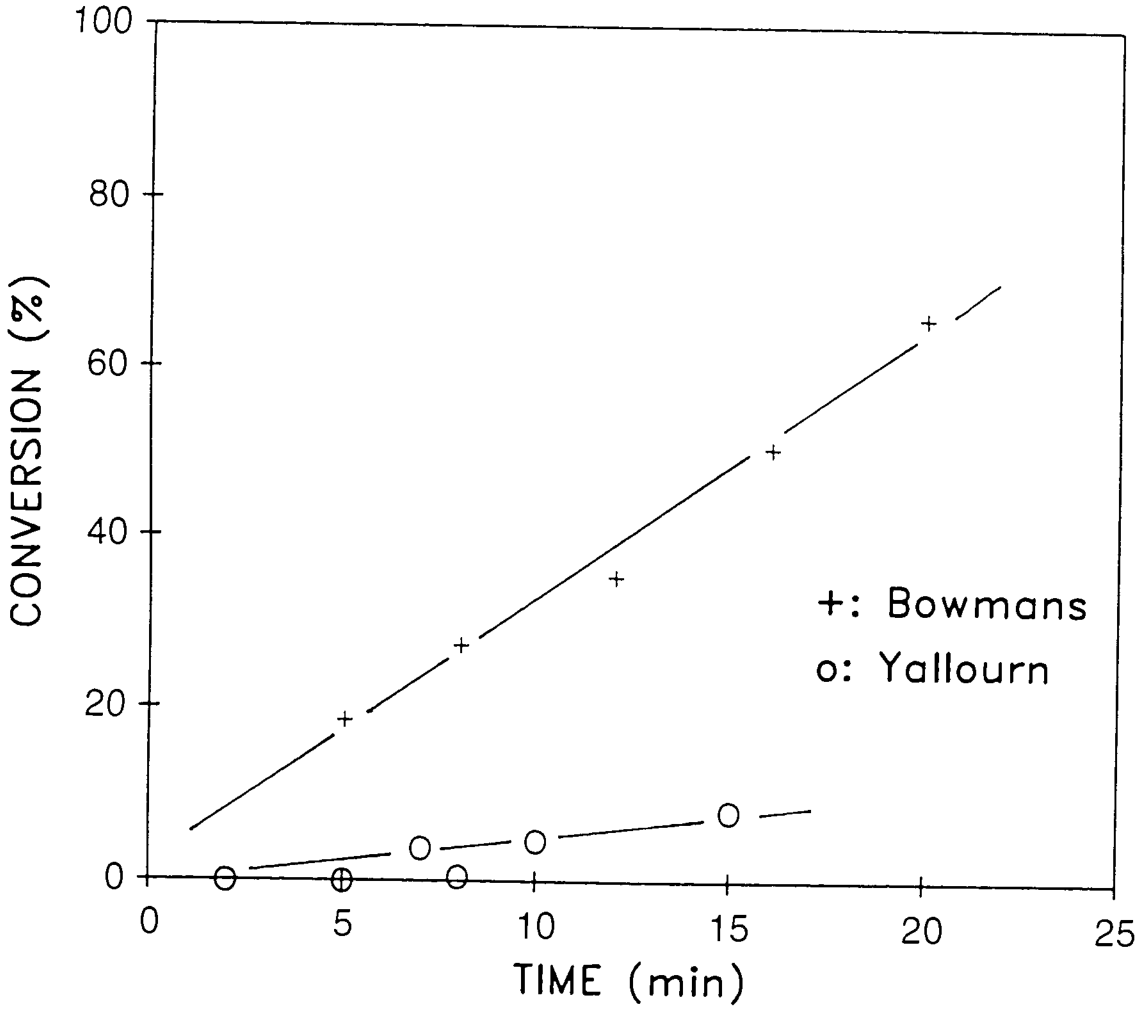


Figure 4-4 Comparison of carbon dioxide gasification behaviour of Bowmans coal with Yallourn coal. (Temp. 765℃, 1.6~3.0 mm size)

Victorian Yallourn coal was obtained using the TGA method which requires low velocity of reactant gases in the reactor. For this method, film diffusion may be significant. Prasad et al. (1990) pointed out that the kinetic data obtained using TGA method invariably includes the effects of gas-film and bulk-diffusional resistances. In the present investigation, in which the coal sample was dropped directly into the reactor which had already been heated to the required temperature (710 ~ 890°C), the heating rate can be very high. Rapid heating promotes the formation of macro-pores in the char, resulting in an increase in gasification rate. Katta et al. (1986) reported that the char produced by rapid heating is almost twice as reactive as that produced by slow heating. Miura et al. (1986) also observed that char formed in this way (fast heating) was 2-10 times more active than the char prepared separately in a conventional charring process. Although estimation of kinetic parameters may be affected by the experimental method used, this influence is much lower than the catalytic effect of inherent minerals.

Experiments were also carried out on Victorian Yallourn coal and the result is plotted in ***Figure 4-4***. It is seen that the gasification rate of Yallourn coal in CO_2 is much lower than that of Bowmans coal. Determined initial reactivity of Yallourn coal is 0.24 (h^{-1}) compared with 2.0 (h^{-1}) for Bowmans coal. The high reactivity of Bowmans coal is attributed to the nature of the coal. There are a number of factors which may affect the reactivity: fixed carbon content, structural characteristics, concentrations of surface functional groups and the quantity and quality of inorganic impurities. From ***Table 3-1*** Bowmans coal contains approximately 12% w/w (d.b.) of ash, much higher than Yallourn coal (***Table 3-2***) which has an ash content of only 1.3 % w/w (d.b.). The inherent alkali and alkaline-earth metal (Na, K and Ca) content of coal Bowmans coal is about 12 times that in Yallourn coal.

4.2.4 Effect of Temperature

Gasification rates with carbon dioxide and steam are considered to be controlled by chemical reaction at temperatures up to 900°C. The influence of mass transfer on the overall reaction rate will become significant for reaction temperatures above 900°C (Johnson 1979, Adschiri et al. 1986, Riley and Judd 1987). To obtain a satisfactory reaction rate, most of the coal gasification experiments were conducted at temperatures above 700°C. The temperatures used in this study for the gasification of raw coal with carbon dioxide were 765, 803, 852 and 891°C. ***Figure 4-5*** illustrates the relationship between carbon conversion and time at various temperatures. ***Figure 4-5*** shows that carbon conversion is very sensitive to temperature. Typical values of first-order rate constant, k, at temperatures of 765, 803, 852 and 891°C are 2.77, 3.56, 5.20 and 8.85, respectively. The high dependence of gasification rate on the reaction temperature indicates that chemical reaction plays an important role in the overall reaction rate. No experiments were performed at higher temperature (over 900°C) in the present study because of equipment limitations.

The observed influence of temperature on the gasification rate is in good agreement with the results published by other investigators (Kasaoka et al. 1984, Miura et al. 1989). Similar results were also reported by Schmal et al. (1983), in which, they found that the gasification rate of a Brazilian-high-ash-content coal with steam, in the temperature range of 700 ~ 900°C, was very sensitive to the reaction temperature, indicating chemical reaction rate control. Barrett (1984) also found that the rate of gasification of some Australian coals with CO_2 was sensitive to temperature variation in the range 750 to 1000°C. He indicated that up to 850°C, chemical reaction between carbon and gas reactant is the rate controlling factor; between 850 and 950°C, the rate was controlled by both diffusion and chemical reaction; and at temperatures greater than 950°C, film diffusion is controlling. In this work, as the gas velocity was sufficiently high, film diffusion was indicated to have minor influence. Detailed calculation on mass transfer is given in **Section 4.2.6**.

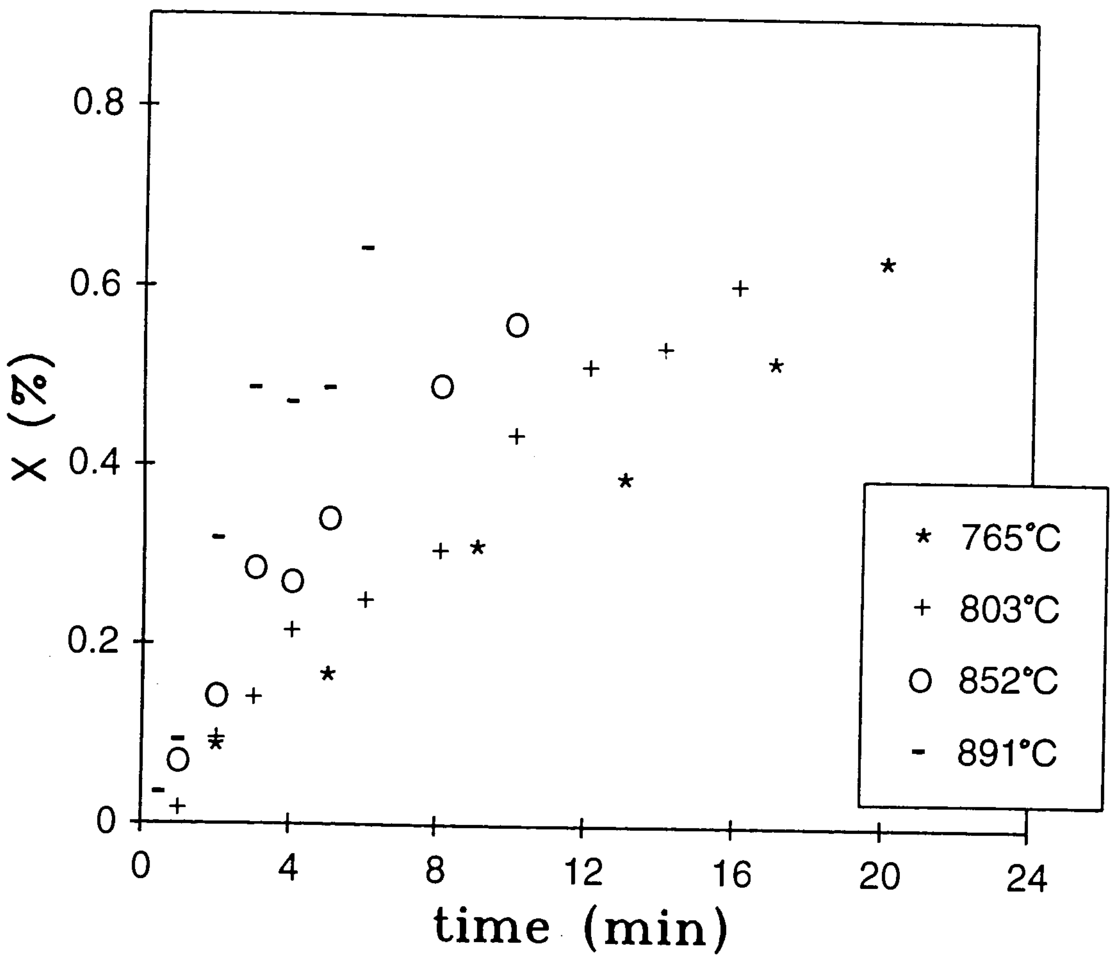


Figure 4-5 Fixed carbon conversion vs. time relationship for gasification of Bowmans coal with carbon dioxide at various temperatures (size: 1.6 ~ 2.4 mm)

4.2.5 Effect of Particle Size

Additional experiments were conducted to identify the influence of particle size of coal on the reaction rate. Three size fractions (0.8~1.6, 1.6~2.4 and 2.4~4.1mm in diameter) of Bowmans coal were tested at 765°C with carbon dioxide. ***Figure 4-6*** illustrates the profiles of fixed-carbon conversion (*X*) versus reaction time (*t*) for different particle sizes. Results show that particle size has only a small influence on the reaction rate over the range studied. For lignite, the pore surface area is several orders of magnitude larger than the outside surface area of the coal particle. Changing particle size influences the outside surface area of the coal particle but has little effect on specific surface area. The specific pore surface area is expected to be constant for the same coal with varied particle size. Present results indicate that the contribution of external surface area of coal on gasification is small, and the carbon-gas reactions mainly occur on the pore surface. ***Figure 4-6*** shows that the gasification rate of smaller particles (0.8~1.6mm) is only slightly higher than those of larger particle (2.4~4.1mm).

Barrett (1984) examined the effect of particle size on the reactivities of some Australian coals with carbon dioxide and found that particle size had little effect on gasification rate within the kinetic-controlling regime (low temperature). Tomita et al. (1988) also observed that the gasification rate of Yallourn coal with carbon dioxide was independent of the particle size in the range from 0.6 to 2.1mm. However, some investigators obtained a contrary conclusion. They found that particle size does have some influence on the gasification rate. For example, Fung et al. (1988) found that the gasification reactivity of some anthracites increased with decreasing particle size from 300 to 89 μm. Kasaoka et al. (1986) also reported that, at a high temperature (1400°C), the reactivities of coals decreased with increasing particle size, but the significant difference had not been observed for the lower temperature regime (less than 1200°C). Other studies (Knight and Sergeant 1982 and Adanez et al. 1985) also indicated that, under relatively

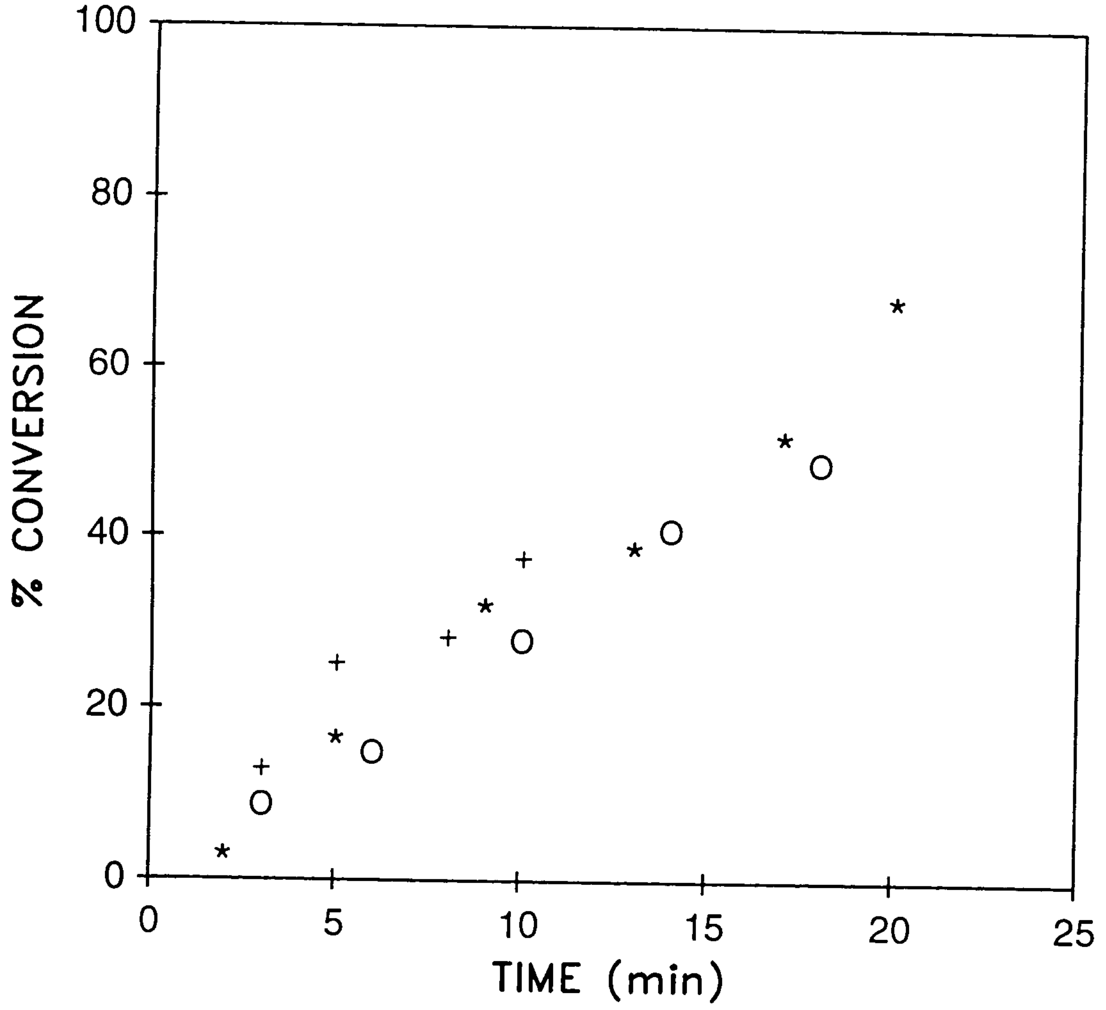


Figure 4-6 Comparison of gasification conversion of Bowmans coal with carbon dioxide at 765℃ for different particle sizes (+: 0.8~1.6, *: 1.6~2.4, o: 2.4~4.1 mm)

high temperature conditions, gasification of coal with carbon dioxide was significantly influenced by particle size, indicating an increase in the effect of diffusion at higher temperature.

The independence of the gasification rate on particle size also implies that the reaction of coal gasification mainly occurs on certain carbon atoms - the 'active sites'. Such 'active sites' are uniformly distributed in the whole volume of the coal particle. With the progress of reaction, new 'active sites' are continually created until all carbon atoms to be converted. Gasification rate is mainly dominated by the concentration of such active sites. The low reaction rate enables gas reactants to diffuse through the whole particle to reach the active sites.

Increasing particle size should result in a decrease in overall reaction rate if intraparticle diffusion is significant. In the chemical reaction control region, where the reaction rate is relatively low, the effect of diffusion can be neglected and the overall process is dominated by the rate of the chemical reaction. At high temperatures, the intrinsic reaction rate is so high that the effect of intraparticle diffusion must be taken into account. In this case, the gasification rate decreases with increasing particle size. The gasification rate of high-rank coal is more sensitive to particle size rather than low-rank coal. Intraparticle diffusion plays a more important role in the gasification of higher rank coals. In the present study, particle size does not significantly affect gasification rate over the range of temperatures and sizes examined.

4.2.6 Mass Transfer

For C-CO_2 reaction

$$C + CO_2 \rightarrow 2CO \tag{4.2.7}$$

At steady-state condition, rate of transfer of CO_2 to surface = rate of reaction of carbon in pellet.

Rate of transfer of CO_2, r_g (mol/s), is:

$$r_g = k_g S_x (C_b - C_s) \qquad (4.2.8)$$

Mass transfer resistance is:

$$\frac{1}{k_g \cdot S_x} \qquad (4.2.9)$$

where S_x is external surface area of pellet, C_b and C_s are the mole concentrations of CO_2 which would be present in fluid phase and surface, k_g is mass transfer coefficient which is expressed:

$$k_g = \frac{2.0D}{d_p} + 0.6\left(\frac{v\rho}{d_p\mu}\right)^{0.5} Sc^{0.33} \qquad (4.2.10)$$

D is diffusivity, ρ is density, μ is viscosity, v is velocity, Sc is Schmidt number, $Sc = \mu/\rho D$.

Rate of chemical reaction of carbon in pellet, r, is:

$$r = kC_c V_p \qquad (4.2.11)$$

Chemical reaction resistance is:

$$\frac{1}{k \cdot V_p} \qquad (4.2.12)$$

here k is first-order reaction rate constant, V_p is volume of pellet.

The ratio of mass transfer resistance and chemical reaction resistance is:

$$\Phi = \frac{k \cdot V_p}{k_g \cdot S_x} \qquad (4.2.13)$$

For a sphere:

$$\frac{V_p}{S_x} = \frac{d_p}{6} \qquad (4.2.14)$$

Equation 4.2.13 can be rearranged to obtain:

$$\Phi = \frac{k \cdot d_p}{k_g \cdot 6} \qquad (4.2.15)$$

Equation 4.2.15 provides a criterion to identify the role of diffusion. For mass transfer to be controlling:

$$\Phi = \frac{k \cdot d_p}{k_g \cdot 6} \gg 1 \tag{4.2.16}$$

In the present study, at T = 1037K, relevant parameter are:

$$d_p = 0.002 \text{ m}$$

$$k = 2.2 \text{ s}^{-1}$$

$$D = 1.43 \text{ x } 10^{-4} \text{ m}^2/\text{s}$$

$$k_g = 0.34 \text{ m/s}$$

$$\Phi = \frac{k \cdot V_p}{k_s \cdot S_x} = \frac{0.002}{6} \cdot \frac{2.2}{0.34} = 2.2 \times 10^{-3} \ll 1$$

At T= 1165K (the highest temperature in this study), $k=7.3s^{-1}$, assume k_g same as above, $\Phi = 0.017 \ll 1$.

Consider the limiting case, v=0, k_g is 0.14 m/s, $\Phi = 0.005 \ll 1$. Therefore, it is safe to conclude that, in the present investigation, CO_2 gasification is under chemical-reaction-rate control. External diffusion has a negligible effect.

4.2.7 Kinetics of CO_2 Gasification

4.2.7.1 Kinetic Models

The experimental data for CO_2 gasification of the raw coal were tested with seven kinetic models. The correlation coefficients for the linearized model equations were used to indicate the suitability of these models. ***Table 4-3*** provides the comparison of the different models fitted to the same experimental data. From the correlation coefficients, the models which best fit the experiment data are Homogeneous and Shrinking-Core models with the assumption of chemical reaction rate control. Numerous investigators (Chan et al. 1979, Schemal et al. 1982, Kwon et al. 1989, and Adanez and de Diego 1990) have reported similar results. Kwon et al. (1989) found that at higher temperature, the shrinking-core model fitted the experimental data better, but at lower temperatures (less than 850°C) the homogeneous model was found to be more appropriate. Models, based on the assumptions of pore structure and its variation during reaction, were found to be less appropriate. This strongly suggests that chemical reaction is the dominating factor for the gasification of Bowmans coal with carbon dioxide, and the structure of the coal and its variation during reaction is of minor importance.

The Homogeneous model assumes that the gas-solid reaction occurs uniformly throughout the whole volume of the particle on sites which are uniformly distributed in the particle; with the progress of reaction, the size keeps constant (equation ***2.5.2***). Conversely, the Shrinking-Core model assumes that the reaction occurs only on the surface of the unreacted core; with the progress of reaction, the unreacted core is "shrinking". Various assumption can be made about the rate-controlling step, e.g. whether chemical reaction, interparticle diffusion resistance or intraparticle diffusional resistance can be ignored. The relevant equations are ***2.5.3*** to ***2.5.8***.

Figures 4-7 and ***4-8*** show predicted conversion against reaction time for the two models (assuming reaction-rate control) at four temperatures, together with experimental data. Lines of best fit were used to estimate constants for prediction of fractional conversion against time, shown in ***Figures 4-9*** & ***4-10***. Both models fit the experimental data reasonably well. Both Kwon et al. (1988) and Adanez et al. (1990) reported that these two models described CO_2 gasification well in the chemical-reaction-control region, but they did not investigate the effect of particle size on the rate of gasification.

Both Homogeneous and Shrinking-Core models have been widely used to describe coal gasification (Schmal et al. 1983, Fung and Kim 1983). The results from both the present study

Table 4.3 Comparison of different models for experimental data fitting

Models	Linearized equation	Correlation coefficient
Homogeneous model [1]	$-\ln(1-X) = kt$	0.897
Shrinking-Core model [2]	$t/\tau = 1-(1-X)^{1/3}$	0.896
Lindner-Simonson model [3]	$\ln(dX/dt) = \ln k + m\ln(1-X)$	0.894
Johnson model [4]	$\ln(1/(1-X)^{2/3})dX/dt = \ln k - aX^2$	0.853
Bhatia-Perlmutter model [5]	$(-r)^2 = k\,(1-w\ln(1-X))$	0.851
Agarwall-Seara model [6]	$(-r) = k(1-M\ln(1-X)$	0.845
Simon model [7]	$(-r) = a + bX$	0.834

1: Wen et al. (1968), Jensen et al. (1975) and Fung et al, (1983); 2: Schmal et al. (1982), Goyal et al. (1989), and Kwon et al. (1989)1; 3: Linder and Simonson; 4: Johnson (1980) 5: Bhatia and Perlmutter (1980); 6, 7: Adanez and de Diego (1990)

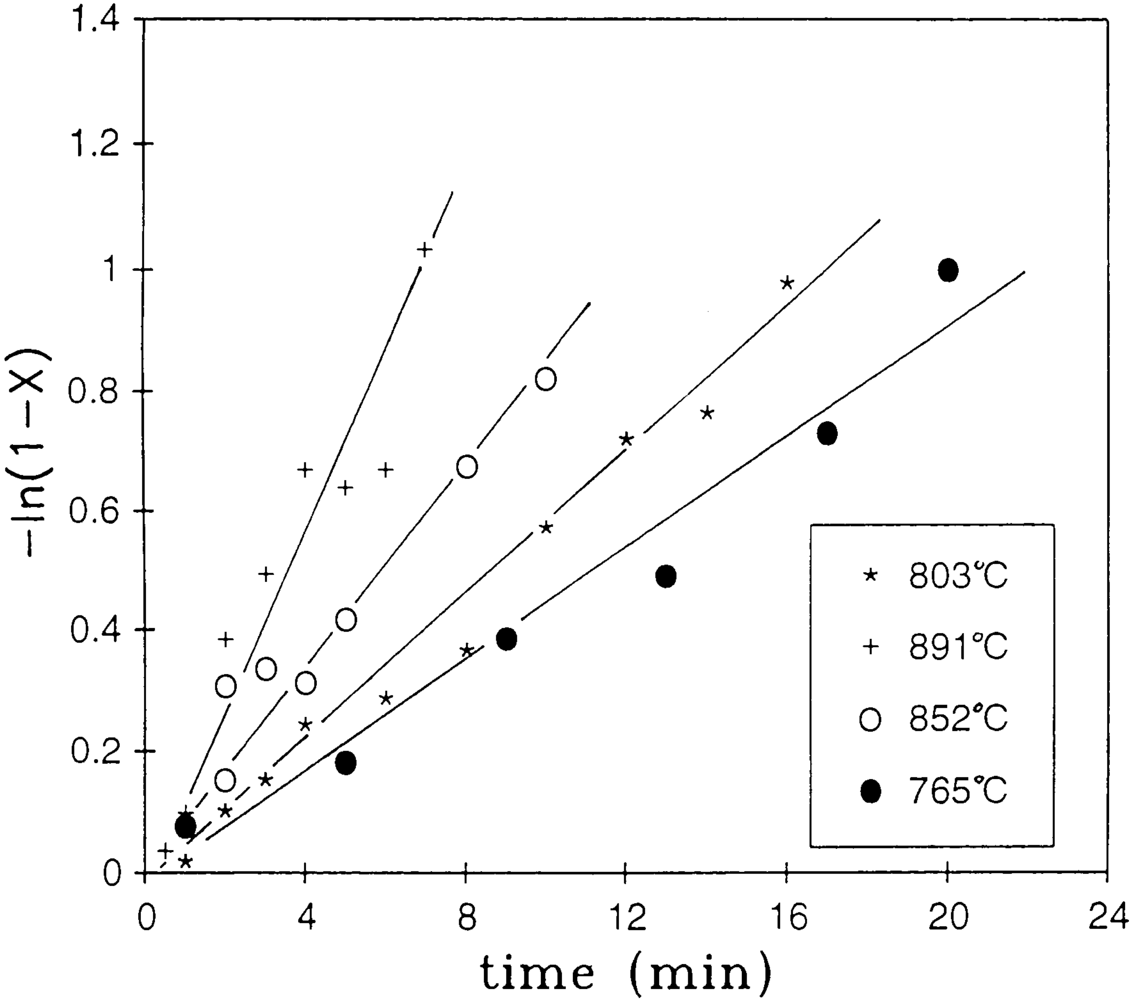


Figure 4-7 Experimental conversion data plotted according to Homogeneous model for gasification of Bowmans coal with carbon dioxide at different temperatures, (size: 1.6~2.4mm).

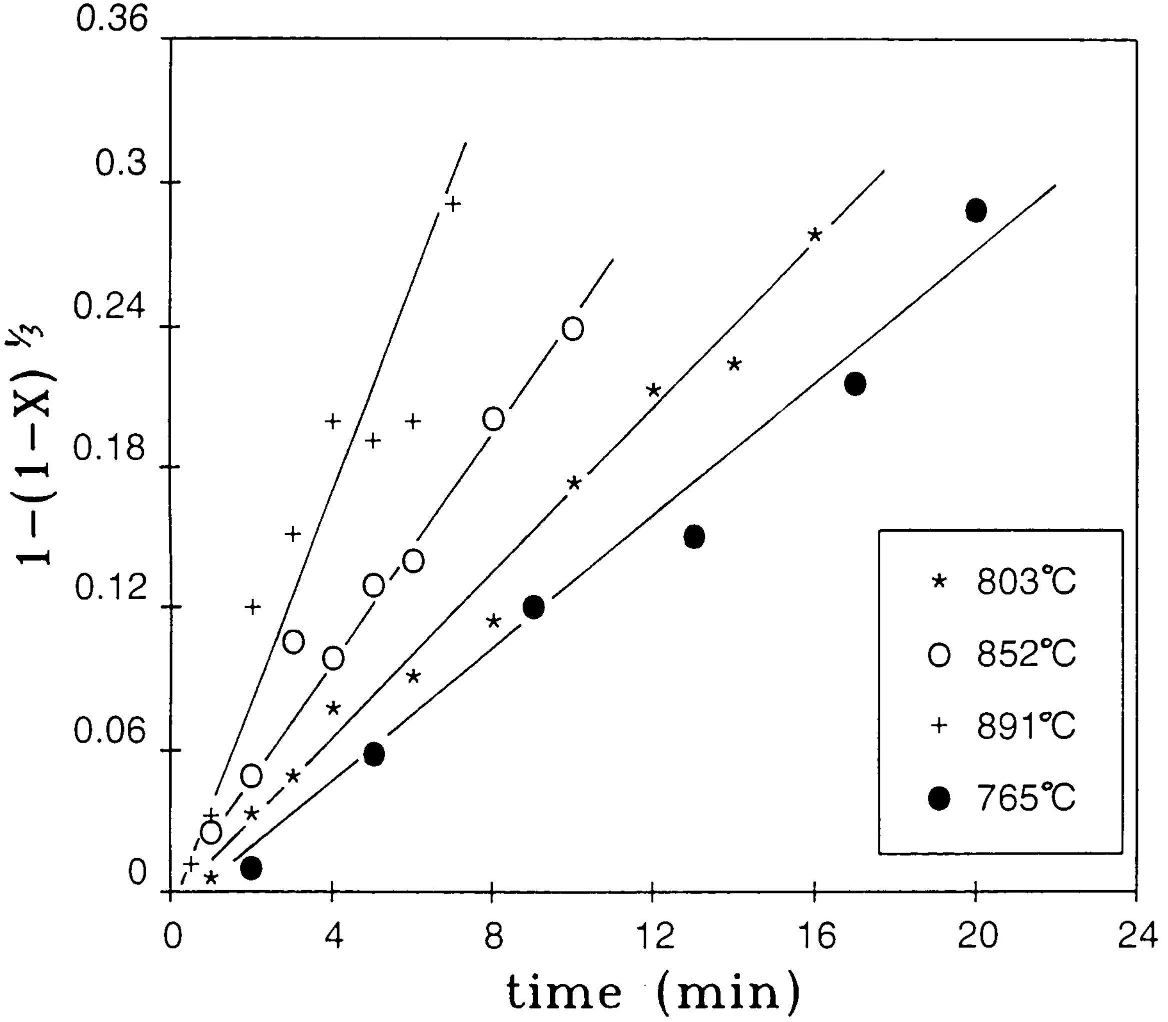


Figure 4-8 Experimental conversion data plotted according to Shrinking-Core model for carbon dioxide gasification of Bowmans coal at different temperatures. (particle size: 1.6~2.4mm)

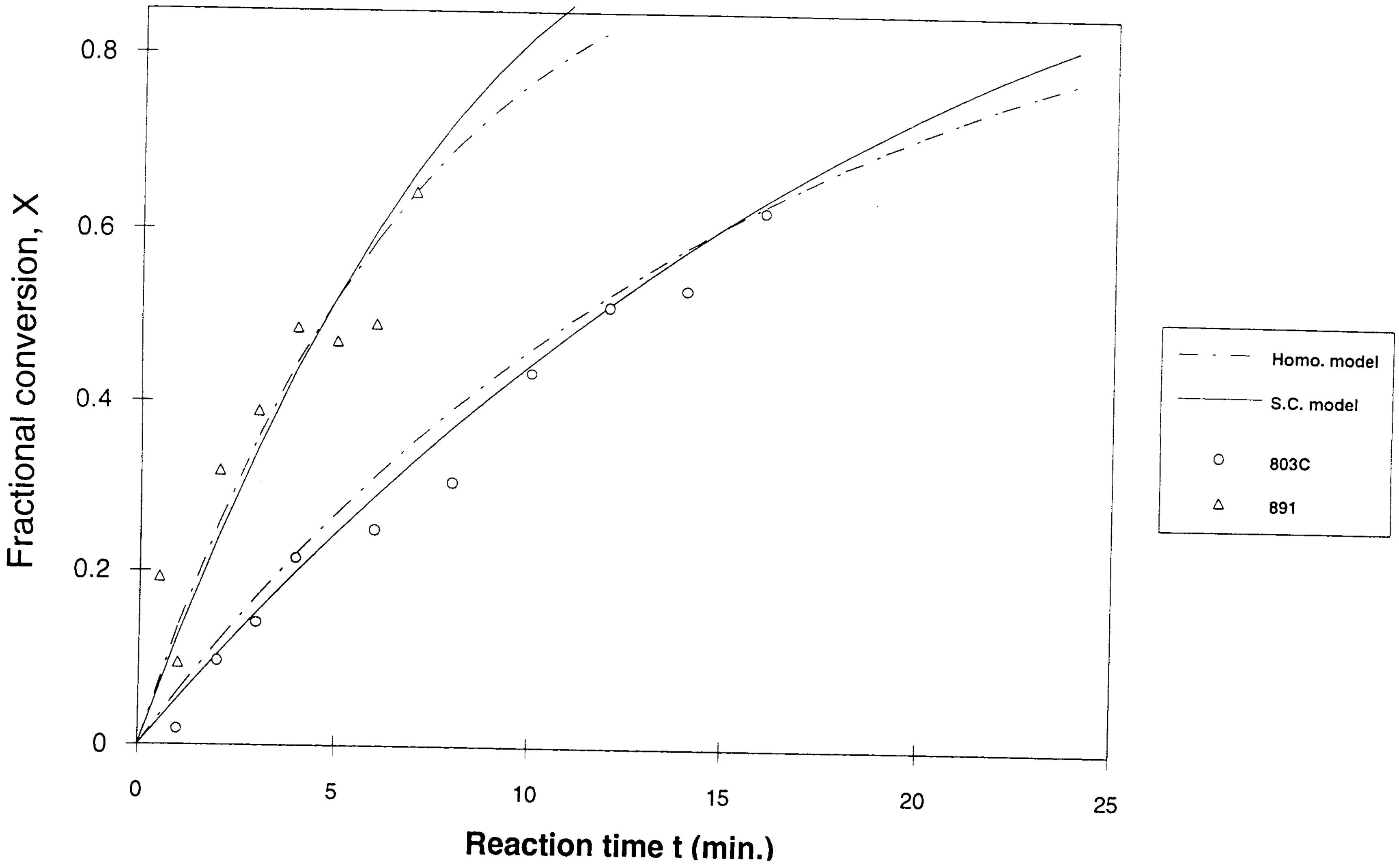


Figure 4-9 Comparison of mdel prediction with experimental data (size 1.6~2.4mm).

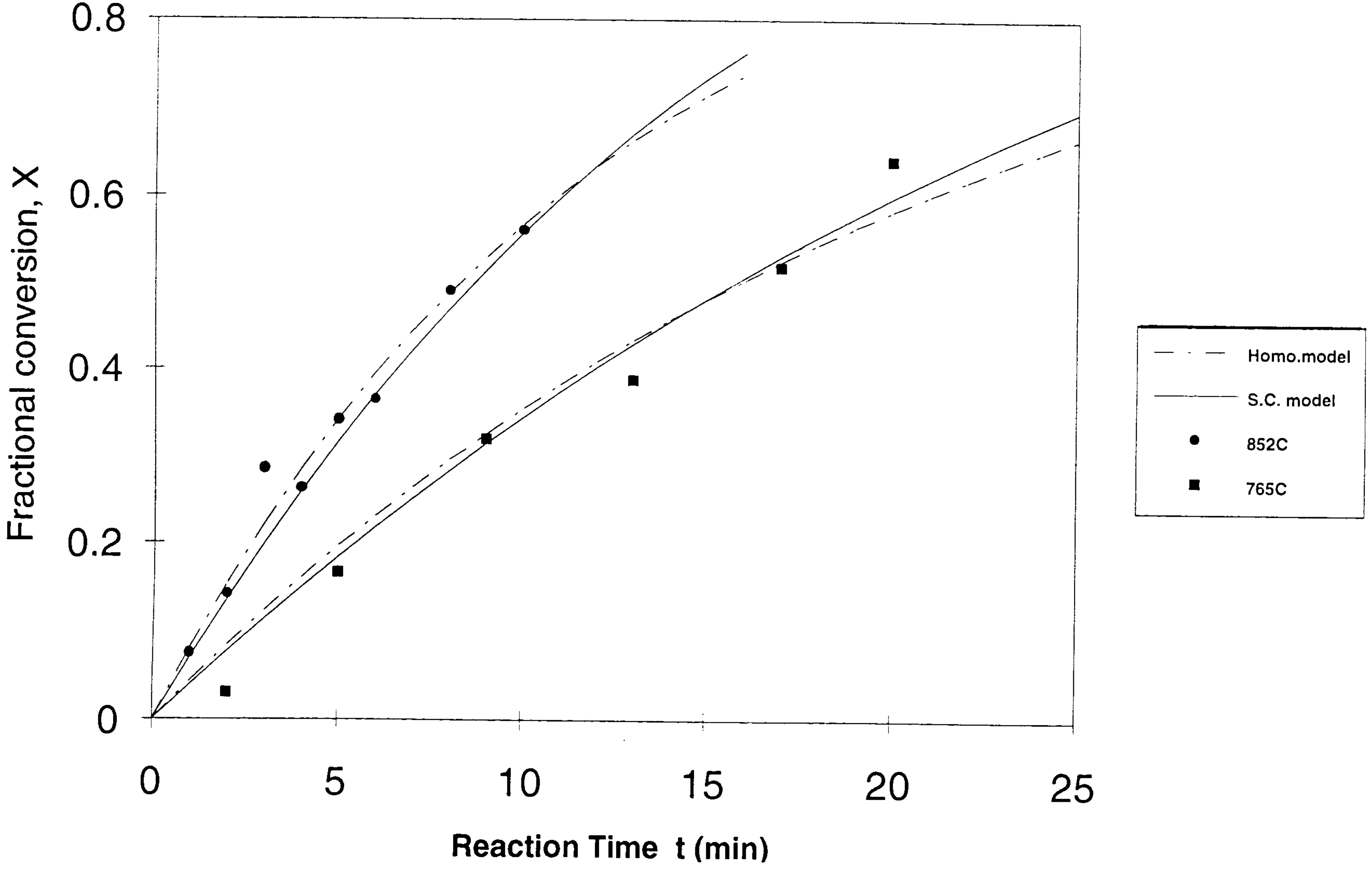


Figure 4-10 Comparison of model prediction with experimental data of Bowmans coal (size 1.6~2.4mm).

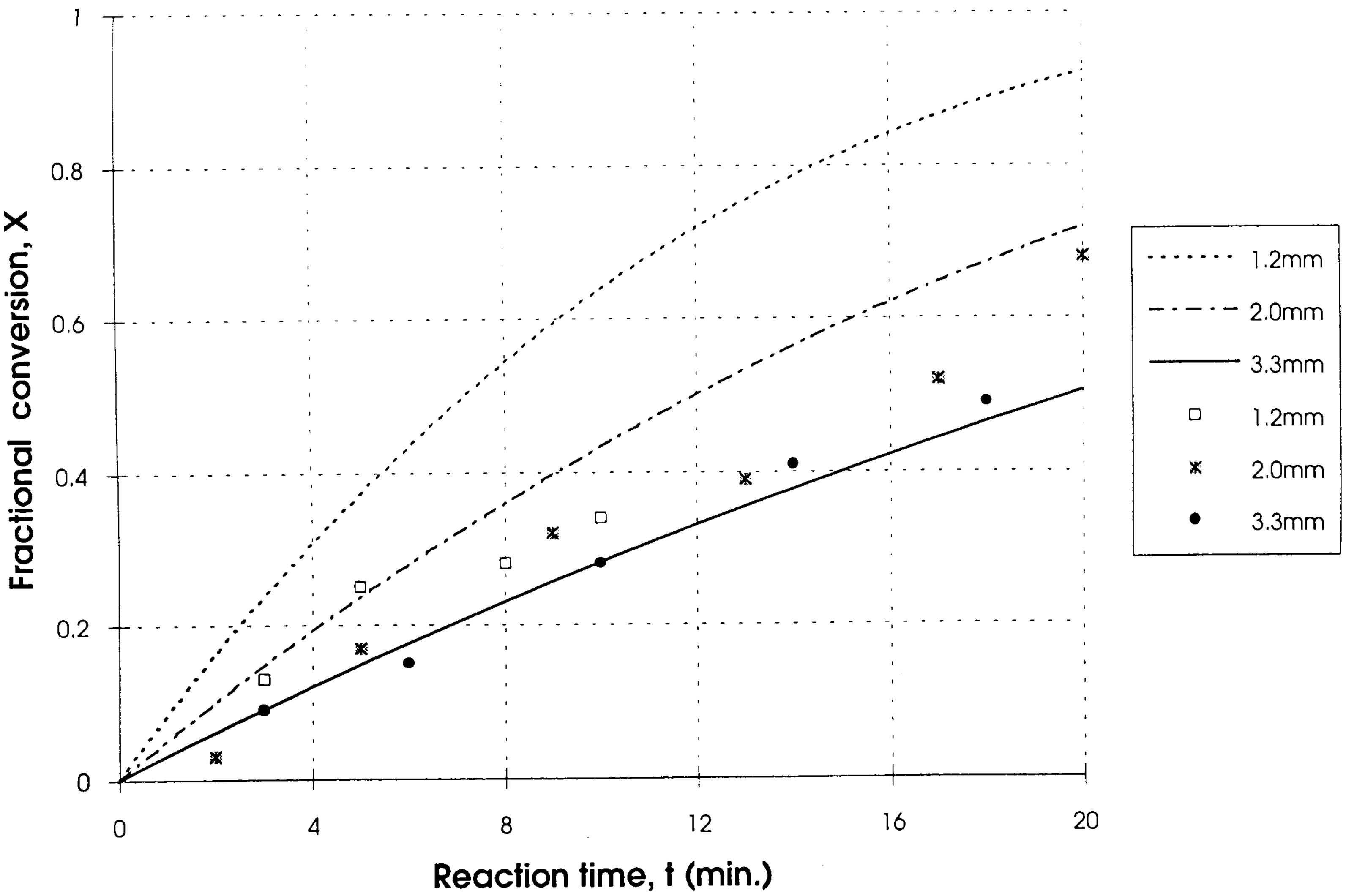


Figure 4-11 Model prediction for Shrinking-Core model for various particle size together with experimental data

and previous investigations indicate that both models appear to describe coal gasification equally well. The question raised is why these two conceptually different models can predict the same gasification process. If the reaction follows the Shrinking-Core model, the reaction rate must be proportional to the reaction surface area which depends on the particle size, and as shown in ***Figure 4-11***, change in particle size should significantly affect predicted conversion. If the reaction follows the Homogeneous model, the reaction rate is independent of particle size. Unfortunately, other investigators (Kwon et al. 1988 and Adanez et al. 1990), who had reported that Shrinking-Core model describes coal gasification well, did not study the effect of particle size on the reaction rate. As discussed in **Section 4.2.5**, particle size does not significantly affect the gasification rate in the present study, so that the Homogeneous model would seem to be the better model, but only marginally so. Other investigators, who reported that both homogeneous and shrinking-core models equally describe the gasification process, did not give detailed discussion on the nature of the models.

Another possible reason is that both models are ideal theoretical models and may not match reality well. The visual observation of the gasification experiments showed that, at low conversion level ($X < 35\%$), the particle size remained relatively constant; at high conversion level ($X > 40\%$), some particles broke into smaller particles; with the conversion further increasing and reaching the level of $X > 50\%$,' most particles broke. Neither Homogeneous model nor Shrinking-Core model considers the influence of breakage on rate, although the Homogeneous model would be expected to cover breakage because it is size-independent.

4.2.7.2 Correlation of Reactivities

Gasification kinetics are strongly influenced by experimental conditions. Current CO_2 gasification experiments were conducted for different particle sizes, temperatures, and gas velocity conditions. It is important to clarify whether all the data support the same mechanism.

Equations for the two models given previously (***2.5.1 - 2.5.8***) relate time with conversion and a parameter, τ, which is the time for complete conversion. As it is not possible to measure τ accurately, a dimensionless reaction time $t^* = t/\tau_{0.5}$ was employed, where $\tau_{0.5}$ is the reaction time required to achieve 50 percent conversion. The relationships between $\tau_{0.5}$ and X for various models are:

Homogeneous model

$$k = \frac{1}{(1-X)} \cdot \frac{dX}{dt} \tag{4.2.17}$$

$$\tau_{0.5} = k \cdot \ln 2 \tag{4.2.18}$$

$$t^* = \frac{1}{\ln 2} \cdot \ln\left(\frac{1}{1-X}\right) \tag{4.2.19}$$

Shrinking-Core model, film diffusion controls

$$t = \frac{\rho_p R_o}{3bk_g P_g} \cdot X \tag{2.5.8}$$

$$\tau_{0.5} = \frac{\rho_p R_o}{3bk_g P_g} \cdot 0.5 \tag{4.2.20}$$

$$t^* = 2X \tag{4.2.21}$$

Shrinking-Core model, ash diffusion controls

$$t = \frac{\rho_p R_o^2}{6bDP_g}(1 - 3(1-X)^{2/3} + 2(1-X)) \tag{2.5.6}$$

$$\tau_{0.5} = \frac{\rho_p R_o^2}{6bDP_g} \cdot (1 - 3(1-0.5)^{2/3} + 2(1-0.5)) \tag{4.2.22}$$

$$t^* = 9.08(1 - 3(1-X)^{2/3} + 2(1-X)) \tag{4.2.23}$$

Shrinking-Core model, chemical reaction controls

$$t=\frac{\rho_p R_o}{b k_s P_g}\cdot(1-(1-X)^{1/3}) \tag{2.5.3}$$

$$\tau_{0.5}=(1-0.5^{1/3})\frac{\rho_p R_o}{b k_s P_g} \tag{4.2.24}$$

$$t^{*}=4.85(1-(1-X)^{1/3}) \tag{4.2.25}$$

The relevant equations used to correlate the experimental data are summarized in ***Table 4-4***.

The theoretical relations of X *vs.* t^* are shown in ***Figure 4-12***, together with experimental data obtained under various conditions for raw Bowmans coal. The best fit appears to be given by the Homogeneous model and the Shrinking-Core model with the assumption of chemical-reaction-rate control. ***Figure 4-12*** indicates that all the experimental data, obtained for two different particle sizes, four reaction temperatures and gas velocities, could be correlated by a single curve. ***Figure 4-13*** shows the relationship of X *vs.* t^* for catalysed Bowmans coal. It can be seen that some of the first-order models fit the data well over entire range. Miura et al (1985) (**Section 2.7.6**) found that for samples with K or Na added, a zero-order Homogeneous model fitted their data. Such a model would yield the equation $t^*=2X$, which corresponds to the Shrinking-Core model with the assumption of film-diffusion control. This model also gives a good fit to the data.

Good agreement has been found between the present investigation and the results reported by Fernandez-Morales et al. (1985), Kasaoka et al. (1986) and Raghunathan et al (1989). Raghunathan et al (1989) directly used the half-life ($\tau_{0.5}$) as a reactivity index for characterizing the char-gas reaction. With an extension of unification approach, they reported that the average reactivity is nearly a constant with a value of 0.38. Kasaoka et al. (1986) studied the gasification kinetics of coal with CO_2 and H_2O. Numerous coals from different countries were tested. They

Table 4-4. Conversion-time expressions for various models

Models	Reaction order	Equations
Shrinking-Core, film diffusion. control	1	$t^* = 2X$
Shrinking-Core, ash diffusion. control	1	$t^* = 4.85(1-(1-X)^{1}/3)$
Shrinking-Core, reaction control	1	$t^* = 9.08(1-3(1-X)^{2/3}+2(1-X))$
Homogeneous model	1	$t^* = 1.44\ln\left(\frac{1}{1-X}\right)$
Homogeneous model	0	$t^* = 2X$
Homogeneous model	2	$t^* = \frac{X}{(1-X)}$

where, t^* is reduced reaction time, $t^*=t/\tau_{0.5}$; X is fractional fixed carbon conversion, $\tau_{0.5}$ is reaction time to achieve 50% conversion.

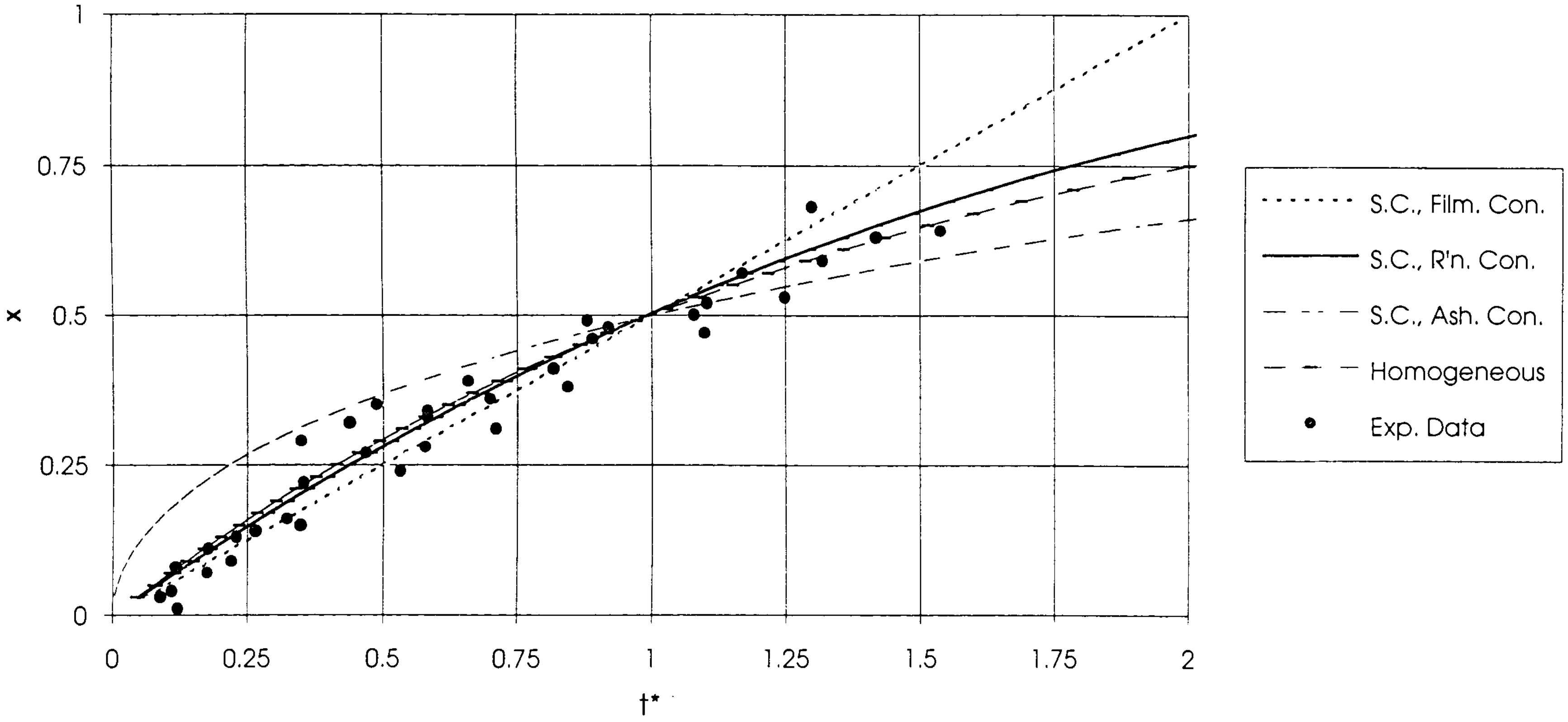


Figure 4-12 X-t* relationship for different models together with experimental data for CO2 gasification of raw Bowmans coal

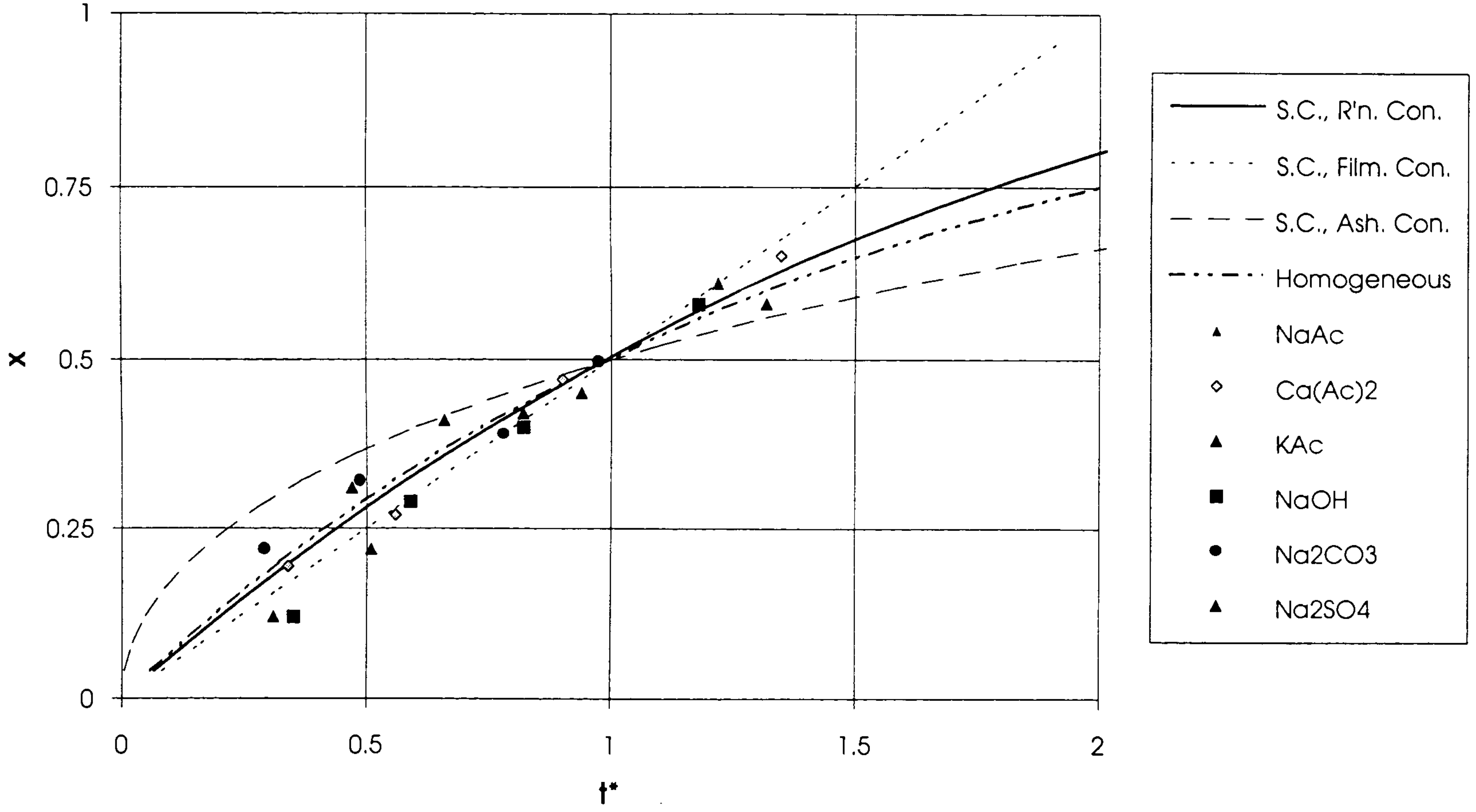


Figure 4-13 X - t* relationship for different models together with experimental data for CO2 gasification of catalysed Bowmans coal

found that, in the chemical-reaction-controlling regime (< 1000°C), all experimental data were correlated with a single curve. They therefore concluded that the same mechanism applied to all their results. An empirical equation was proposed to correlate their experimental data:

$$X = A\frac{t}{\tau_{0.5}} + B\left(\frac{t}{\tau_{0.5}}\right)^2 + C\left(\frac{t}{\tau_{0.5}}\right)^3 \qquad (4.2.26)$$

where A, B and C are constants which need to be experimentally determined.

It is not surprising that all results should support a reaction-control mechanism in this investigation because all experiments were conducted at temperatures below 1000°C, which is the generally accepted limit for chemical reaction rate control. Also, gas velocities employed were high.

4.2.7.3 Activation Energy

Figure 4-14 presents Arrhenius plots of reaction rate constants k over the range of 710-891°C for gasification of raw Bowmans coal with CO_2. The experimentally obtained activation energy for CO_2 gasification is 91 kJ/mol, which is within the range of reported values (Guo and Zhang 1986, Kwon et al. 1988). Kwon et al. (1988) found the activation energy was in the range of 79 to 155 kJ/mol depending on coal type and experimental conditions.

As an important parameter of gasification kinetics, activation energy of coal gasification has been widely investigated. Reported values of activation energy vary widely. Factors affecting the activation energy are: coal rank, amount and state of inorganic impurities, pore structure, experimental method used and method of analysis. Kasaoka et al. (1985) measured the activation energies of CO_2 gasification for 25 coals (75<C<91 wt%, daf) under varied experimental conditions. Their results showed that, at temperatures <1000°C, the activation energy ranged

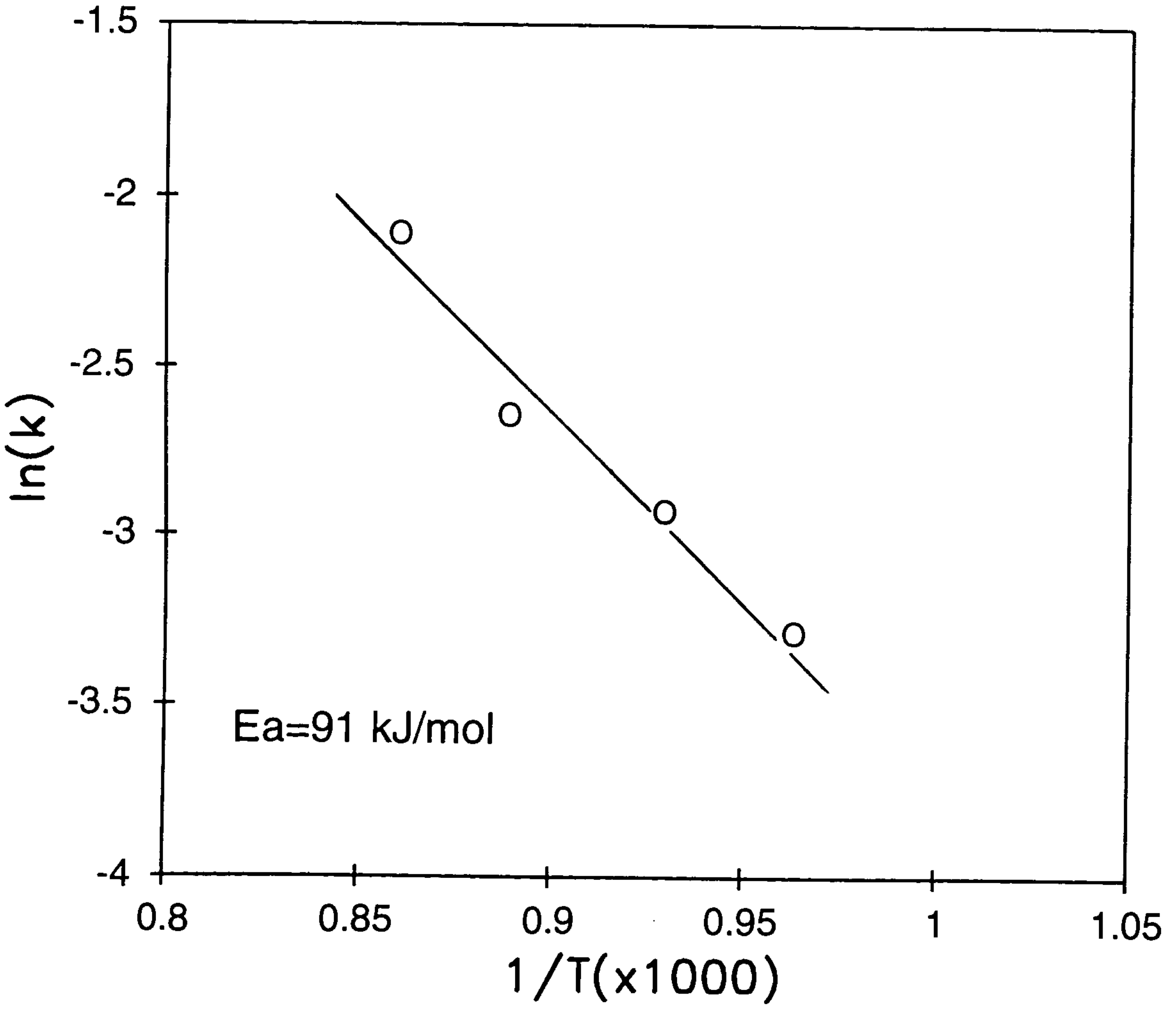


Figure 4-14 Arrhenius plots of reaction rate constants of gasification of Bowmans coal with carbon dioxide (size 1.6~2.4mm).

Table 4.5 Summary of Activation Energy of Gasification with CO_2 for Some Australian coals

Investigator	Coals	Activation Energy (kJ/mol)
Knight et al.(1988)	Millmerran (Qld)	233
Knight et al.(1988)	Liddell (NSW)	219
Knight et al.(1988)	Lithgow (NSW)	222
Knight et al.(1988)	Merriown (VIC)	227
Knight et al.(1988)	Yallourn (VIC)	175-185
Barrett (1986)	Yallourn (VIC)	135
Barrett (1986	Metallurgical coke (VIC)	200
Dodds (1986)	Metallurgical coke (VIC)	207
Kwon et al.(1986)	Yallourn (VIC)	146
Present Study	Bowmans (SA)	91

Note: Pressure is 101 kPa for all investigators from 197 to 310 kJ/mol; they found no significant difference between the activation energy of C-CO_2 reaction and C-H_2O reactions. Knight et al. (1988) reported values ranging from 219 to 233 kJ/mol for gasification of four Australian black coals with carbon dioxide; the value for Yallourn brown coal was lower, at 175-185 kJ/mol, which is higher than the value reported by Kwon et al. (1988). A brief summary of the activation energies of some Australian coals and cokes with carbon dioxide is listed in ***Table 4-5***.

In the present investigation, the particle size, reaction temperature and gas flow rate were selected to minimize the influences of internal and external diffusion. The rate of coal gasification can partly be explained by the activation energy of reaction. In general, a high reactivity corresponds to a low activation energy. The activation energy of CO_2 gasification from the present study is lower than most of the results which have been published in the literature. This can be attributed to the presence of high concentrations of inherent alkali metals (Jenkins et al. 1973, Johnson 1976, and Knight et al. 1982). As discussed in **Chapter 2**, active metal elements accelerate the reaction by reducing the activation energy. The effect of alkali catalyst on activation energy of coal gasification has been investigated by Ruan et al. (1987). who found that the apparent activation energy of gasification of lignite could be reduced from 59.6 to 37.9 kJ/mol by adding alkali catalyst to the raw coal. Similar results have also been reported by Guo and Zhang (1986), who determined kinetic parameters of CO_2 gasification of some Chinese bituminous coals using a thermogravimetric technique at elevated pressure. Measured activation energy was reduced from 45.8 to 39.1 kJ/mol by adding various alkali and alkaline-earth compounds. Knight (1982) also found that the presence of ash constituent impurities accelerated the C-CO_2 reaction rate and reduced activation energy.

Other investigators also reported that demineralization could increase activation energy. Burham (1984) found that the activation energy can be increased from 205-234 for raw coals to 327-354 kJ/mol by acid washing. Fernandez-Morales et al. (1985) also pointed out that demineralization brings about an increase in activation energy.

In the present study, various catalysts were added to the demineralized coal by cation-exchange. The gasification rate of catalysed-coal samples was greatly increased. Demineralization significantly reduces the reactivity. But the activation energy of the demineralized coal was not measured due to the low reactivity of the acid-washed coal and the high temperature, which was not available in the present reactor, required to achieve measurable carbon conversion.

4.2.8 Effect of Demineralization on Gasification Rate

4.2.8.1 Transformation of Inorganics During Demineralization

Demineralization is a process in which coal is treated with acid or water to remove inherent minerals. Water-leaching of low-rank coal removes the water-soluble salts and may cause some dissociation of cations from the surface functional groups. Acid-leaching results in the exchange of cations with hydrogen from surface carboxyl groups.

In the present study, Bowmans coal has been treated with water or hydrochloric acid to evaluate the transformation of inorganics during the process of demineralization. The distribution of inorganic matter in raw, water-washed and acid-washed coals was determined by analysing the ash composition using Atomic Absorption Spectrophotometry. The ash contents of raw coal, water-leached and acid-washed coal were 12%, 6.3% and 2.6% (d.b.), respectively. ***Tables 4-7*** and ***4-9*** show the ash analyses of these samples. Substantial quantities of sodium, calcium, potassium, aluminium and magnesium of coal were removed by water-washing. About 98% of alkali, alkaline-earth and other metals such as Na, K, Ca, Fe, Al and Mg were removed by treating the coal with HCl. The major element remaining in acid-washed coal was Si which is known to have no catalytic effect on gasification.

Evaluation of these results indicated that most of the inorganic matter can be effectively

Table 4-6 Ash content of the different Bowmans coal samples

	Raw Coal	Water-Washed Coal	Acid-Washed Coal
ash fraction d.b. %	12.0	6.3	2.6

Table 4-7 Ash analysis of different coal samples (weight percentage in ash %)

Inorganics % d.b.	Na	K	Ca	Mg	Fe	Al	Si
raw coal	11.25	0.25	5.75	6.63	1.90	1.43	9.00
water-washed coal	6.40	0.19	6.20	8.51	2.65	2.25	8.85
acid-washed coal	0.67	0.17	0.49	0.20	0.85	<0.01	27.00

Table 4-8 Ash analysis of Bowmans coal (Data from Dunne 1988)

	Na	K	Ca	Mg	Fe	Al	Si
M/ash (%)	14.69	0.33	4.93	9.95	10.5	1.48	17.92

Table 4-9 Ash analysis of Bowmans coal

M_xO_y/ash (%)	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2
raw coal	15.16	0.30	10.35	11.05	2.73	2.70	19.29
water-washed coal	8.63	0.23	11.16	14.18	3.78	4.25	18.96
acid-leached coal	0.90	0.20	0.88	0.33	1.19	0.01	57.86

Table 4-10 Ash composition analysis of raw coal (Data from Dunne 1988)

	Na_2O	K_2O	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2
M_xO_y/ash (%)	19.8	0.4	6.9	16.5	15.0	2.8	38.4

Table 4-11 Percentage of the inorganics removed from Bowmans coal by washing

Iorganics % d.b.	Na	K	Ca	Mg	Fe	Al	Si
water-soluble	60.2	46.8	5.36	10.15	2.37	-1.74	31.17
acid-soluble	98.6	84.1	98.17	99.3	89.56	99.98	30.00
acid-insoluble	1.4	15.9	1.83	0.70	7.20	0.02	70.00

replaced by H^+ from an aqueous HCl solution. Present results show that about 83% of total sodium can be removed by water-washing and about 99% can be removed by acid-washing. These results also indicated that, for Bowmans coal, 83% of sodium is present in the water-soluble forms (i.e. as NaCl), the remainder being insoluble in water. Water-insoluble sodium is essentially associated with organic acid groups as R-COONa (Readett and Quast, 1986, 1989 and 1991, Manzoori et al. 1990). Considerable amounts of calcium, magnesium, aluminium and iron are also water-insoluble. These cations associate with carboxyl groups or other oxygen-containing function groups to form organic acid salts. ***Table 4-11*** shows that only 5.4% of the total calcium and 2.4% of total iron can be removed by water-washing. Aluminium was found to be mainly present in water-insoluble form. Most silicon is present in the acid-insoluble form. For comparison, reported experimental data for Bowmans coal from other investigation (Dunne 1988) is also listed in ***Tables 4-8*** and ***4-10***.

The present results are in good agreement with the results reported by Readett and Quast (1986, 1988, 1991), Dunne and Agnew (1988), Manzoori (1990) and Wright (1992). Readett and Quast (1990) found that approximately 70% of the total sodium of Bowmans coal is in water-soluble form and 30% of sodium is bound to surface functional groups and can be removed by acid leaching. Acid washing reduced the sodium content from 1.2% to 0.03% (Na/coal d.b.). They further pointed out that the water-soluble sodium was presented in the form of salt (NaCl) in the water retained within the pores of coal. Dunne and Agnew (1989) also found that the main inorganic constituents removed from Bowmans coal during the process of dewatering were sodium, chlorine and potassium. Most calcium and magnesium were water-insoluble. Iron and silicon were not affected by water-leaching, either.

Cations which are present in water-insoluble form are inferred to be bonded on coal surface functional groups. Such organically bonded cations play an important role in the reactivity of coal. Bowmans coal contains high concentrations of inorganic impurities. Sodium, which is the most abundant alkali element in the coal, is also the major contributor to ash agglomeration in fluid-bed gasifiers. But sodium is not the element which has the highest content in water-washed coal. ***Table 4-11*** shows that up to 60% of sodium, 47% of the total potassium, 10% of the total magnesium, 31% of silicon, 21% of the total aluminium and 3% of the total iron can be removed by water-leaching. From ***Table 4-7*** the sequence of contents of major inorganic elements in water-washed coal is: Si > Mg > Ca > Na > Fe> Al > K. Among them, Si, Al, and Mg are inactive and make no contribution to the gasification; Na, K and Ca are good catalysts for gasification; Fe only has a catalytic effect in its metallic form. Since water-washed Bowmans coal contains approximately the same calcium and sodium content, both of which are good catalysts for gasification, it is concluded that sodium is not the only active element which causes the high gasification reactivity of Bowmans coal.

4.2.8.2 Effect of Acid-washing on Reactivity

Gasification experiments were conducted using the demineralized coal samples to investigate the effect of inherent impurities on gasification reactivity. The relationships between fractional fixed-carbon conversion, X, and reaction time, t, of raw, water-washed and acid-washed coal samples, is shown in ***Figure 4-15***. The carbon conversion rate of raw coal is much greater than that of the acid-washed sample. The X-t profile shows that, under current experiment conditions (1.6~2.4mm particle size, 765°C temp. and CO_2 atmosphere), 70% of total fixed carbon conversion can be achieved within 20 minutes for raw coal. There is no significant carbon conversion with the reaction time extended to 40 minutes. Measured gasification reactivities, under current experiment conditions (765°C, 1.6~2.4mm, and pure CO_2), are 3.6 and 0.21 (h^{-1})for raw and demineralized coal samples, respectively. It clearly indicates that the inherent minerals play an important role in the gasification of Bowmans coal with carbon dioxide. Other investigators (Mahajian et al. 1979, Fernabdez-Morales et al. 1985, and Adanez et al. 1990) have reported results similar to ***Figure 4-15***. Kopsel et al. (1990) examined the catalytic effect of coal ash components on the gasification of some lignites with carbon dioxide. They found that the reaction rates of the ash-containing lignites were 30-50 times higher than that for demineralized

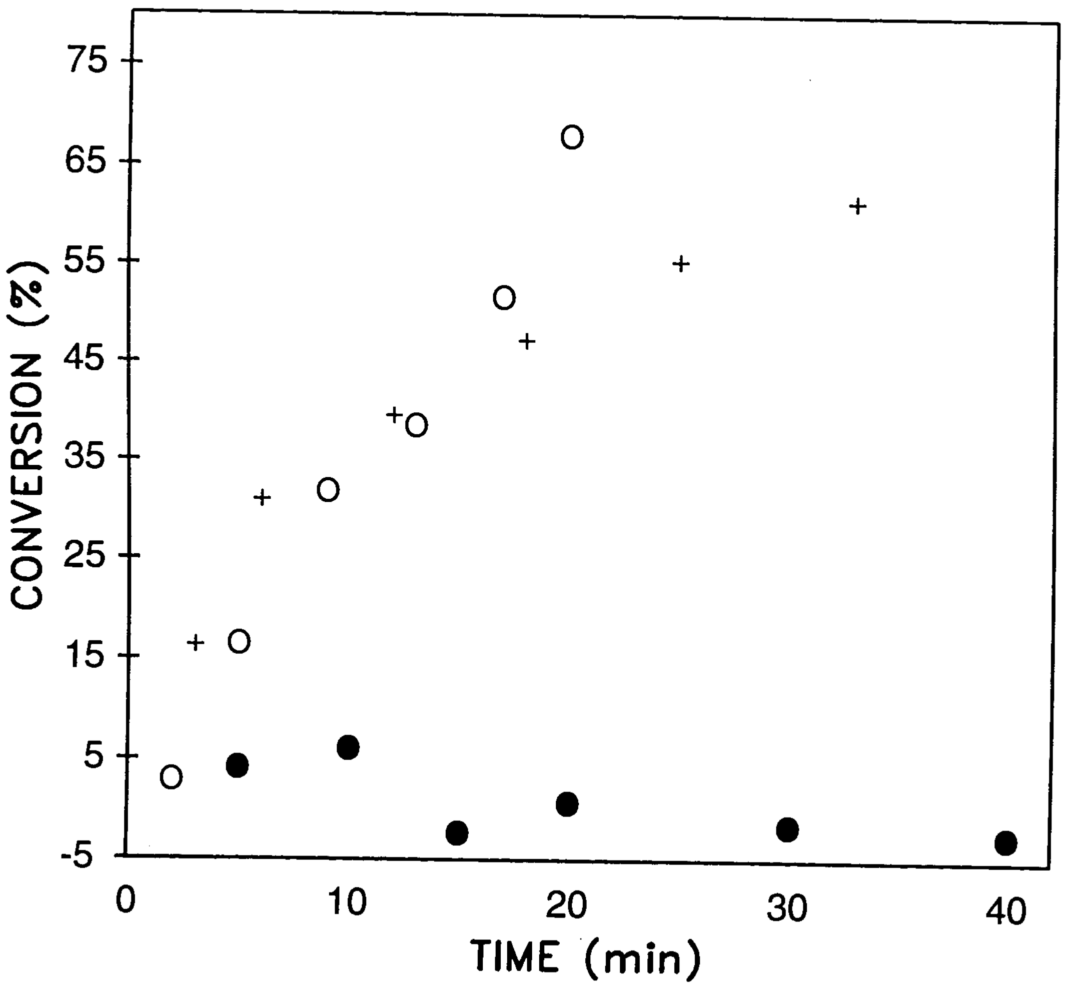


Figure 4-15 Comparison of carbon dioxide gasification behaviour for raw coal (o) with acid washed (●) and water washed (+) coal samples, (temp. 765°C, size 1.6~2.4 mm).

lignites. Detailed studies of the catalytic effects of *added* inorganics on the gasification of Bowmans coal with carbon dioxide and steam are given in **Sections 4.2.8** and **Section 4.3.4,** respectively.

It is known that carboxyl groups connecting active cations form the 'active sites' on the surface of coal and that the gasification reactions mainly occur on these 'active sites'. Gasification rate is proportional to the number of active sites. Treating the coal with acid decreases the concentrations of 'active sites'.

The present results also show that not all the inorganic elements have a catalytic effect. Silicon, the major component remaining in the acid-washed coal, is known to be a poor catalyst for gasification (Walker et al. 1986). Total ash content of coal shows poor correlation with its gasification rate (Adschiri et al. 1991). The catalytic activities of different elements follows the order of K > Na > Ca > Fe. The major inorganic components, Si and Al, have no catalytic effect. The chemical form for the inorganics of coal has not been investigated in this work. The variation of metal elements during the reaction was unknown, so it is difficult to explain the activities of inherent metals on gasification at the molecular level.

A parameter named "*alkali index*" (*B*) has been defined to indicate the catalytic abilities of inherent minerals of coal. *B* value is calculated from the ash analyses by the equation (Sakawa et al. 1982):

$$B = ash(wt\%) \cdot \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O}{SiO_2 + Al_2O_3} \tag{4.2.27}$$

Examination of extensive experimental data by Sakawa et al. (1982) confirmed the relationship between gasification reactivity and *B* (***Figure 2-5***, see **Section 2.6**).

In present study, for raw, water-washed and acid-washed Bowmans coal samples, the values of *B* are 18.6, 6.46 and 0.24, respectively. The alkali index of raw coal is only three times higher than water-leached sample, and is 78 times higher than acid acid-washed coal sample.

Although alkali index provides a useful parameter in describing the role of coal ash in gasification, the concept of alkali index is far from perfect. For example, Mg is well known to be a poor catalyst for gasification, and Fe also has less catalytic effect. The alkali index assumes that Mg and Fe have the same activities as that of alkali and alkaline-earth metals. Another drawback of the alkali index is that the interaction of metals with coal surface functional groups has not be taken into account. In other words, the water-insoluble and the water-soluble cations are not distinguished in the *B* index. Various results indicate that only the water-insoluble cations of coal have the principle catalytic effect. This is also supported by the results from this work.

4.2.8.3 Effect of Water-washing on Reactivity

Figure 4-15 shows that water-washing only slightly affects the gasification rate of Bowmans coal. ***Tables 4-7*** and ***4-9*** show that, after water treatment, considerable amounts of active inorganics still remain in the coal. Sodium and calcium are known to be the excellent catalysts for gasification. The catalytic activity of metal in gasification depends on the association of metal with coal surface and the amount of the metal (the ratio of metal/carbon). The mole ratios of metal/carbon in water-washed coal for Na/C, Ca/C and Fe/C are 0.0032, 0.0019 and 0.0006, respectively. The presence of high concentrations of Na and Ca exerts a strong catalytic effect on the gasification of Bowmans coal. Although water-washed Bowmans coal contains considerable iron content, it appears that inherent Fe does not contribute to the high reactivity of water-washed coal. Iron is reported to have catalytic activity only in the metallic form and not in the oxide form (van Heek et al. 1985).

Figure 4-15 shows that, at t < 10 min, the gasification rate of the water-washed sample was slightly higher than that for the raw coal. The 'anomalous' increase of reaction rate at the initial stage could be attributed to two reasons: (i) the changing of coal surface area due to water-leaching; water-leaching removes approximately 50% of the total inherent inorganic impurities from raw coal which may cause the increase in surface area; (ii) experimental error. In this work gasification rate is calculated by analysing the ash content of raw and reacted coal samples. The distribution of inherent minerals may not uniform. Small differences in the measured ash contents may result in a significant deviation of calculated carbon conversion. Knight and Sergeant (1982) found that the surface areas of some Australian coal chars increased by treating the parent coals with acids. The reactivity of the acid-treated coal chars also increased. Linares-Solano et al. (1986) found that the CO_2 reactivity of two Spanish high-ash coals increased after the samples had been washed by acids. They attributed that behaviour to the change in porous texture produced by the acid treatment.

It has been reported that demineralization may affect the surface area of char. The surface area of demineralized lignite can be larger or smaller depending upon the lignite (Mahajan et al. 1979, Hengle et al. 1984). Readett and Quast (1985) reported that the porosity, surface area and surface functional groups of lignite could be influenced by treating the coal with water. Others (Wood et al. 1983) found that the change of surface area did not influence the reactivity of coal. The effect of changing surface area on reactivity is much smaller than that due to the loss of catalyst by demineralization.

4.2.9 Role of Added Catalyst in Gasification

4.2.9.1 Adsorption of Cations

There are various ways to add catalyst to coal. The widely used methods are (i) physical-mixing of catalysts with fine coal and (ii) impregnation of coal in solutions of salts - cation-exchange. Physical-mixing requires small particle size of coal. The latter achieves better dispersion of catalyst in coal.

In this work, catalysts were added to the coal by the impregnation method. Various salts were selected for impregnation tests. The amounts of cations absorbed on the deashed Bowmans coal were measured by Atomic Absorption Spectrophotometry. The effect of solution concentration on catalyst loading is shown in ***Figures 4-16*** and ***4-17***, where it is indicated that, for all the cations (e.g. Na, K, Ca, Mg and Fe) tested, the loading increases linearly with increasing concentrations of solution. Two types of salts, chlorides and acetates, were used in the work. The acid-washed Bowmans coal samples were put in solutions ranging in concentration from 0.1 to 1.0 M. Obtained cation absorptions were: 0.15~3.1, 0.18~1.81, 0.50~3.10, 0.24~2.51, and 0.36~3.0 mmol/g for Na, Ca, K, Mg and Fe, respectively. Coal samples were also impregnated in the solutions of acetate salts of sodium and calcium. The cation loadings were 0.49~2.2 and 0.33~2.18 mmol/g for Na and Ca, respectively. ***Figure 4-17*** also shows that immersing coal sample in the solution of acetate salts results in higher absorption than for impregnating in solution of chloride salts. This can be attributed to the interaction between cation and coal. Cation, replacing hydrogen, connects to carboxylic function groups to form humic salts. Impregnating coal in the solution of chloride salts only causes physical absorption of cation on the structure or surface of coal without reacting with functional groups. On the other hand, impregnating the coal in solutions of acetate salts results in chemical reaction to give weakly dissociating acetic acid.

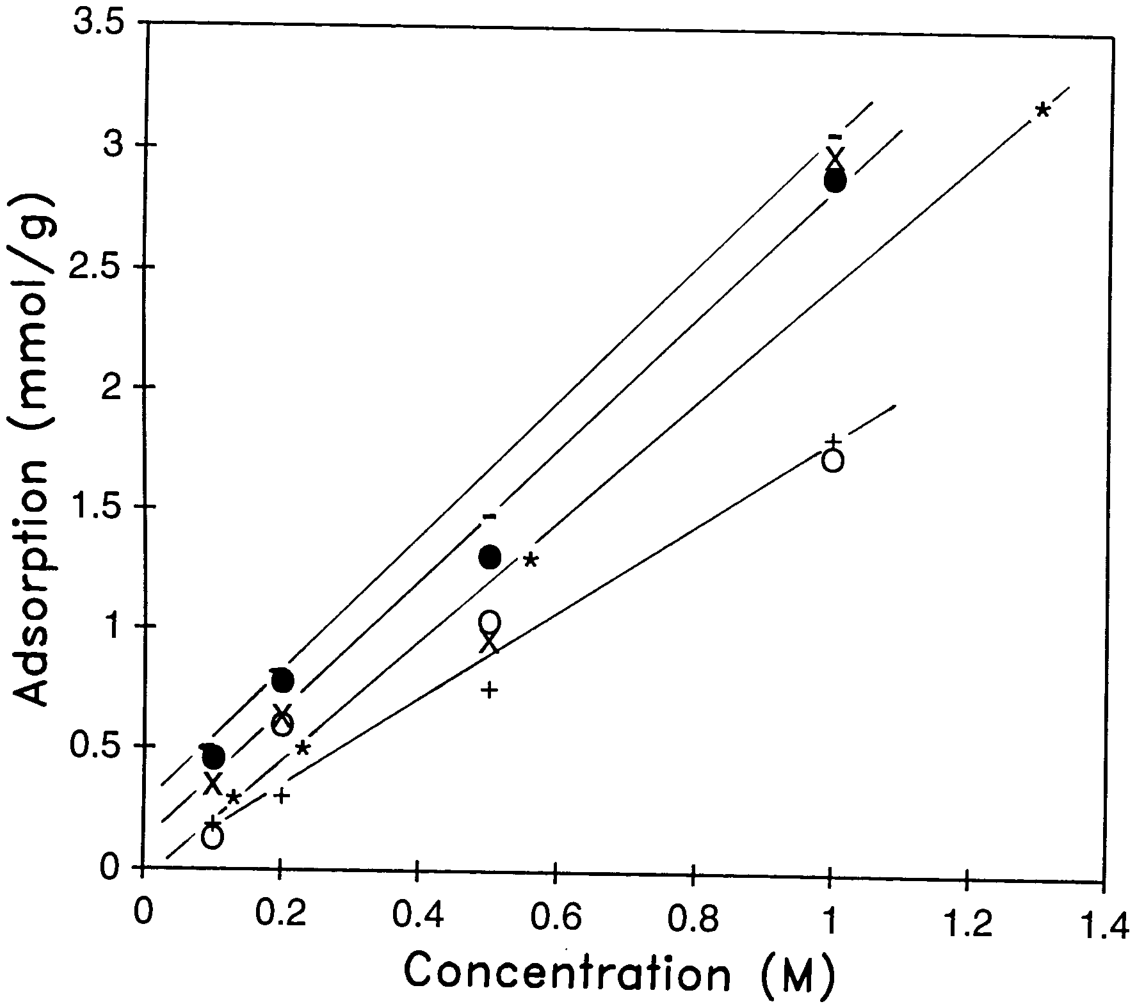


Figure 4-16 Effect of solution concentration on amounts of cations loaded onto the acid washed Bowmans coal o,Na; +,Ca; -,K; *,Mg; x,Fe (Ferric); ●,Fe (Ferrous) , material: chloride salts, particle size: 1.6~2.4mm.

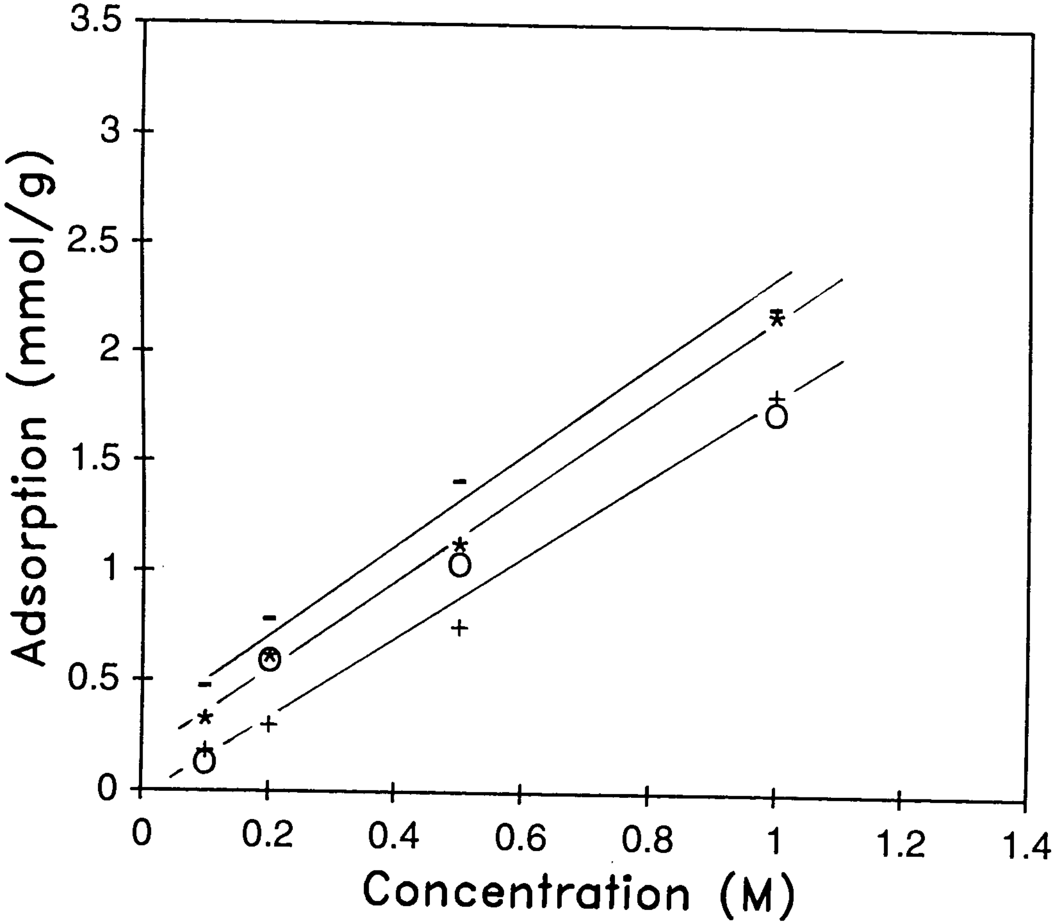


Figure 4-17 Effect of solution concentration on amounts of cations loaded onto the acid washed Bowmans coal with acetate or chloride salts -:NaAc, *:CaAc2, o:Nacl, +:CaCl2 , size 1.6~2.4mm

Although the impregnation method has been widely used for the addition of catalyst on coal, few investigators conducted a quantitative measurement of cation absorbed by coal during the process. Walker (1979) and Hippo et al. (1983) reported similar results to the present study. Hippo et al. (1979) impregnated coal in solutions of calcium acetate, ranging from 0.1 to 2.0M and found that the loading of calcium on the acid-treated lignite ranged linearly from 0.10 to 2.14 mmol/g coal (daf). Walker et al. (1983) tested several cations (Na, K and Ca) and found that the cation absorption linearly increased with increasing the solution concentration.

The present results indicate that impregnation provides a good method for catalyst loading. For the cations used, the order of absorption is $K \sim Fe^{2+} \sim Fe^{3+} > Mg > Na \sim Ca$, and the absorption of metal acetate is better than metal chlorides.

4.2.9.2 Catalytic Effect of Added Cations

Preliminary experiments established that cation loading increases linearly with increasing concentration of solution. The catalytic effect of major elements (Na, Ca, K and Ni) on the reactivity of coal was then determined. The concentration of the solution was selected to add approximately the same amount of element (e.g. Na, K and Ca) to the lignite as that in the original coal. Sodium chloride, sodium acetate and calcium chloride were used. To examine the catalytic effect of the different cations on reactivity, the CO_2 gasification behaviour of deashed lignite was selected as the basis for the comparison.

The results show that sodium, calcium and potassium are excellent catalysts for the gasification of Bowmans coal with carbon dioxide. ***Figure 4-18*** shows that these three elements exhibit strong catalytic effect. For coal impregnated in solutions of KAc, NaAc and $Ca(Ac)_2$ at a concentration of 0.3M, the gasification rates were found to be higher than for raw coal. All the acetates, except nickel acetate, exhibited strong catalytic effect. For all the catalysts used, the rate of catalysed gasification was 10 to 100 times faster than uncatalysed reaction. Alkali and alkaline earth metals exhibited similar catalytic effect.

It is notable that potassium only has the same catalytic activity as sodium and calcium in this work. Some investigators (Spiro et al. 1983 and Huhn et al. 1983), have reported that K is more active than Na and Ca. It is difficult to explain this difference, because the catalytic activity of catalyst depends on the particular experimental conditions such as reaction temperature, type of salt, concentration of solution and the interaction between catalyst and inherent minerals (Huhn, et al. 1983, Holstein et al. 1983, and Kasaoka et al. 1986). Among all these factors, reaction temperature plays an important role on the activation of catalyst. High temperature can cause melting and decomposition of added salt. The interaction between alkalis and inherent minerals may consume the artificially added catalyst. It is known that potassium may react with inherent minerals of coal to form inactive components and thus lose its catalytic activity (Kuhn et al.1983. Formella, et al. 1986). The acid-washed Bowmans coal has an ash content of 3% (mainly are Al and Si). Added potassium may react with Si and lose its catalytic activity.

The present results show that calcium has similar catalytic efficiency with alkali metals. Some publications (Haynes et al. 1974, Otto et al. 1979), have shown that Ca has less catalytic effect on coal gasification compared with K and Na. Reported results on the role of calcium are confusing. For example, in some cases, CaO was reported to be an effective catalyst, while in other cases Ca was found completely ineffective (Kayember et al. 1976). Calcium was considered as the most important inherent catalyst for the some U.S. lignites (Walker et al. 1983). The strong catalytic effect of calcium obtained in the present work can be attributed to the good distribution of Ca in coal and possibly the transformation from $Ca(CH_3COO)_2$ to $CaCO_3$ and from $CaCO_3$ into CaO at elevated temperature (Otto et al. 1983).

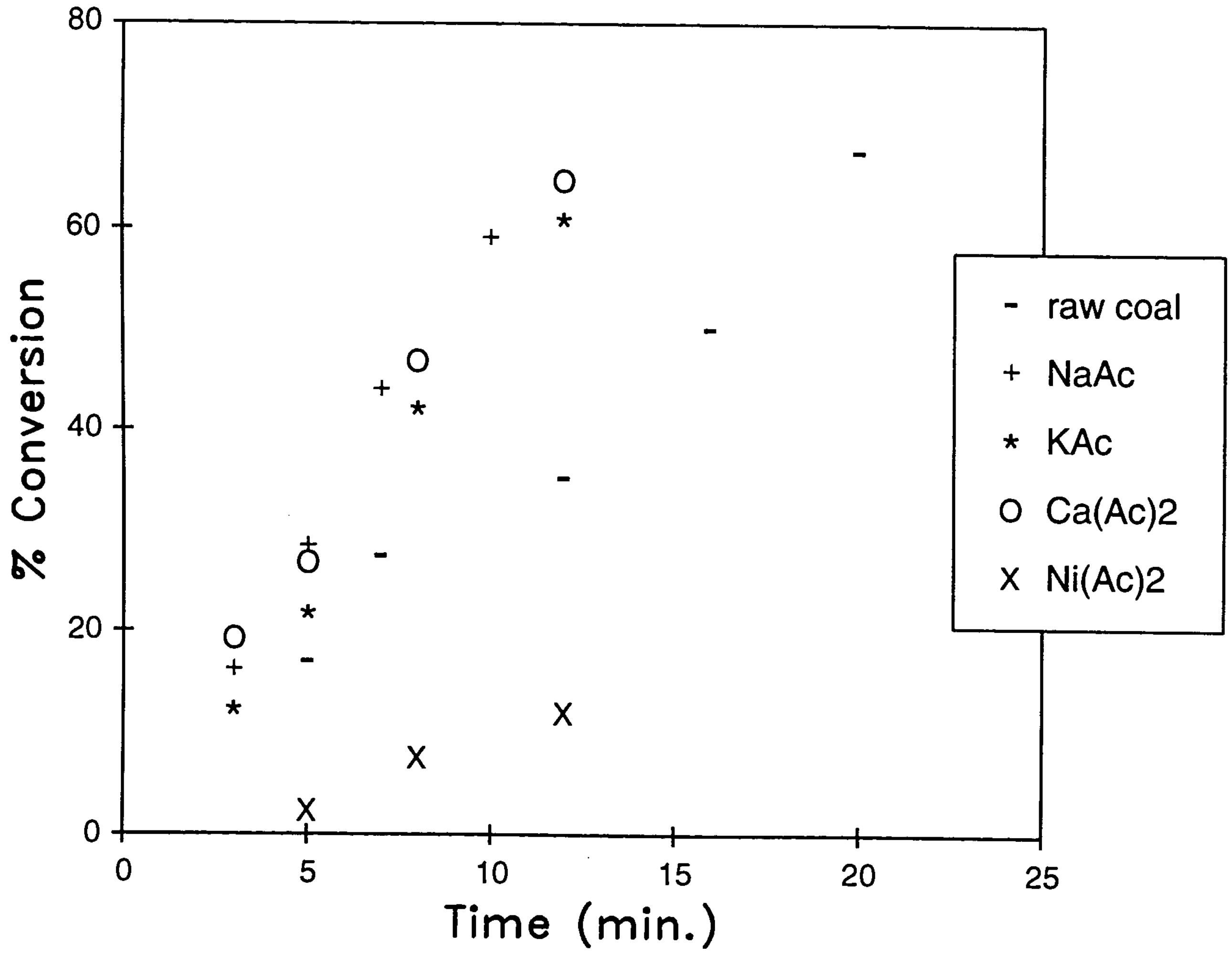


Figure 4-18 Gasification behaviour of raw and treated Bowmans coal with carbon dioxide (temp. 765℃, size 2.0~3.0mm, concentration 0.3M).

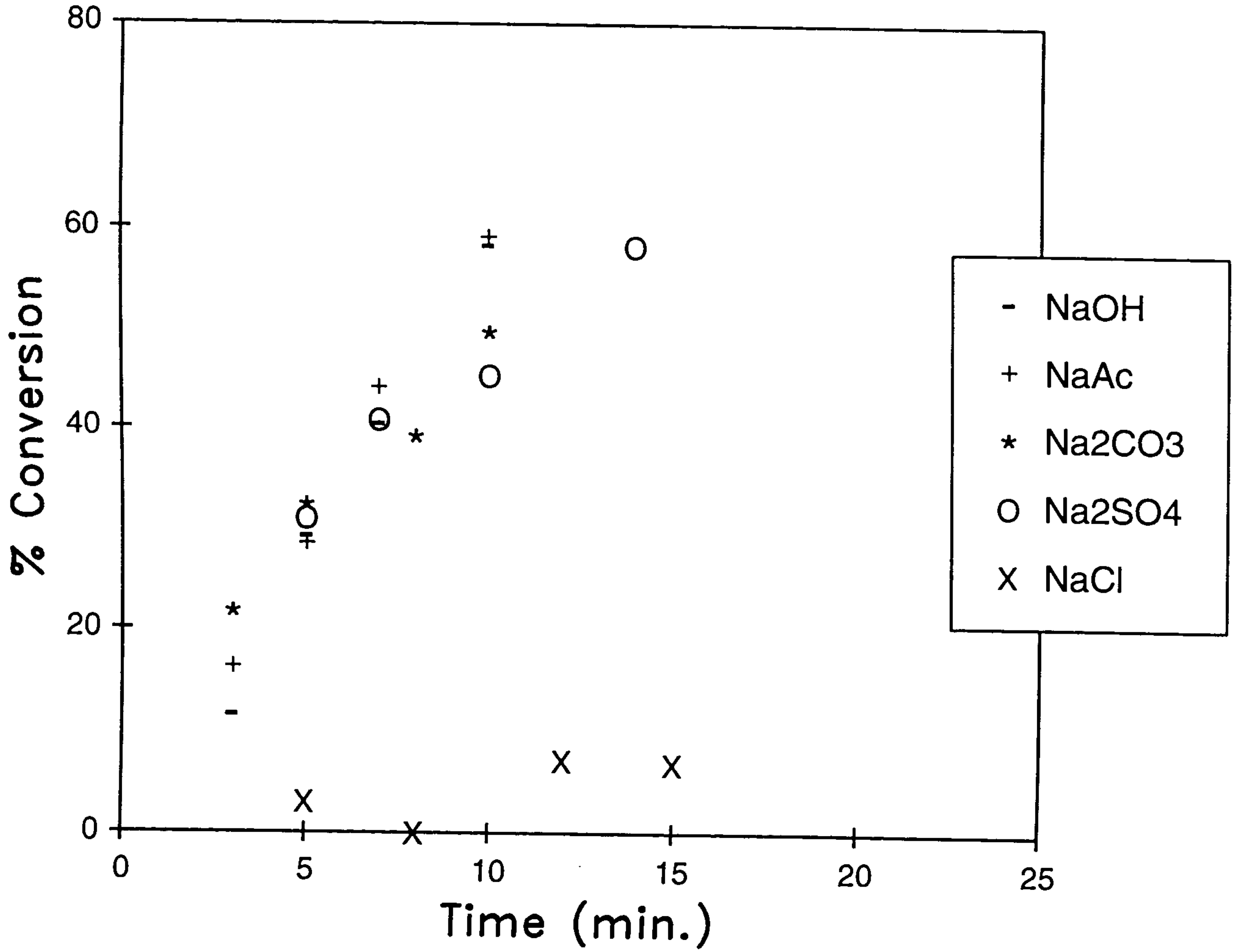


Figure 4-19 Gasification behaviour of treated Bowmans coal with carbon dioxide temp. 765°C, size 2.0~2.8mm, concentration 0.3M.

Table 4-12 Catalytic activities of salts in the gasification of Bowmans coal with CO_2

Added Salt	Concentration of Solution (M)	Reaction time (min.)	Reactivity (h^{-1})
NaAc	0.3	5	6.10
NaOH	0.3	5	6.01
Na_2CO_3	0.3	5	5.82
Na_2SO_4	0.3	5	3.46
NaCl	0.3	5	0.86
$Ca(Ac)_2$	0.3	5	5.01
KAc	0.3	5	5.50
$Ni(Ac)_2$	0.3	5	1.33
raw coal	-	5	3.06
demin. coal	-	10	0.21

Note: raw and demineralized coals were not impregnated in solution of salt.

Catalytic activities of alkali and alkaline-earth elements were also determined using other salts (e.g. chlorides and carbonates). Various alkalis were added to coal by impregnating demineralized Bowmans coal in the solution of chloride salt. It was found that alkalis, added as chlorides, have much lower catalytic activity than acetate salts, as shown in ***Figure 4-19***. The high catalytic activity of alkali acetate salts on C-CO_2 reaction can be attributed to the good dispersion of cations on coal and the association of these cations with carboxyl groups.

The significant catalytic activity of alkali and alkaline-earth metals in gasification has been widely reported (Hippo et al. 1979, Huhn et al. 1983, Spiro et al. 1983, McKee et al. 1983, Barthe et al. 1986, Hashimoto et al. 1986 and Joly et al. 1990). The enhancement of the reactivity of a U.S. lignite to CO_2 and steam by the addition of calcium was studied by Linares-Solano et al. (1986). They found that the reactivities were greatly enhanced, the reactivity increasing linearly with increasing Ca loading. Using wide-ranging catalysts and under varied experimental conditions, Spiro et al. (1983) showed that all alkali and alkaline-earth carbonates were effective catalysts for CO_2 gasification. Catalysts were added by physical mixing ranging from 2 to 25 % w/w. The reaction rates were 10 to 100 times faster than for uncatalysed reactions, depending on the amount of catalyst. The gasification rates were also found to increase linearly with increasing cation-to-carbon atom ratio for most alkali and alkaline-earth carbonates within low loading (less than 13% w/w).

It is known (Carrasco-Marin et al. 1991) that an important parameter which describes the behaviour of catalytic activity of metals is active site formation. The addition of catalyst to coal can be considered as the creation of active sites on the coal surface. Some hold the view that active sites occur where the particular carbon atom locates itself (i.e. edge, crystal site in the coal structure). Others (Carrasco-Marin et al. 1991) believe that active sites are the carboxyl functional groups associated with active metals on the surface of coal. Both of them agree that gasification reaction of coal only occurs at these active sites. Present results provide evidence to support this. The actual concentration of active sites may be determined by measuring the adsorption of gases on the surface of coal under various conditions. Some investigators (Hashimoto et al. 1988) reported that good correlations have been found between the gasification rate and oxygen or other gases trapped on coal and the metals added to coal. This study is not going to go through the definition of active sites and its argument. The present results suggest that active sites are the carbon atoms associated with oxygen-containing functional groups, particularly carboxyl group, associated with active metals.

4.2.9.3 Catalytic Effect of Nickel

Coal samples which were impregnated in the solution of $NiAc_2$ only slightly increased the gasification rates within the range of low carbon conversion, as shown in ***Figure 4-18***. ***Table 4-12*** shows the reactivities of the various salts examined. The present results indicate that nickel is a poor catalyst for gasification of Bowmans coal with carbon dioxide, its catalytic activity being much lower than alkali and alkaline-earth metals.

In contrast, some investigators reported that nickel exhibits a strong catalytic effect on gasification at low temperatures (<700°C). A possible reason for the discrepancy is that nickel could have lost its activity at the reaction temperature (765°C) used in the present study conditions. Nickel is reported as having a strong catalytic activity in the temperature region from 500 to 750°C (McKee,1981). Nishiyama (1986) indicated, however, that nickel was active only over two temperature regions, one is between 400 to 700°C and the other above 800°C. Tomita et al. (1983) also found that nickel catalyst exhibited an extremely high activity in the gasification of some lignites (e.g. Yallourn coal) at temperatures as low as 500°C. Conversely, investigators (Yamada et al. 1983) reported that nickel was inactive for $C-CO_2$ reaction under normal gasification conditions.

Spiro et al. (1983) reported that $NiCO_3$ was totally inactive for coal gasification with carbon dioxide. Marsh and Rand (1971) found that nickel ($Ni(NO_3)_2$) had limited catalytic effect and beyond 16% carbon conversion it was no longer active. They concluded that nickel loses its catalytic efficiency by converting from metallic to oxidized form. The behaviour of nickel acting as catalyst during gasification appears to be similar to iron.

Another possible reason for the low catalytic efficiency of Ni could can be that the nickel was used alone. Some investigators indicated that nickel can only exhibit a significant catalytic activity when it was combined with other metals such as Ca and Fe (Haga and Nishiyama 1983). Nishiyama (1986) proposed that some metals such as Ca and Fe, enhance the interaction between nickel and carbon.

4.2.9.4 Effect of Anion on Catalytic Activity

To examine the influence of anion on the catalytic activity of cation, sodium acetate, sodium chloride, sodium sulphate, sodium carbonate and sodium hydroxide were used as the impregnation salts. Acid-treated Bowmans coal was impregnated in the solutions of these sodium salts. ***Figure 4-19*** shows that NaAc, Na_2CO_3 and NaOH exhibit strong catalytic activities, with small difference between the three. The order of reactivity is NaOH > Na_2CO_3 > NaAc. Sodium hydroxide, sodium acetate and sodium carbonate are much more active than sodium chloride. The sodium sulphate has slightly less catalytic activity, while, sodium chloride has almost no catalytic effect on gasification. For all the catalysts used, the sequence of catalyst activity is NaOH ~ NaAc ~ Na_2CO_3 > Na_2SO_4 > NaCl.

These results are in agreement with published results from other investigations. Kuhn et al. (1983) reported that alkali cations exhibit catalytic effect only when the elements are present in the form of certain salts, in which, carbonate and acetate salts have been found to show strong catalytic effect. Vera and Bell(1978) also found potassium exhibits strong catalytic activity in the form of KOH and K_2CO_3; KCl had a much lower activity. Lang (1986) pointed out that alkali salts of weak acids are good catalysts for gasification, while the alkali salts of strong acids are poor catalysts. Similar work had been conducted by Huttinger and Minges (1986) to examine the influence of potassium catalyst precursor anion on steam gasification. They found that the anion of the catalyst "precursor" controls the catalytic activity of potassium. For all the potassium salts used, the sequence of catalytic activity was found to be $KOH \sim K_2CO_3 \sim KNO_3 > K_2SO_4 > KCl$. They further indicated that the sequence of catalyst activity is independent of the gasification medium (e.g. carbon dioxide or steam). Similar results were also reported by Hashimoto and co-workers (1986), in which, the reactivity of coal in steam was measured by the TGA method. Metal salts as K_2CO_3, KOH, KNO_3 K_2SO_4 and Na_2CO_3 were found to greatly accelerate the gasification with steam over the total process, while the catalytic effects of KCl and NaCl were much lower. Initially, NaCl and KCl did not show any catalytic effect, but their reactivity increased gradually as reaction proceeded.

The present results show that sodium acetate has higher activity than sodium carbonate (***Figure 4-19***), but the difference between these two catalysts is small. This behaviour is difficult to explain. One reason is that the anions may influence the distribution of sodium in coal. Because sodium acetate is more soluble than sodium carbonate, therefore it could achieve better distribution of Na in coal during impregnation. Temperature can also influence the catalytic activity of added cation. The reaction temperature of 765°C is lower than the melting point of most selected cation salts. The present results also show that sodium sulphate is more active than sodium chloride. The activity of Na_2SO_4 is difficult to explain since both NaCl and Na_2SO_4 are strong acid salts. A possible explanation is that the anion also participates in some chemical reactions during gasification. Another possibility is that the sulphate may be reduced to a weak-acid such as sulphide under gasification conditions. Na_2S has been reported to be a good catalyst for the gasification (Lang 1986).

Figure 4-19 also shows that sodium hydroxide exhibits catalytic activity similar to carbonates and acetates. This phenomenon can not be explained by the weak/strong acid theory. The chemical property of OH^- differs from that of Ac^- and CO^{2-}. Huttinger and Minges (1986) found that alkali hydroxide was the key component in the activation of all alkali salts.

From the above discussion we can conclude that alkali and alkaline-earth compounds such as carbonates, acetate and hydroxide exhibit strong catalytic effect on gasification, while sulphate salts also have catalytic effect (Huttinger and Minges 1986, Lang 1986). The catalytic activity of chloride salts is much lower than weak acid salts. The mechanisms for the activation of alkali carbonate and hydroxide have been well studied, but the reason for the low catalytic efficiencies of alkali chloride are not clear. Anions are believed to participate in some chemical reactions rather than acting only as a cation carrier.

4.2.9.5 Effect of Thermal Treatment on Activation of Cations

Thermal treatment causes the loss of carboxylic functional groups. Acid-washed Bowmans coal samples were maintained at 600°C, under nitrogen atmosphere to remove all the organic acid groups (as suggested by Laurendeau, 1978).

Experiments were carried out on the thermally-treated coal samples to compare activities of the catalysts added to the original and thermally-treated coal samples. The same amounts of $Ca(Ac)_2$ and NaAc were added to both original deashed and thermally-treated deashed coal samples. The results are shown in ***Figure 4-20***. It is seen that, for the heat-treated coal samples (chars), the added cations do not exhibit any significant catalytic effect. The gasification rate of the catalysed heat-treated coal sample is almost equal to that for uncatalysed demineralized samples. The obvious explanation for this phenomenon is the loss of carboxyl functional groups. Added cations can not then be chemically associated with surface groups to form active sites. For the heat-treated coal, added cations are only physically adsorbed by coal.

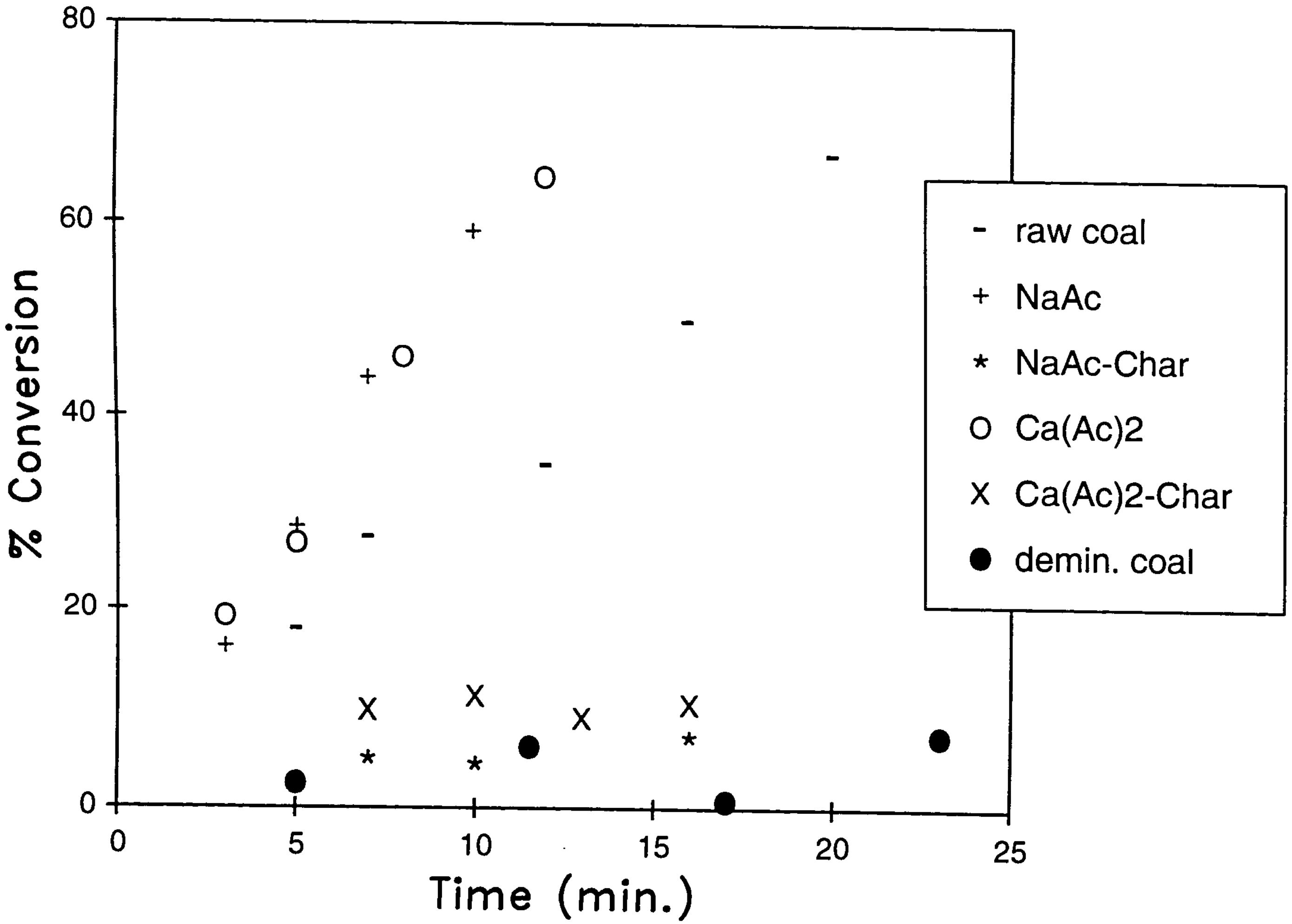


Figure 4-20 Gasification rates of different coal samples with carbon dioxide at 765°C, char is heat-treated coal, (size 2.0~2.8mm, concentration 0.3M).

Carboxylic functional groups therefore play a critical role in catalysed gasification of coal because they provide locations for cation-exchange to form active sites. Low-rank coal is more sensitive to catalyst loading than high-rank coal because low-rank coal contains high concentrations of carboxyl functional groups (Nishiyama 1986). The main role of surface functional groups, then, is to provide the sites onto which catalyst can deposit.

There is a strong influence of thermal treatment on coal surface. It is well known that char is more porous than parent coal (Tomkow et al. 1977). The charring process increases surface. As indicated by many investigators (Laurendeau 1978, Walker 1981), increasing surface area brings about increasing coal/char reactivity. Results of this work indicate that the chemical interaction between active metal and oxygen-containing functional groups is the crucital factor, while, the surface of coal/char has minor importance.

4.2.9.6 Kinetics and Mechanisms of Catalytic Gasification

When catalysts are added to acid-washed coal, the gasification behaviour is strongly influenced by the type and amount of catalyst loading. ***Figure 4-18*** shows the carbon conversion at 765°C as a function of gasification time *t*, catalysed by NaAc, KAc and $CaAc_2$. The carbon conversion increases linearly with reaction time, indicating apparent reaction order of zero with respect to carbon (see ***Equation 2.7.6***). This can be attributed to the high mobility of alkali metals on the coal surface (Mins et al. 1983). As previously discussed the kinetic model of gasification varied depending on the nature of the added cations. The addition of Na and K resulting a zero order reaction (Miura et al. 1986, see **Section 2.7.6**). The present results are in agreement with the results obtained by Klein et al. (1983), who found that the kinetics of alkali-catalysed gasification of a bituminous coal is changed from a first-order reaction to zero-order reaction.

Compared with non-catalysed gasification, catalytic gasification sometimes exhibits irregular and far from simple rate pattern. This can be explained by reaction between catalyst and inherent minerals which results in the deactivation of the catalyst. ***Figure 4-29*** (see **Section 4.3.3**) shows that, for the Ni-catalysed H_2O gasification, the reaction rate was initially high but decreased as the reaction progressed. This phenomenon can be explained by the variation of nickel catalyst during gasification. Similar results have also been reported by other investigators. For example, Nishiyama (1986) concluded that the '*normal pattern* 'of catalytic gasification is large initial reaction rate decreasing monotonously as the reaction proceeds. Linares-Solano et al. (1986) pointed out that most of carboxyl groups in coal undergo exchange of their hydrogen by cations during catalyst loading. Heating the coal to the gasification temperature, the carboxyl groups decompose and form well dispersed M_xO_y on the surface of coal. CO_2 or other reactant gases are chemisorbed on the these M_xO_y sites.

Many investigators (McKee 1982, Klein et al. 1983, and Linares-Solano et al. 1986) agree that, during gasification, alkali catalysts are involved in chemical changes including oxygen or electron transfer. Results from this work show that alkali hydroxide exhibits similar catalytic activity to alkali carbonates. This behaviour can not be explained by the degree of exchange between hydrogen and cation on the carboxyl groups. Since Na_2CO_3 is only a weak acid salt, but NaOH is a strong base, the use of NaOH solution for catalyst loading achieves a higher level of cation-exchange between Na and H^+ than Na_2CO_3. The possible reason is that sodium hydroxide participates in the catalysed reaction in a different way from that of sodium carbonate. The chemical sequences for sodium carbonates and sodium hydroxide during the gasification may be expressed as:

for Na_2CO_3:

$$Na_2CO_3 + C = Na_2O + 2CO \tag{4.2.28}$$

$$Na_2O + CO_2 = Na_2CO_3 \tag{4.2.29}$$

for NaOH:

$$2NaOH + 2C = 2Na + 2CO + H_2 \tag{4.2.30}$$

$$2NaOH + C = 2Na + CO_2 + H_2 \tag{4.2.31}$$

Other alkali and alkaline-earth metals such as potassium and calcium catalyse the coal gasification in a similar manner (Huttinger et al. 1986).

Using other salts (e.g. NaCl, $CaCl_2$, $NiAc_2$, NiCl, KCl) as catalysts, the gasification rate increases, but does not show a linear correlation between conversion X and reaction time t. The cations from these salts have much lower catalytic activities than other salts (e.g NaAc). The low efficiencies of chloride salts on the gasification can be attributed to insufficient cation-exchange with carboxyl groups. It implies that the kinetics of catalysed gasification is determined by the properties of the loaded metals and the amount of carboxyl groups which are occupied by cations on the surface of coal.

In the present study, the behaviour of catalysed gasification of coal, as a result of loading with various catalysts, showed irregular reaction pattern. With the loading of the weak acid salts such as sodium acetate and potassium carbonate, the gasification reactions show almost zero order with respect to carbon conversion. For Ni-catalysed gasification, the reaction rate was high at the beginning but decreased as reaction progressed, perhaps due to the reduction of catalyst efficiency. It indicates that rate of catalytic gasification is controlled by the amount and status of catalyst. A general kinetic description of the process of catalytic gasification is beyond the scope of the present study.

In summary, according to the results obtained from this work, the factors causing reduced catalytic activity are: (1) the changes of chemical state of the catalyst (e.g. the reduction of Ni or poisoning by sulphur); (2) the dispersion of catalyst in coal; (3) the amount of catalyst (e.g. potassium consumed by reacting with minerals to form inactive K-containing components); (4) the change in nature of coal (e.g. the amount of carboxyl groups).

Based on the results obtained from present study, the mechanism of catalysed gasification can be summarized as:

- active cations (e.g. Na, K and Ca) associate with carboxyl groups to form active sites on the surface of coal, in which cations act as catalysts for gasification;
- the catalyst participates in some chemical limited reactions by transferring oxygen or electrons during the gasification, which involves absorption of gas and desorption of product;
- the catalyst may create active carbon atoms by perturbing the electronic structure of carbon; or by dissolving carbon into a surface catalyst phase (Spiro et al. 1983), and by forming surface compounds;
- the catalytic activities of added cations depend upon the properties of added metals and the extent of connection between cation and carboxyl groups.

4.3 STEAM GASIFICATION

Experiments for the gasification of Bowmans coal with steam have been conducted at temperatures ranging from 708 to 810°C, particle sizes from 1.6 to 4.1 m, and atmospheric pressure. To compare steam with CO_2 gasification, the experimental conditions were generally kept the same as for CO_2. Investigations of steam gasification also involved using water-leached, acid-washed and catalysed coal samples, although kinetic studies were only carried out for raw coal. Emphasis was given to catalytic gasification in which alkali and alkaline-earths were used.

4.3.1 Kinetics

A number of studies have been conducted to investigate the kinetics of the gasification of Bowmans coal with steam. The reactivity of coal with steam is reported to be higher than that with carbon dioxide under the same experiment condition (Katta et al. 1981 and Ergun 1962). This can be attributed to the difference in nature of $C\text{-}CO_2$ and $C\text{-}H_2O$ reactions.

Preliminary experiments were conducted to measure the initial reactivity of Bowmans coal with steam (size 1.6~2.4 mm and temperature of 756°C) for comparison with that obtained for $C\text{-}CO_2$ gasification (***Figure 4-21***). It indicated that the gasification rate of Bowmans coal with steam is higher than with carbon dioxide under current experimental conditions. The initial rate constant of the $C\text{-}H_2O$ reaction is about 3 times higher than that for the $C\text{-}CO_2$ reaction at 765°C, in which r_{CO2} is 0.034 min^{-1} and r_{H2O} is 0.1 min^{-1}. This is in good agreement with the results obtained from other investigations (Johnson 1981, Datta et al. 1981 and Tomita et al. 1986). Ergun (1962) explained the difference in the rates for these two reactions as being due to a greater number of reaction sites being generated by steam than by CO_2.

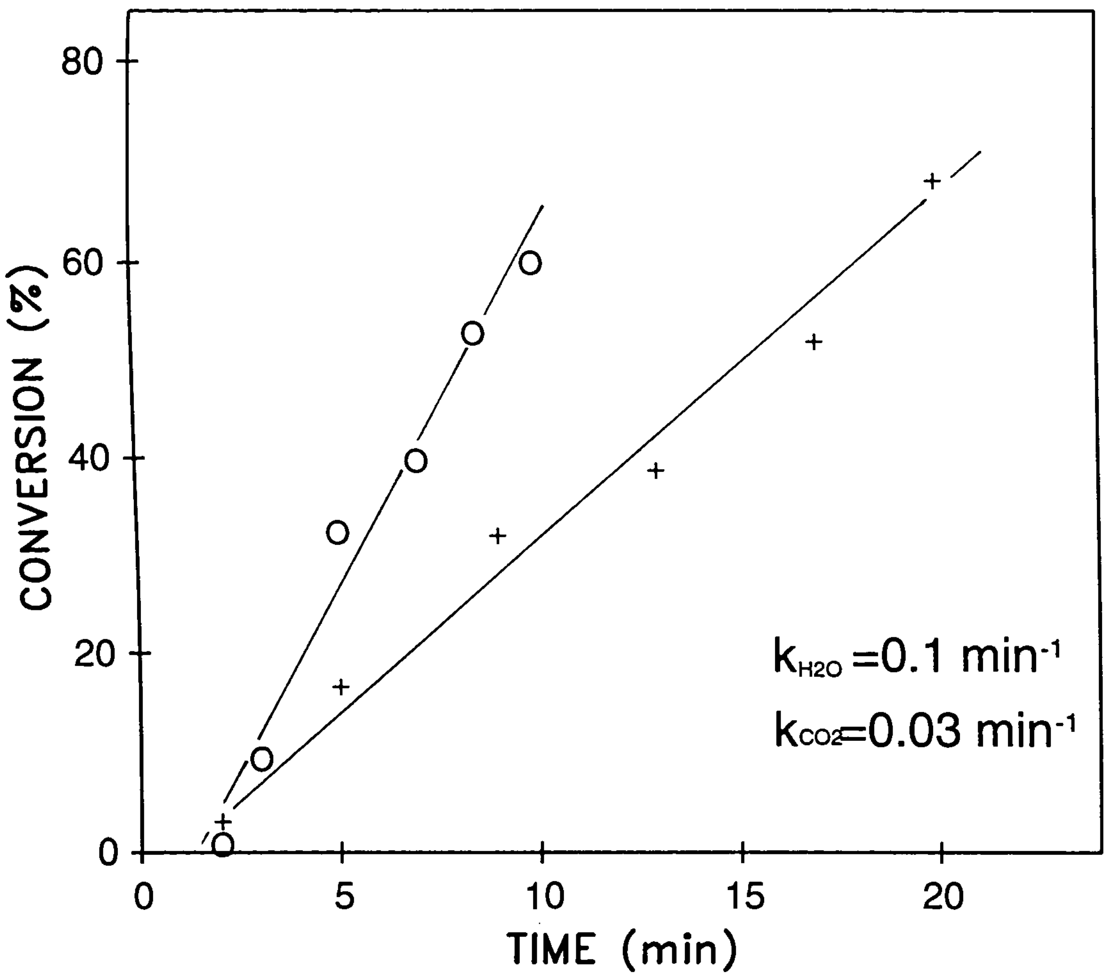


Figure 4-21 Comparison of gasification conversion of Bowmans coal with steam (o) and carbon dioxide (+), (temp. 765°C, size 1.6~2.4 mm).

4.3.1.1 Effect of Temperature

The rate of gasification of coal with carbon dioxide and steam is dominated by chemical reaction at low temperature, e.g. Riley and Judd (1987) indicated chemical reaction rate control at temperatures up to 1000°C. In the present investigation, reaction temperatures were kept below 900°C. The temperatures were 708, 765 and 810°C. It has been shown that for temperature less than 810°C, the effect of intraparticle diffusion on gasification rate can be neglected (Chin et al. 1987). ***Figure 4-22*** illustrates the profiles of carbon conversion versus time at different temperatures. It is seen that the gasification of Bowmans coal with steam is very sensitive to the temperature. The times required to achieve 50% carbon conversion were 18, 8 and 4 min. at the temperatures of 710, 765 and 810°C, respectively. The measured values of initial first-order reaction rate constants are 3, 8 and 17 at the same respective temperatures. This high dependence of gasification rate on reaction temperature is similar to that for carbon dioxide gasification.

The influence of temperature on C-H_2O reaction has been widely investigated (Miura et al. 1986, Hashimoto et al. 1987 and Kwon et al. 1989). The conclusion from most investigations is that the overall rate to be chemical-reaction rate-control at low temperature (<900°C) and becomes diffusion-control at high temperature (>1200°C). Ruan et al. (1987) examined the steam reactivity of coal under various conditions using a Chinese bituminous coal. They concluded that the rate measurements were made at the chemical reaction controlling regime (0.6~4 mm particle size and 700~900 °C). They found that the rate of C-H_2O reaction was very sensitive to temperature, doubling for every 50°C increase. Similar behaviour was also found for the gasification of alkali-catalysed coal.

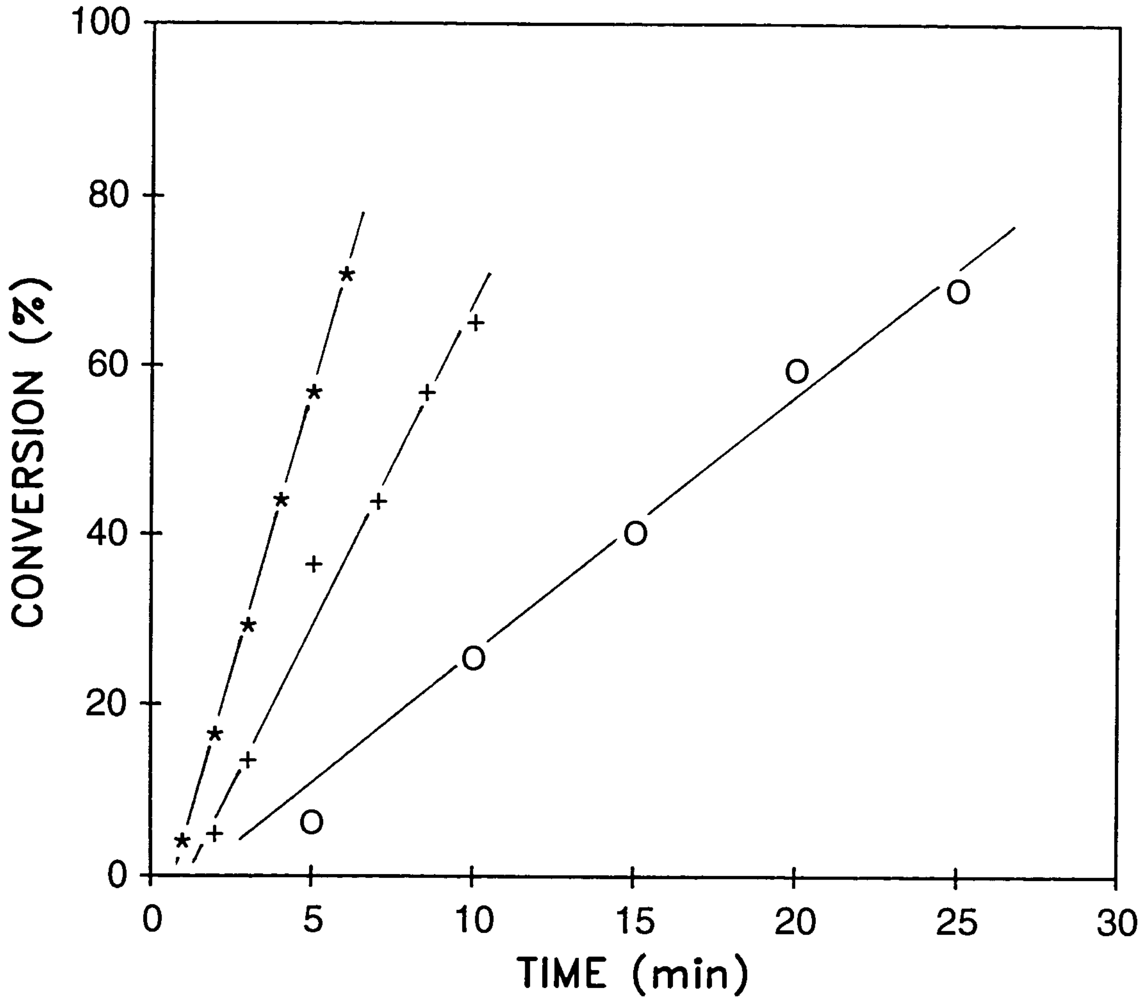


Figure 4-22 Comparison of gasification conversion of Bowmans coal with steam at various temperatures, (*: 806, +: 765, o: 710°C, size 1.6~2.4mm).

4.3.1.2 Activation Energy

Experimental data were analysed using a first-order reaction rate equation. Initial reaction rate constant k, was used to evaluate the activation energy E_a. ***Figure 4-23*** shows the Arrhenius plot over the range 705-810°C. The activation energy estimated for gasification is 131 kJ/mol. This result is in reasonable agreement with values for lignite gasification obtained by other investigators. Mahajian et al. (1986) reported activation energies between 120 to 250 kJ/mol depending on the rank of coal; for low-rank coal, values ranged from 120 to 210 kJ/mol.

Numerous results (Tomita et al. 1986, van Heek et al. 1986 and Hashimoto et al. 1989) indicate that not only the reactivity of C-H_2O reaction but also its activation energy is affected by the presence of Na and Ca. High rank coals, which have low reactivity, have relatively high activation energies ranging from 180 to 260 kJ/mol. In summary, we can conclude that, for Bowmans coal, the presence of high concentrations of inherent alkalis causes the low activation energy and high gasification rate.

Other factors such as temperature, size, amount and composition of mineral also have some influence on the activation energy. In general, high-rank coal has lower reactivity and higher activation energy than low-rank coals. At higher temperature, the influence of intraparticle diffusion and film diffusion become important and the observed activation energy decreases. The activation energy can also be influenced by the process of demineralization in which the catalytic effect of inherent minerals is eliminated. Knight et al. (1988) found that the activation energies of gasification increase from 124 to 154 kJ/mol by washing raw coal with HCl. Other investigators reported similar results (Kohn et al. 1986). These matters will be examined in subsequent sections.

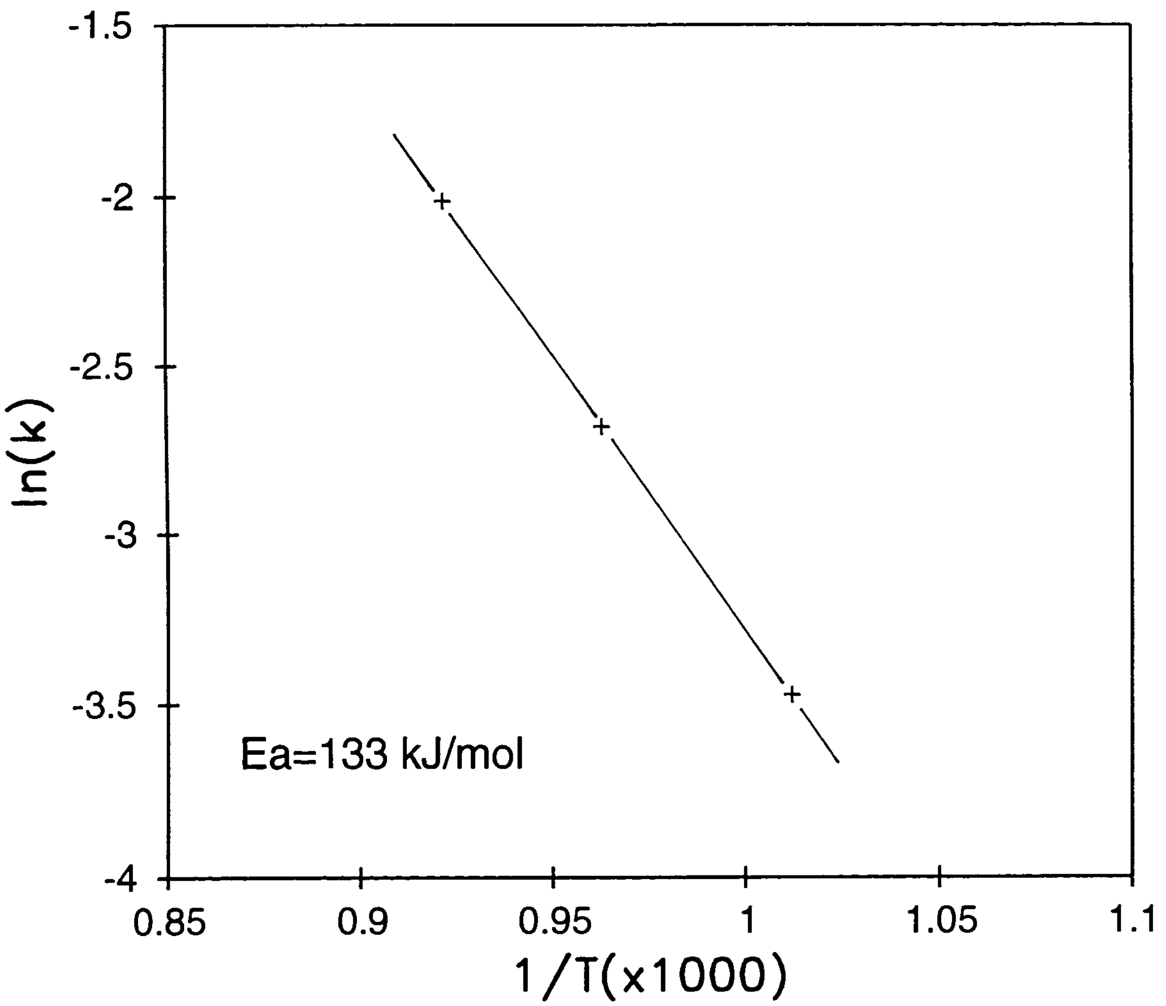


Figure 4-23 Arrhenius plots of reaction rate constants of gasification of Bowmans coal with steam (size 1,6~2.4mm).

4.3.1.3 Effect of Particle Size

The effect of coal particle size on the gasification rate of raw Bowmans coal with steam was investigated using two size fractions, 1.6~2.4 and 2.4~4.1 mm, at 765°C. ***Figure 4-24*** shows the comparison of the plots of the carbon conversion *X* against reaction time *t* for both two size fractions. It is seen that there is no significant difference for the gasification behaviour between these two sizes, confirming the earlier finding for C-CO_2 gasification (**Section 4.2.5**) that gasification rate is not influenced by diffusional effect in the temperature studied.

Other investigators (Datta et al. 1981, Katta and Keairns 1981) reported Kasaoka et al. (1989) examined the steam gasification of coal of different particle sizes fractions (0.5 mm, 1.0 mm and 2.0 mm) and found that the rate of gasification was independent on the particle size at temperatures less than 1000°C; the gasification rate decreased with increasing the particle size at a temperature of 1400°C. Other researchers reported that the gasification rate was significantly influenced by the particle size at high temperatures. For example, Kasaoka et al. (1988) found that the rate of gasification of coal with steam decreased with increasing particle size at 1400°C, for which they explained that intraparticle diffusion was the rate controlling step. Most investigators agreed that the gasification of lignite with steam is independent of particle size in the low-temperature chemical-reaction-controlling regime and is influenced by particle size in the high temperature regime.

As previously discussed for C-CO_2 reaction (see **Section 4.2.5**), increasing particle size result in a decrease in overall reaction rate if intraparticle diffusion is significant. In the low temperature region (less than 850°C), the reaction rate is relatively low and the effect of diffusion can be ignored.

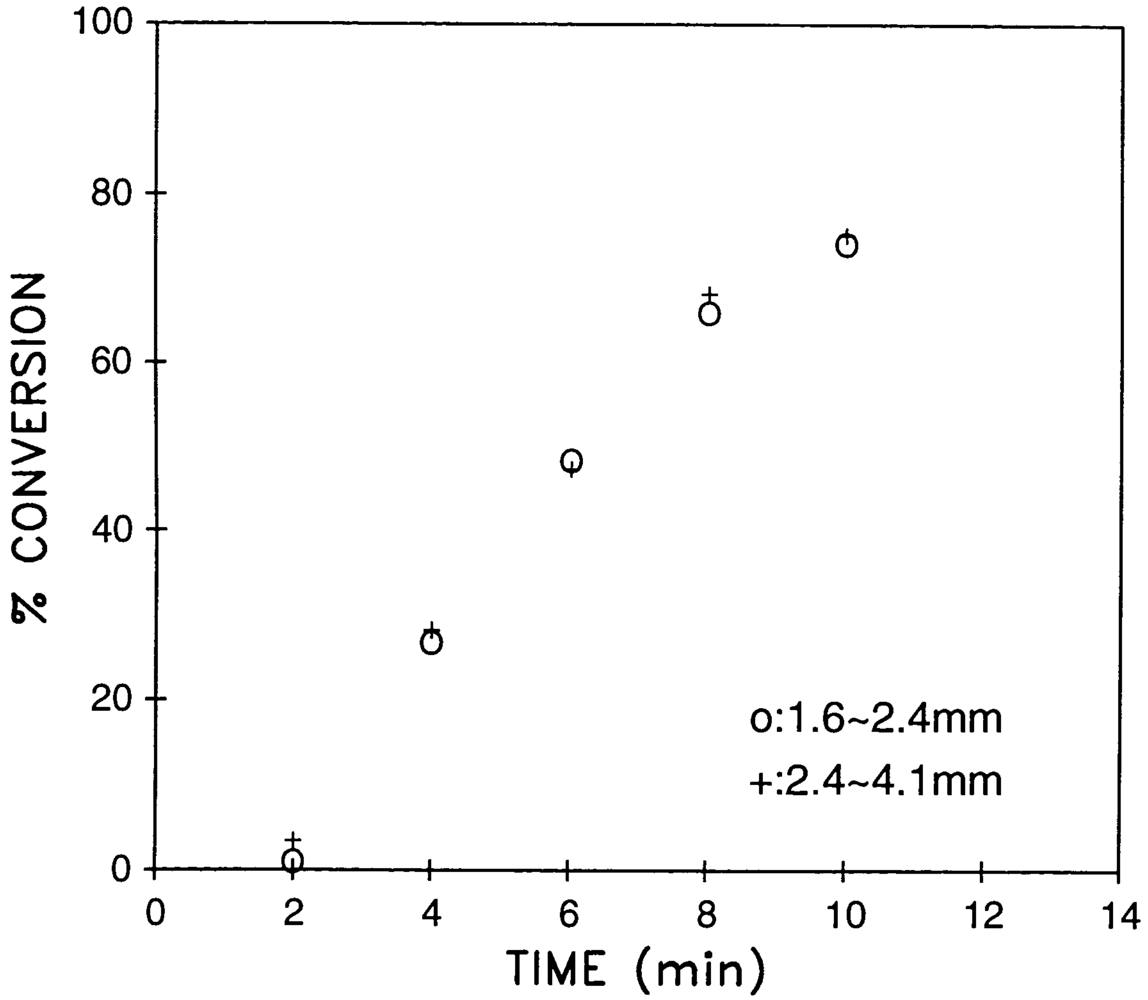


Figure 4-24 Fixed carbon conversion vs. time for steam gasification of raw Bowmans coal at 765°C for two particle sizes

4.3.1.4 Correlation of H_2O Gasification

Since the experiments for steam gasification were carried out at different temperatures and for different particle sizes it is necessary to verify whether all these reactions followed the same reaction mechanism, because increasing reaction temperature and coal particle size may change the overall process from the chemical-reaction control transfer to the mass transfer control. The dimensionless reaction time $t^*=t/\tau_{0.5}$, which had previously been used to correlate the experiment data for the C-CO_2 reactions, was again employed to clarify the mechanism of C-H_2O reactions in the present investigation.

Figure 4-25 shows the relationship of fractional carbon conversion X against t^* of different models together with experimental data for raw Bowmans coal obtained under various experimental conditions, viz. different reaction temperatures and particle size fractions. This result is similar to that obtained for the C-CO_2 reaction. The Homogeneous model, Shrinking-Core model with assumption chemical reaction rate-control and Shrinking-Core model with film-diffusion control, all fit the data reasonably well. This is similar to the results for CO_2 gasification. Unlike CO_2 gasification, experimental data for steam gasification were also close to the Shrinking-Core model for film diffusion control. The possible reason for this is that the C-H_2O reaction is faster than C-CO_2 reaction under the same conditions. So that film diffusion may affect the overall rate. Due to the equipment limitation, experiments at high fixed-carbon conversion (X>75% w/w) could not be conducted. Other investigators made similar observations. Kasaoka et al. (1988) reported that, in the chemical reaction controlling regime (<1000°C), all the experimental data obtained from different coals were found to be correlated with a single curve. For that, they explained that all the coals were gasified according to the same mechanism. Other investigators (Levenspiel 1980, Fernandez-Morales et al. 1985) gave similar explanation for such behaviour.

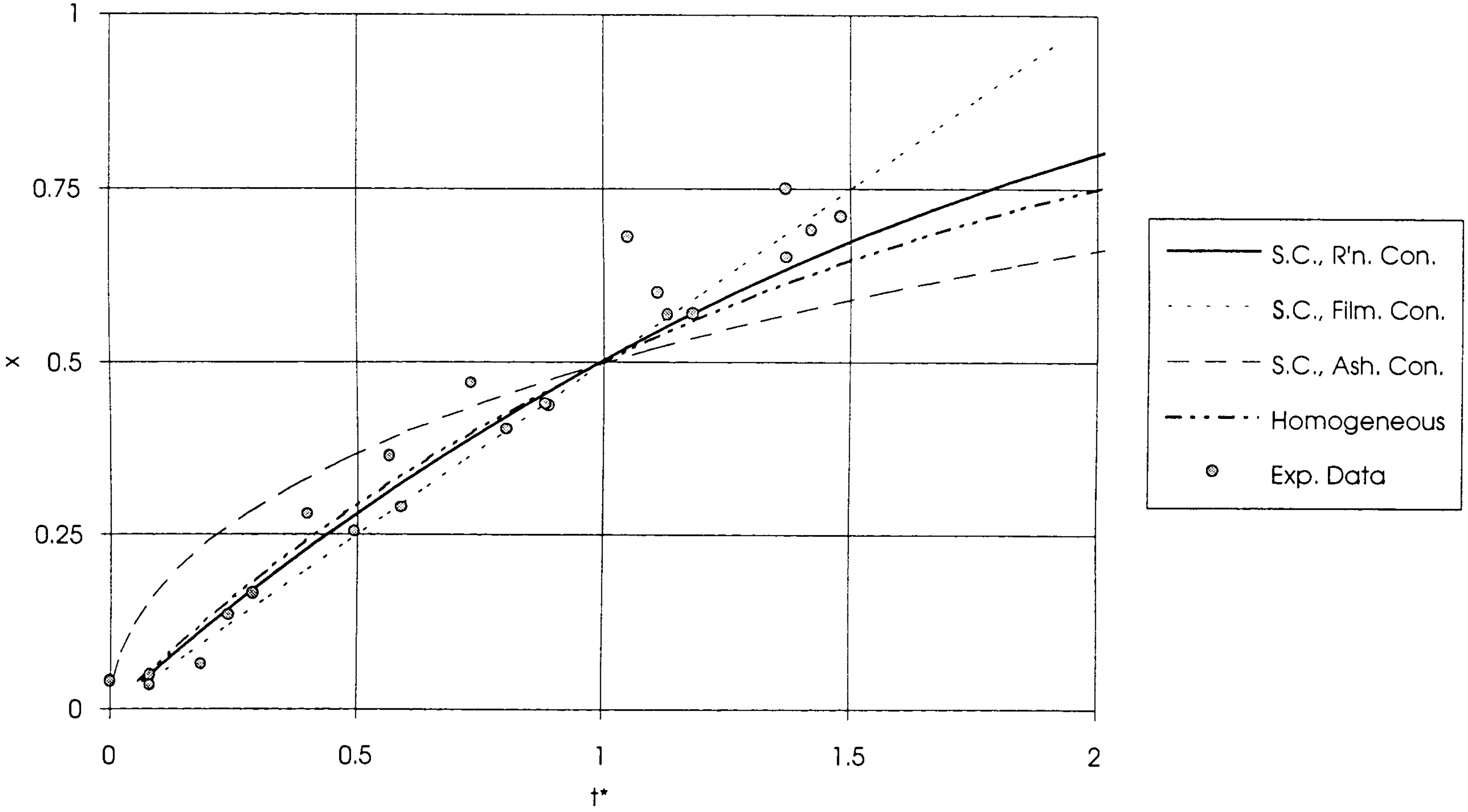


Figure 4-25 X - t* relationship for different models together with experimental data for steam gasification of raw Bowmans coal

4.3.2 Effect of Demineralization

4.3.2.1 Acid-Washing

Experiments have also been conducted to investigate the role of inherent minerals in the gasification of Bowmans coal with steam. Most of these studies involved demineralization by treating raw coal with HCl. All experiments were carried out at 765°C and for 1.6~2.4mm particle size fraction. For the steam gasification of acid-washed lignite, plots of fractional carbon conversion *X*, against time *t* are shown in ***Figure 4-26***. It can been seen that the gasification rate is greatly decreased by acid treatment. The gasification conversion for demineralized coal sample is much lower than that for the raw coal. It suggests that the gasification of Bowmans coal with steam is catalysed by the inherent active minerals. The high reactivity of Bowmans coal with steam can be attributed to the presence of active minerals in the raw coal.

The catalytic effect of inherent minerals on the gasification of coal with steam has been widely reported (Mahajian et al. 1979, Fung et al. 1983, McKee and Spiro et al. 1985 and Riley et al. 1987). The results from other investigations have established that alkali, alkaline-earth and transition metals are the most effective catalysts. For example, Kopasel et al. (1990) studied the catalytic effect of the ash compounds of lignite on steam gasification and found that the gasification rate of ash-containing lignite was 30-50 times higher than that for the demineralized coal. Other investigators reported similar results (van Heek et al. 1988, Miura et al. 1988). Most researchers believe that the inherent cations Na, K and Ca act as catalysts for steam gasification. The rate of gasification is proportional to the concentration of active sites. Acid-washing results in the removal of these active cations from the surface of coal. Decreasing the number of active sites greatly decreases the reactivity of coal.

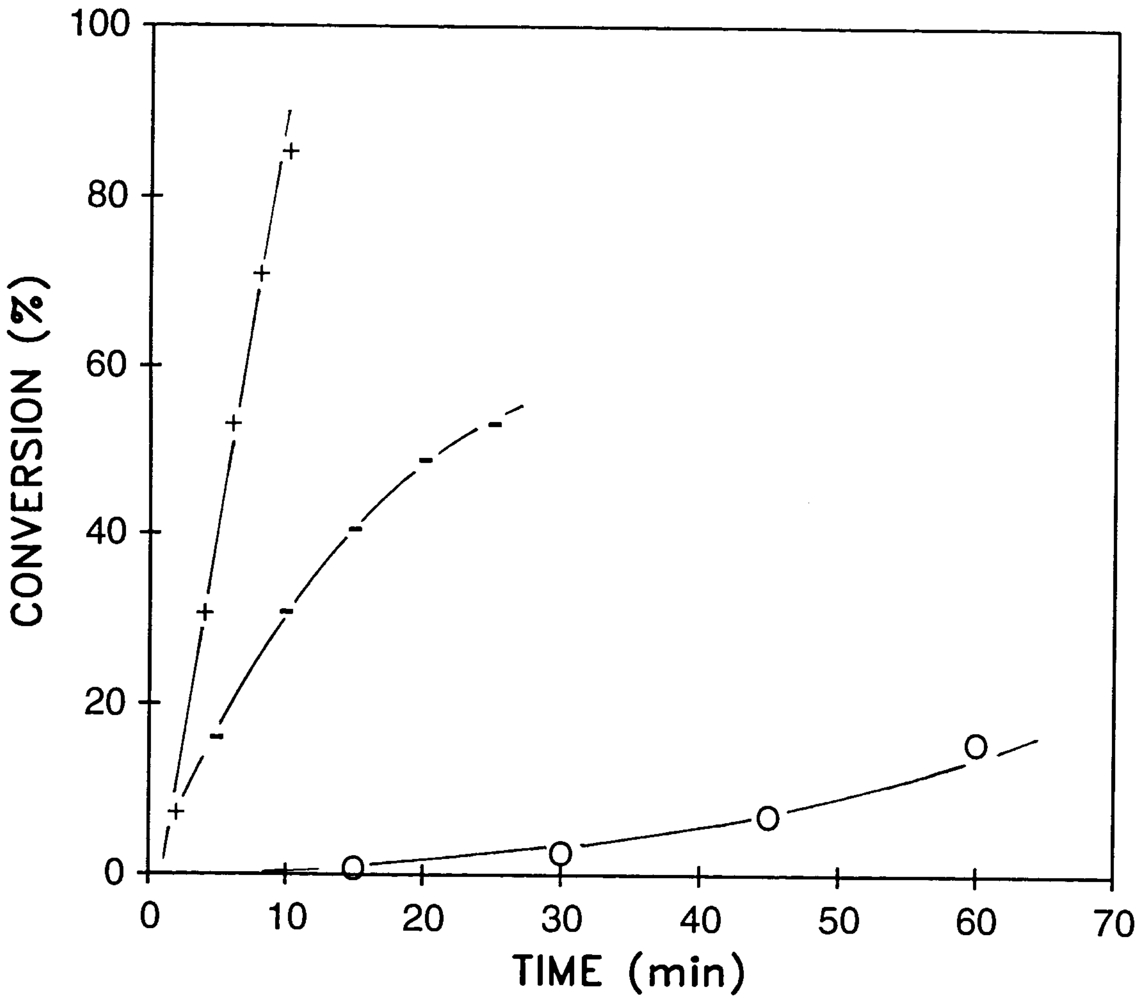


Figure 4-26 Comparison of steam gasification conversion of raw (+) water-washed (-) and acid-washed (o) coal samples. (temp. 765℃, size 1.6~2.4 mm)

Demineralization may affect the surface area of the raw coal, which may have some influence on its reactivity; however it is recognized that changing surface area has a minor effect on the reactivity compared with loss of catalyst.

4.3.2.2 Water-Washing

Bowmans coal (size 1.6~2.4 mm) was washed with water to remove the water-soluble salts. The effect is shown in ***Table 4-11*** (see **Section 4.2.8**). As discussed in **Section 4.2.8**, water-leaching removes approximately 50% of the total minerals. Most sodium in Bowmans coal is present in the form of NaCl and 83% of the total sodium can be removed by water-washing. Other cations such as Ca, K, Fe, Mg and Al, are not as soluble and only smaller amounts can be removed by water washing.

The gasification of the water-washed coal samples with steam was conducted at 765°C. The results are compared with raw coal in ***Figure 4-26***, which indicates that water-leaching has a more significant effect in reducing steam reactivity than on CO_2 reactivity.

Water-washing removes cations which are not associated with the carboxylic functional groups of coal. Organically bonded cations are not affected by the process of water-washing. After water-leaching, considerable amounts of active metal elements still remain in the coal, and they exhibit significant catalytic effect. Similar to the effect of water-washing on the C-CO_2 reaction, the influence of water-washing on the process of steam gasification is small compared to acid-washing.

The ash analysis shows that, for the water-washed coal samples, the mole ratio of metal/carbon for Na, Ca and Fe are 0.013, 0.010 and 0.017, respectively. This level of metal/carbon ratio is high enough to exert significant catalytic effect on the gasification process (Bruno et al. 1986).

Na and Ca are the major elements which catalyse the gasification of water-treated coal with steam. Fe, in the metallic form, has also been reported to exhibit strong catalytic effect on C-H_2O reaction. Manzoori (1990) reported that, in S.A. Lochiel lignite, there is a considerable amount of inherent Fe presented as organic salt of Fe^{++}. Due to the lack of information on the chemical form of iron in Bowmans coal, the role of Fe on the catalytic activity of minerals is not established. Magnesium is another major element which remains in the water-leached coal. In the present study, the catalytic effect of Mg on the C-H_2O was neglected because it is well known as a poor catalyst for steam gasification (Thomas et al. 1984). Other elements such as Al and Si also have no contribution to steam gasification.

The process of water-washing is potentially important for the utilization of South Australian lignite. Although investigations on water-treatment have been extensively carried out to study the beneficiation of South Australian lignites (Readett and Quast 1986, 1987, 1991), there is no report on the influence of water-washing on the gasification reactivity of coal. The present results indicate that water-leaching provides an attractive method for the utilization of these coals. Because water leaching removes about 83% of the total sodium and 50% of total ash, it reduces the potential of agglomeration and defluidization in the fluid bed gasifier and has little influence on the high reactivity. In contrast to water-washing, acid-washing may remove most of the inherent minerals of raw coal but also greatly reduces the reactivity.

4.3.3 Catalytic H_2O Gasification

Various acetate and chloride salts of alkali and alkaline-earth metals have been used as catalysts for H_2O gasification. Catalysts are added to the coal by the ion-exchange method (**Section 4.2.7**). Selected coal samples (size 1.6~2.4 mm) were firstly washed with HCl. The demineralized coal samples were then impregnated in solutions of acetate or chloride salts. Catalysed steam gasifications were performed at 765°C. The catalytic activities of NaAc, $Ca(Ac)_2$,

$Ni(Ac)_2$, NaCl, KCl, $CaCl_2$ and $NiCl_2$ and mixed (Na,Ca)Ac) were examined. Firstly, the coal samples were impregnated into the solutions of required concentrations to add approximately the same amount of cations (Na and Ca) to coal as that in the original coal.

4.3.3.1 Activities of Na and Ca

Knowledge on the catalytic efficiency of Na and Ca on the gasification of Bowmans coal with steam is important because these two metals are the major inherent active elements in this coal. The same amount of sodium as in raw coal was added to the sample by impregnating the coal with solutions of NaCl and NaAc salts. Considering the reaction characteristics with NaAc and NaCl, the catalytic reactivity of NaAc was found to be much higher than NaCl. ***Figure 4-27*** shows that the gasification of Bowman coal with steam was greatly accelerated by the addition of NaAc. The gasification rate of the catalysed sample was also higher than that for raw coal. The explanation for this behaviour is that physically absorbed cation shows a poor catalytic efficiency. Sodium exhibits strong catalytic activity only in the case of connection to carboxyl groups to form active sites. For raw coal, although the concentration of inherent sodium is high, only a small part (approximately 20%) connects with carboxyl groups (Readett and Quast 1986, 1989, 1991, and Ye et al. 1993). The impregnation of acid-treated coal with NaAc solution results in cation-exchange between Na and hydrogen. More Na is exchanged onto carboxyl groups than in raw coal. Therefore the reactivity of NaAc-catalysed coal is higher than that of the raw coal. This agrees well with the CO_2 gasification reactivity results in the present study.

The same amount of Ca as that in raw coal was added to the acid-treated coal sample by impregnating coal in solution of $CaCl_2$ with required concentration. ***Figure 4-27*** shows that the reactivity of $CaCl_2$-catalysed coal is very low. It does not mean, however, that the added Ca is not active for C-H_2O reaction, or that the inherent Ca does not catalyse the steam gasification. As the impregnation of coal in the solution of $CaCl_2$ only results in the physical absorption of

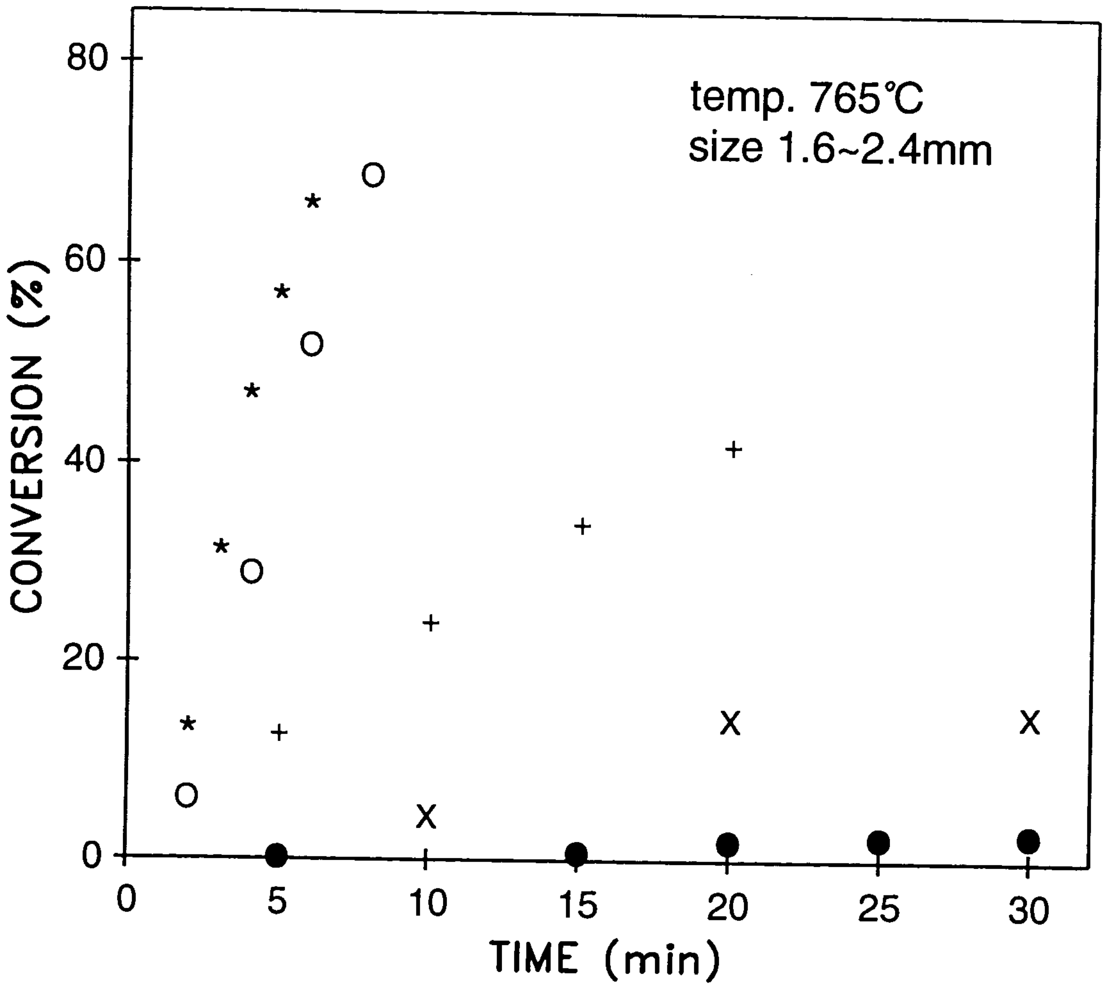


Figure 4-27 Comparison of steam gasification conversion of raw coal (o) with acid-washed (●) and catalysed acid-washed coal samples (*:0.34M NaAc; +:0.34M NaCl and x:0.07M Ca(Cl)2)

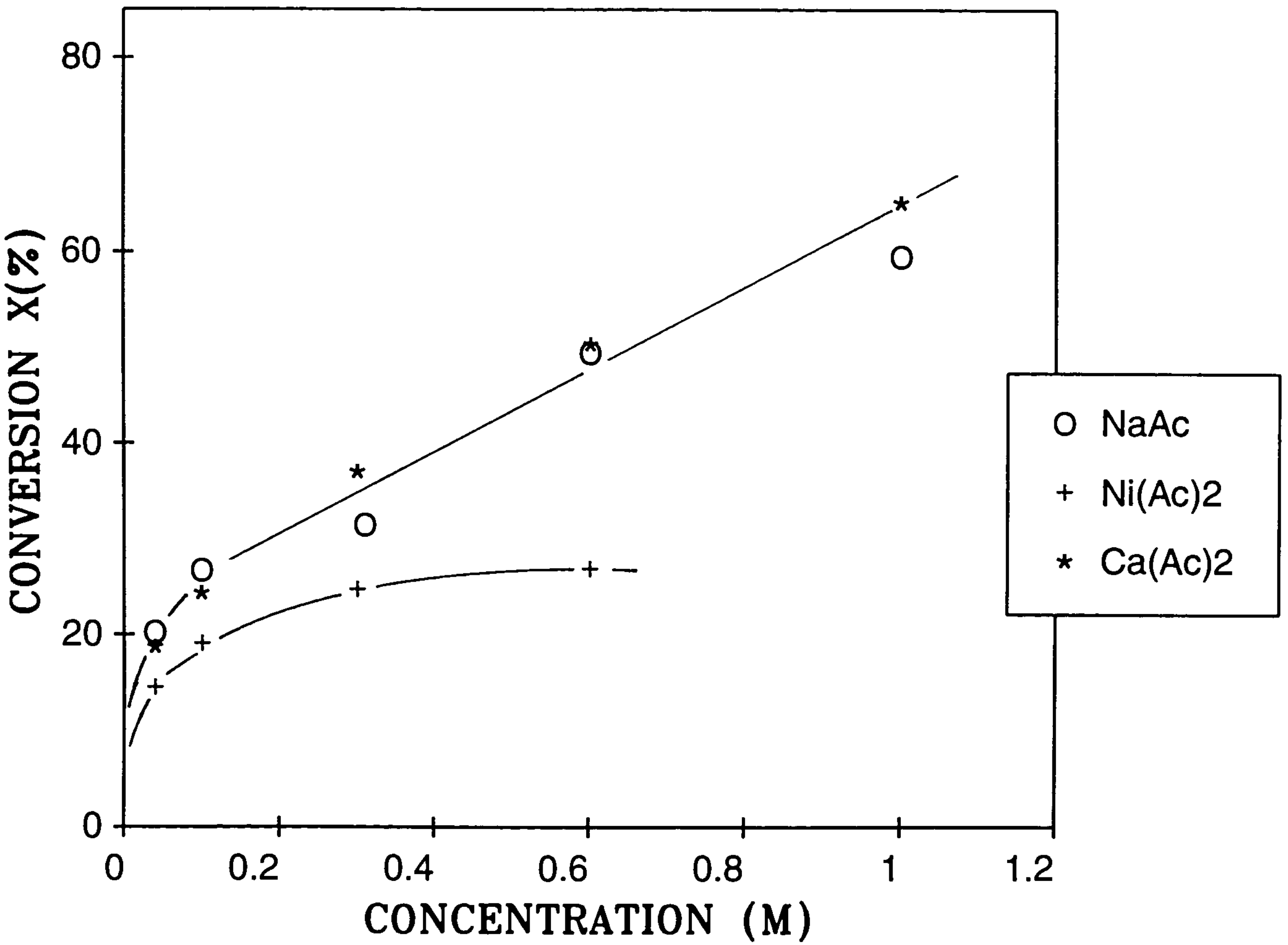


Figure 4-28 Steam gasification conversion (at 765℃) of Bowmans coal prepared from various concentrations (solution) of catalyst. Reaction time is 3 min. size: 1.6~2.4mm

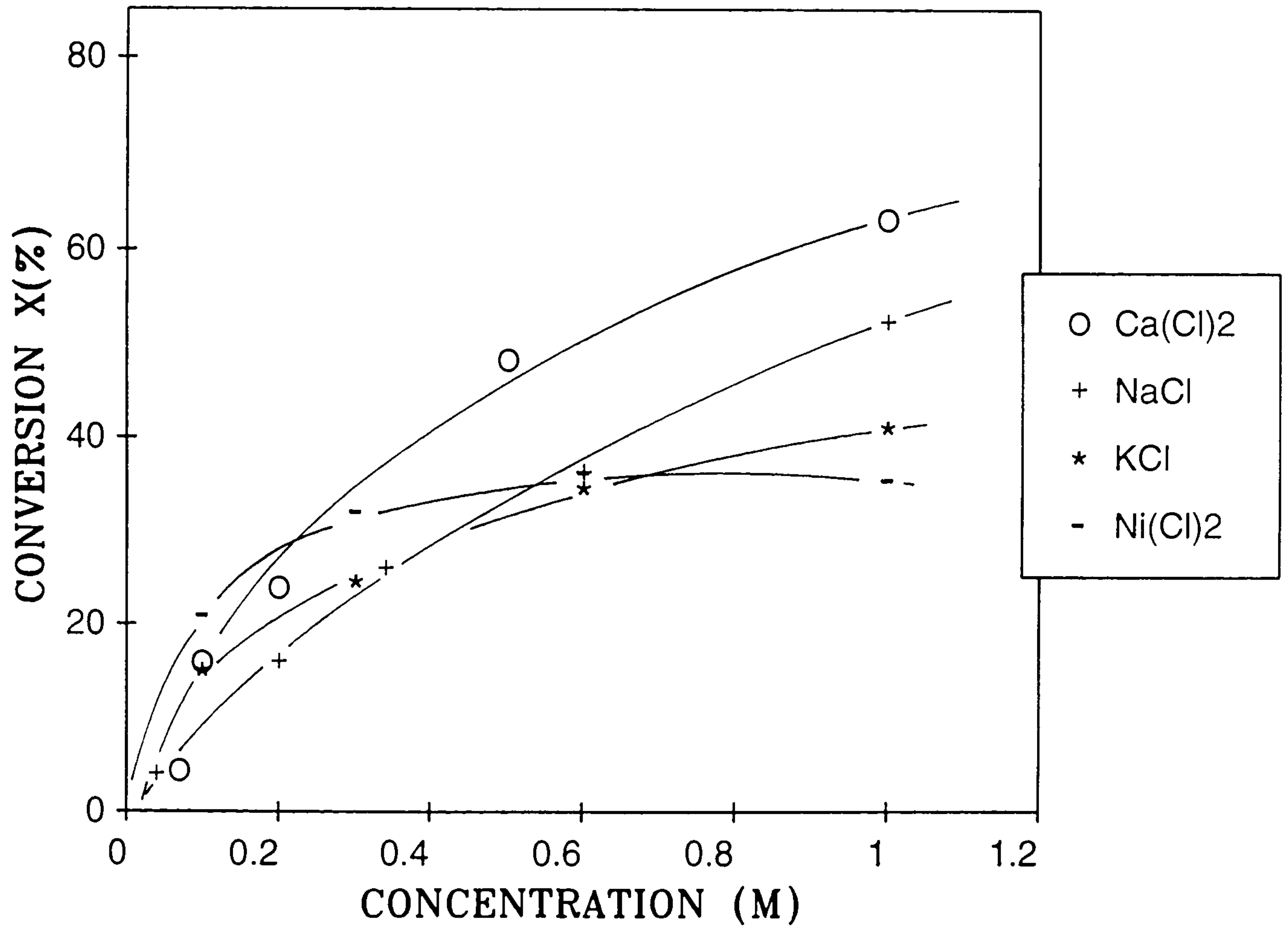


Figure 4-29 Steam gasification conversion (at 765 C) of Bowmans coal prepared in various concentrations (solution) of catalysts. Reaction time is 10 min, particle size 1.6~2.4 mm.

Ca, the low catalytic efficiency of $CaCl_2$ in steam gasification in this work can be attributed to the poor connection between the added Ca and carboxyl functional groups on the surface. ***Figure 4-28*** indicates that calcium, added by acetate salt, has a similar catalytic activity to that of sodium in steam gasification. Thomas et al. (1984) also found that the Ca-exchanged demineralized lignite has a higher reactivity than that of raw coal.

4.3.3.2 Comparison of Chloride and Acetate Salts

To examine the influence of the anion on the rate of catalysed steam gasification, experiments were performed using both acetates and chlorides under the same experimental conditions. ***Table 4.13*** compares the catalytic activities of all the salts used. Demineralized Bowmans coal was impregnated in solutions of various concentrations. Reactivity was determined at 765°C, 10 and 3 min for chlorides and acetates, respectively. It is seen that, the catalytic activities of alkali and alkaline-earth acetates are much higher than that chloride salts. Ca and Na acetates exhibit strong catalytic effect on the C-H_2O reaction and have similar activities. Compared with alkali acetates, alkali chlorides have less catalytic effect. Also, Na, Ca and K were found to have a higher catalytic effect than Ni. ***Figure 4-28*** shows that, no significant difference was observed between the activities of NaAc and $Ca(Ac)_2$. Both are excellent catalysts for steam gasification. Nickel acetate has relatively low activity compared with alkali acetate salts. ***Figure 4-29*** illustrates gasification conversions of coal samples using $CaCl_2$, NaCl, KCl and $NiCl_2$ as the catalyst. It shows that, at low levels of catalyst loading (<0.4M), $NiCl_2$ is found to have an activity similar to NaCl, KCl and $CaCl_2$. No significant difference was observed for NaCl, $CaCl_2$ and KCl. At high levels of catalyst loading (>0.4M), $CaCl_2$ was the most active catalyst.

These results agree reasonably well with the observations of other investigations. Huttinger et al. (1986) examined the influence of the precursor anion on the catalytic activities of various potassium salts and found that potassium carbonate, acetate and hydroxide exhibit strong catalytic effect on steam gasification; alkali chloride was found almost inactive. The activities of all the catalysts used was found to follow this sequence: KOH ~ KAc ~ K_2CO_3 ~ KNO_3 > K_2SO_4 > KCl. Other investigators (Hippo et al. 1980) also observed a similar sequence for the catalytic effect of salts of other alkali and alkali-earth metals such as Na and Ca on steam gasification. Takarada et al. (1987) found that the gasification rate of the sodium-catalysed Yallourn coal with steam increased with increasing the pH value of NaCl solution used for ion-exchange. They pointed out that sodium, in contrast, was a poor catalyst unless it is well dispersed by ion-exchange with carboxyl groups. Ohtsuka and Tomita (1986) also studied the calcium-catalysed gasification of Yallourn coal with steam and found that calcium hydroxide, carbonates, acetates and nitrate exhibited strong catalytic activities. The reaction rate increased linearly with the increase of the catalyst loading. Calcium chloride and sulphide were found to have less activity.

Comparing with the results on carbon dioxide gasification, the steam gasification results are similar (see discussion on **Section 4.2.6**). The general conclusion is that alkali salts of weak acids have strong catalytic activities on gasification, while the salts of strong acids are less effective. The high catalytic activities of weak salts are attributed to the effective cation-exchange between hydrogen and cations in the carboxylic functional groups. Cations act most effectively as catalysts when associated with the carboxyl functional groups. The only difference of the catalysed gasification behaviour between C-CO_2 and C-H_2O reactions is the effect of NaCl on the reactions. Experimentally obtained results showed that sodium chloride has some catalytic effect on C-H_2O reaction, but it was completely inactive for the C-CO_2 reaction. In general, for all the catalysts used for the catalytic gasification of Bowmans coal with steam, NaAc, KAc and $Ca(Ac)_2$ were excellent catalysts. $Ni(Ac)_2$ shows less activity and NaCl, KCl and $CaCl_2$ and $NiCl_2$ were poor catalysts.

Figures 4-28 and ***4-29*** show that, for the gasification of Bowmans coal with steam, nickel has less catalytic efficiency than alkali and alkaline-earth metals in both acetate and chloride forms. The gasification behaviour of the Ni-catalysed coal samples was also different from that of the alkali-catalysed coal samples. For $Ni(Ac)_2$ and $NiCl_2$-catalysed steam gasification reactions, the gasification rate of coal significantly increased with the addition of a small amount of nickel. Substantial results are obtained from the initial nickel loading, beyond this level, the reaction rate appears not to be influenced by further loading. The present results do not agree with other investigations. Hashimoto et al. (1989) reported that nickel exhibited a strong catalytic effect on the gasification of Yallourn coal with steam at low temperatures (500~700°C). As mentioned in **Section 4.2.8,** nickel only has the catalytic effect in its metallic form, and loses catalytic activity when changed to an oxidized form. In the present study, the relatively low activity of nickel can be attributed to the high temperature. Under current temperature (765°C) condition, at the beginning of reaction, nickel acts as the catalyst. With the progress of reaction, it is reported to changes from metallic form to oxidized form and lose catalytic efficiency (Tomita et al. 1989).

The present study also indicates that nickel has different catalytic activities for steam and carbon dioxide reactions. For steam gasification, nickel acetate at certain levels exhibits similar catalytic activity as sodium acetate and calcium acetate. For carbon dioxide gasification nickel acetate was almost inactive. This indicates that nickel is an effective catalyst for steam gasification rather than for carbon dioxide gasification. Other investigators (Hashimoto et al. 1988) have reported similar results

Figure 4-29 shows that KCl has a similar activity to that of NaCl and $CaCl_2$. Some observations (McKee et al. 1983, Huttinger and Minger 1986) indicated that K has a higher activity in steam gasification than Na and Ca. It has been confirmed that potassium only exhibits a catalytic effect on gasification in the form of certain salts and may lose its catalytic activity by reacting with inherent minerals of coal (Kuhn et al. 1986, Bruno et al. 1986, Kuhn and Plogmann 1986). Since acid-treated Bowmans coal contains a considerable amount of silicon, this may react with potassium to form inactive compounds and therefore result in a decrease in its catalytic effect.

In conclusion, the present results indicate that alkali and alkaline-earth metals exhibit strongest catalytic activity when added in the form of weak-acid salts. The salts of strong acids are not as active due to the failure of connection between cation and carboxyl groups. Cations act as catalysts if they are well dispersed in coal and associate with carboxyl groups to form active sites on coal. ***Table 4-13*** shows that, for all the catalysts used for this study, the relative effectiveness of the various salts on the steam gasification are found to follow this sequence: NaAc ~ $Ca(Ac)_2$ > $Ni(Ac)_2$ > $CaCl_2$ > NaCl > KCl > $NiCl_2$.

4.3.3.3 Dependence of Reaction Rate on Catalyst Loading

Figure 4-30 shows the relation between reactivity and the concentration of the solution of salts. It is seen that, for acetate salts, within the loading range from 0.1 to 1.0 M, the reactivity increases linearly with increasing the NaAc and $Ca(Ac)_2$ loading. A possible explanation for this behaviour is that as gasification rate is proportional to the number of active sites on the surface of coal, increasing the concentrations of the alkali acetate solution results in increasing the number of active sites. For $Ni(Ac)_2$-catalysed gasification, the reactivity increases rapidly with cation loading at low concentrations, but the catalytic effect of nickel seems to approach saturation at about 0.3M. Beyond this point, further catalyst loading does not increase reaction rate.

A linear relationship between gasification rate and catalyst loading has also been reported by other investigators. Fung and Kim (1983), Bruno et al. (1986), Ruan et al. (1987) observed that alkali and alkaline-earth metals strongly catalyse steam gasification and the gasification rate is proportional to catalyst loading. Thomas et al. (1984) studied the catalytic gasification of some U.S. lignites by adding exchangeable calcium. They found that the gasification of the ion-exchanged lignites was strongly catalysed by Ca and that the reactivity increased linearly with

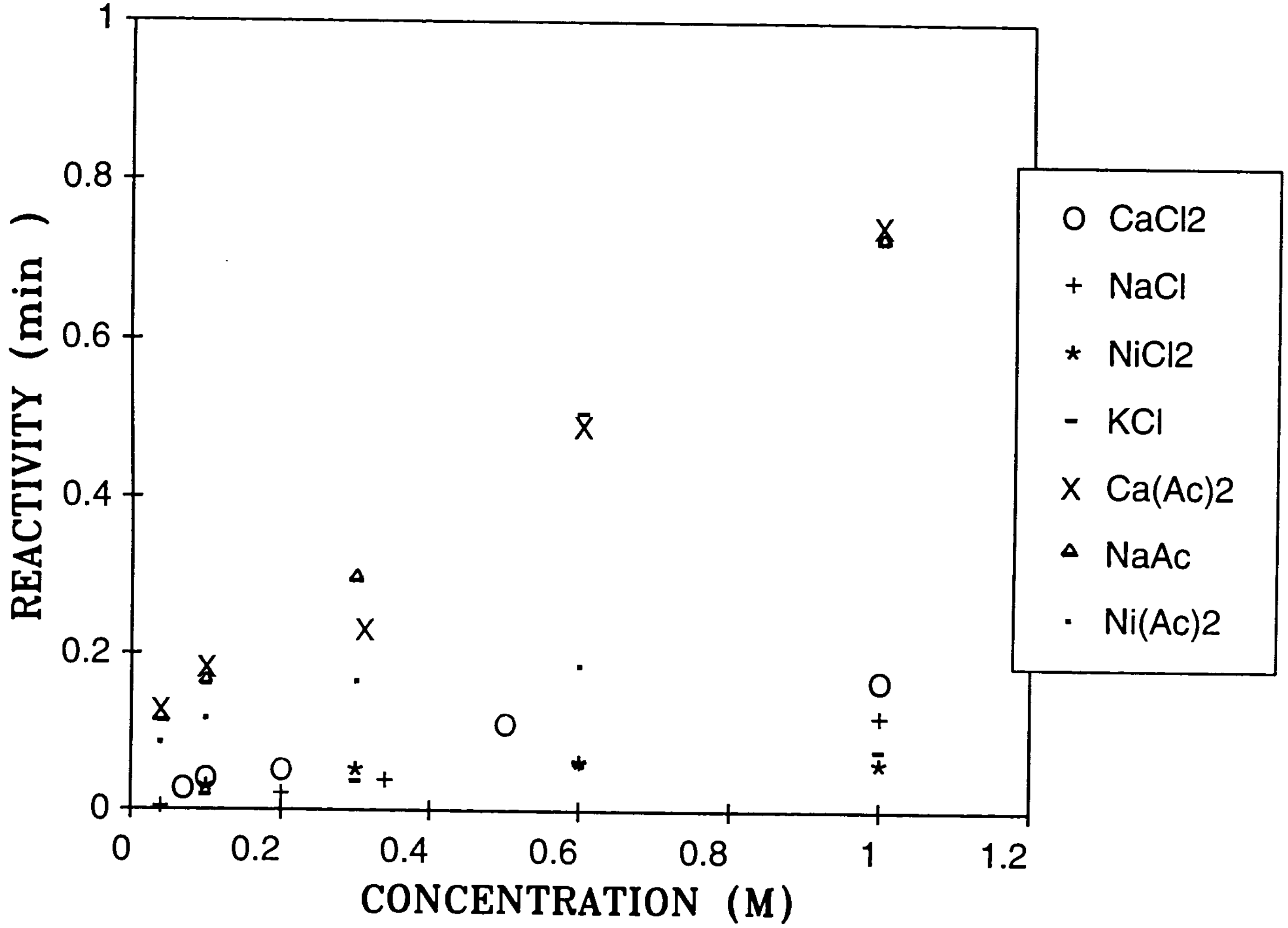


Figure 4-30 Reactivity of steam gasification (at 765°C) for Bowmans coal prepared in various concentrations (solution) of catalysts. Reaction time is 10 min, particle size 1.6~2.4 mm.

Table 4-13 Activities of catalysts on H_2O gasification of Bowmans coal

Added Salt	Concentration (M)	Reaction time (min.)	Reactivity (h^{-1})
NaAc	0.3	3	12.2
$Ca(Ac)_2$	0.3	3	10.5
$Ni(Ac)_2$	0.3	3	7.8
NaCl	0.3	10	2.2
$CaCl_2$	0.3	10	2.8
KCl	0.3	10	2.2
$NiCl_2$	0.3	10	2.7
raw coal	-	3	9.5
demin. coal	-	10	0.2

Note: the raw and demineralized coals were not impregnated in solution of salt.

increasing concentrations of Ca up to a certain level. Bruno et al. (1986) indicated that at sufficient high C/M (M is Na, K and Ca) ratio the rate of the steam gasification depends on the concentrations of the well dispersed alkali elements.

The dependence of gasification rate on catalyst loading was also tested for alkali chloride salts. ***Figure 4-30*** shows the relationship between reactivity and the concentration of chloride salts solution. For the KCl, NaCl and $CaCl_2$ catalysed gasification reactions, the reactivity slightly increased with the increase in the concentration of the salt, but not linearly. For $NiCl_2$, the behaviour was found to be similar to that observed for $Ni(Ac)_2$, the reactivity reaching the saturation at a concentration of about 0.3M. The catalytic activities of chloride salts are much lower than acetate salts. The gasification of Bowmans coal seems to be not sensitive to chlorides.

The catalytic steam gasification experiments were only carried out on the acid-washed coal samples (ash content 2.6% d.b.). The major inorganic element remaining in the acid-washed coal sample is silicon which is known to be catalytically inactive. Inherent minerals may react with alkali additives during the gasification cause deactivation of the catalyst.

4.3.3.4 Addition of Several Active Elements

Raw Bowmans coal contains several active elements e.g. Na, Ca, K and Fe. The contents of sodium and calcium are sufficiently high to cause pronounced catalytic effect. Therefore, it is necessary to know whether the catalytic contributions of the individual elements are additive or whether there is some interactive effect. It has been reported that the combined catalytic effect of several active elements on coal gasification was higher than the sum of individual catalysts (Ruan et al. 1987, Kopesl and Zabawski, 1990). Kopsel et al. (1990) studied the catalytic effect of ash components in a high sodium content lignite. Active elements of the original coal were, individually or in combination, impregnated. Their results showed that none of the individual elements controls the gasification rate of the original lignite. The significant catalytic effect of the original coal was dominated by the combination of several individual metal elements. Other investigators indicated that if Na and Ca were used together, their catalytic activities are higher than the sum of Na and Ca used alone.

In the present study, acid-treated Bowmans coal was treated with sodium/calcium acetates. Three solutions, one was 0.15M Na + 0.15M Ca, others were 0.15M Na and 0.15M Ca alone, were made for the catalyst loading. ***Figure 4-31*** shows the gasification conversion of treated coal samples. As Ca has a catalytic activity similar to Na, the profiles of conversion versus time were plotted as **A** (0.15M Na and 0.15MCa) and **B** (0.15M Na + 0.15M Ca separately). The third plot **C** represents the sum of the individual Na and Ca data. The results show that the conversion of lignite impregnated in Na/Ca is considerably lower than the sum of conversion for the coal samples which were impregnated with each elements alone. This finding conflicts with the early finding that the gasification reactivity increases linearly with increasing Na and Ca loading.

Other investigators report synergistic effects. Kopsel et al. (1990) evaluated a quantitative relationship between the gasification rate and the content of the catalytically effective element of coal. They found that the gasification rate of lignite for simultaneous impregnation with 2.6% sodium and 1.4% calcium was higher than the sum of gasification rate obtained by impregnating only one of these elements (with same quantity). Similar results were also reported by Ruan et al. (1987).

The present result can be explained by the saturation of the active elements absorbed by coal. As mentioned earlier, the gasification reactivity is proportional to the amount of cations which are associated with carboxyl groups. Impregnation of the deashed coal in high concentration alkali solutions results in the saturation of active elements absorbed on the surface of coal. Total number of carboxyl groups are occupied by added metal cations at certain concentration levels.

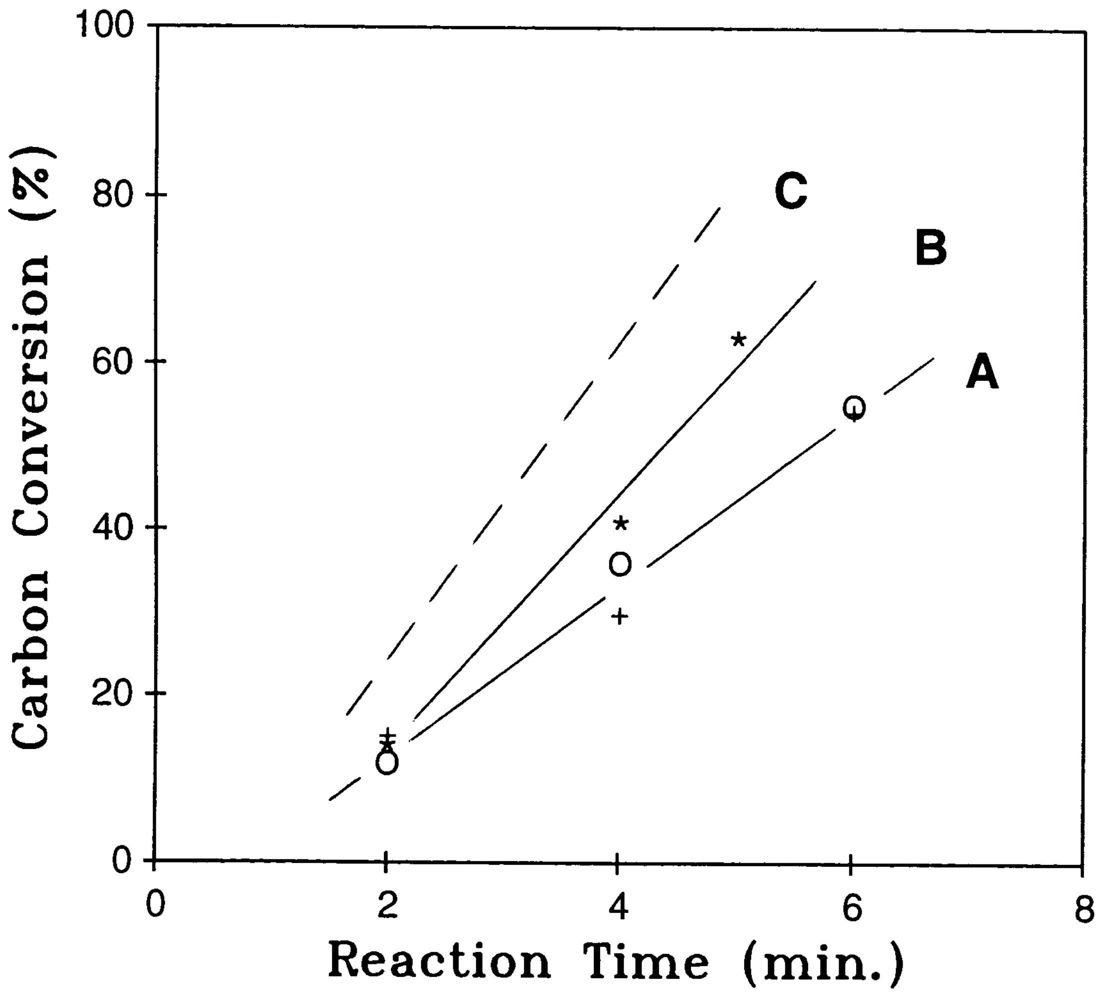


Figure 4-31 Comparison of steam gasification conversion of catalysed coal samples
o: 0.15M Na, +: 0.15M Ca, *: 0.15 Na + 0.15 Ca,
(temp. 765 C, size 1.6~2.4 mm)

In this case, increasing the concentration of solution only results in the physical adsorption of cation which results in little or no further increase in catalytic effect. It is expected that the synergistic effect of combined cations will become significant by impregnating coal in the solutions which their concentrations are lower than the saturation point. Further effort is needed in this area to obtain full understanding of the combined catalytic effect of the different cations.

Another example of the combined catalytic effect of different catalysts on steam gasification is the work conducted by Long (1983) in which the combination of cations was related to the effect of anions. Long found that the mixture of K_2SO_4 and Na_2CO_3 has surprisingly high catalytic activity in comparison to either pure component used alone. Similar behaviour was also observed for the mixture of K_2SO_4 and NaCl. The reason for these phenomena, Long explained, was that K_2SO_4 reacts with Na_2CO_3 or NaCl to form Na_2SO_4, which is reduced to Na_2S during the gasification. Na_2S exhibited strong catalytic effect on gasification.

4.4 Gasification of Yallourn Coal

A limited investigation of the gasification behaviour of Yallourn coal has also been carried out for comparison of the reactivities between Bowmans coal and other lignites. Since Yallourn coal is well known for its attractive properties such as low ash and sulphur contents, investigations of this lignite have been widely carried out on various aspects. Reported values of the gasification reactivity of this coal vary, depending on the particular experimental conditions used (Tomita et al. 1983, Suzuki et al. 1985 and Kwon et al.

Yallourn coal (V.M.: 44.2, F.C.: 54.5, and Ash: 1.3, d.b.) was crushed and sieved to 1.6~3.0 mm in size. All the gasification experiments were carried out in the quartz-tube reactor at atmospheric pressure; the experimental conditions and operational procedures were kept the same as for Bowmans coal.

Gasification conversion data for Yallourn coal in steam are compared with Bowmans coal in ***Figure 4-32***. Clearly, it is seen that the gasification rates of Yallourn coal with steam are much lower than those of Bowmans coal. ***Figure 4-32*** shows that, at 765°C, for Bowmans coal, approximately 80% (due to the limitation of the present reaction system, this is the maximum carbon conversion which could be achieved) of fractional fixed carbon conversion was achieved in 10 min reaction time; in contrast, less than 10% conversion was observed for Yallourn coal. The initial reactivities, were 9.6 and 0.9 (min^{-1}) for Bowmans coal and Yallourn coal, respectively.

Figure 4-33 shows the gasification behaviour of Yallourn coal with steam at 805°C, comparing with data obtained by other investigators Takarada et al. (1985) at 787°C using the TGA method. The data of this work were also corrected to 787°C as shown in ***Figure 4-33***. It can be seen that the present results are very close to those obtained by Takarada et al. (1985) after temperature correction (based on E_a=133 kJ/mol). The difference can be attributed to the difference in method of determination (fluid-bed vs TGA) and experimental error. Other results reported in literature are in general agreement with the general finding of low reactivity of raw Yallourn coal with steam (Takarada et al. 1985, and Suzuki et al. 1985). Kwon et al. (1988) also observed low gasification reactivity of Yallourn coal with steam and carbon dioxide.

The low reactivity of Yallourn coal with steam and carbon dioxide is attributed to its low inorganic matter content. Investigations have also been made of the catalysed gasification of Yallourn coal (Tomita et al. 1983 and Suzuki et al. 1985). Their results showed that the gasification rate with CO_2 and H_2O could be greatly increased by adding Na, Ca, K and Ni, to the raw or demineralized coal, thus confirming the importance of active inorganic matter in coal gasification.

Due to the low reactivity of Yallourn coal, it is difficult to achieve high carbon conversion under the current experimental conditions. The investigation has concentrated on determining the initial reactivity of this low-ash raw lignite. Since Yallourn coal has low inherent mineral content, demineralization does not significantly influence its gasification behaviour.

The results for Yallourn coal provide evidence to support the conclusions obtained for Bowmans coal. The reactivity of low-rank coal is mainly dominated by the catalytic effect of inherent minerals. The gasification rate of lignite can be greatly affected by changing the mineral content. A more detailed comparison of reactivities and properties of Yallourn and Bowmans coals is given in **Section 5.1**

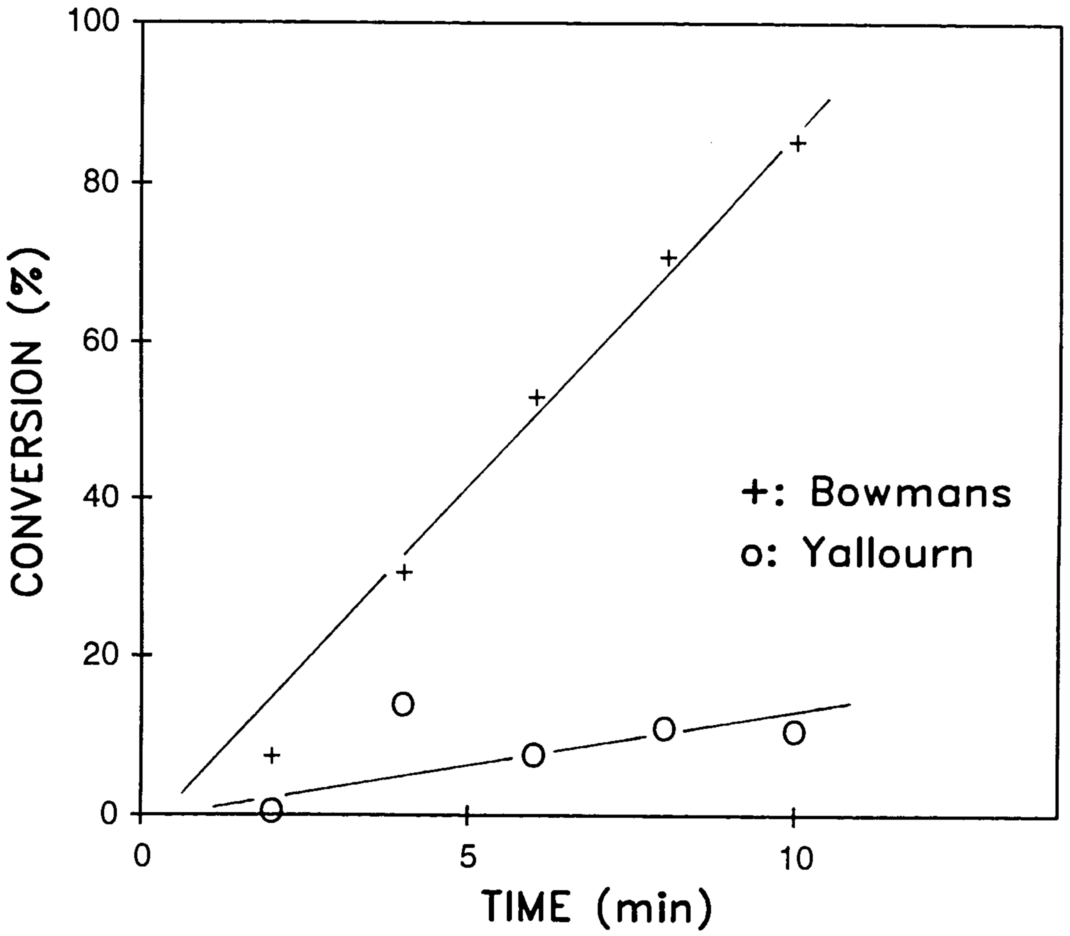


Figure 4-32 Comparison of steam gasification behaviour of Bowmans coal and Yallourn coal. (temp. 765℃, particle size 1.6~3.0mm)

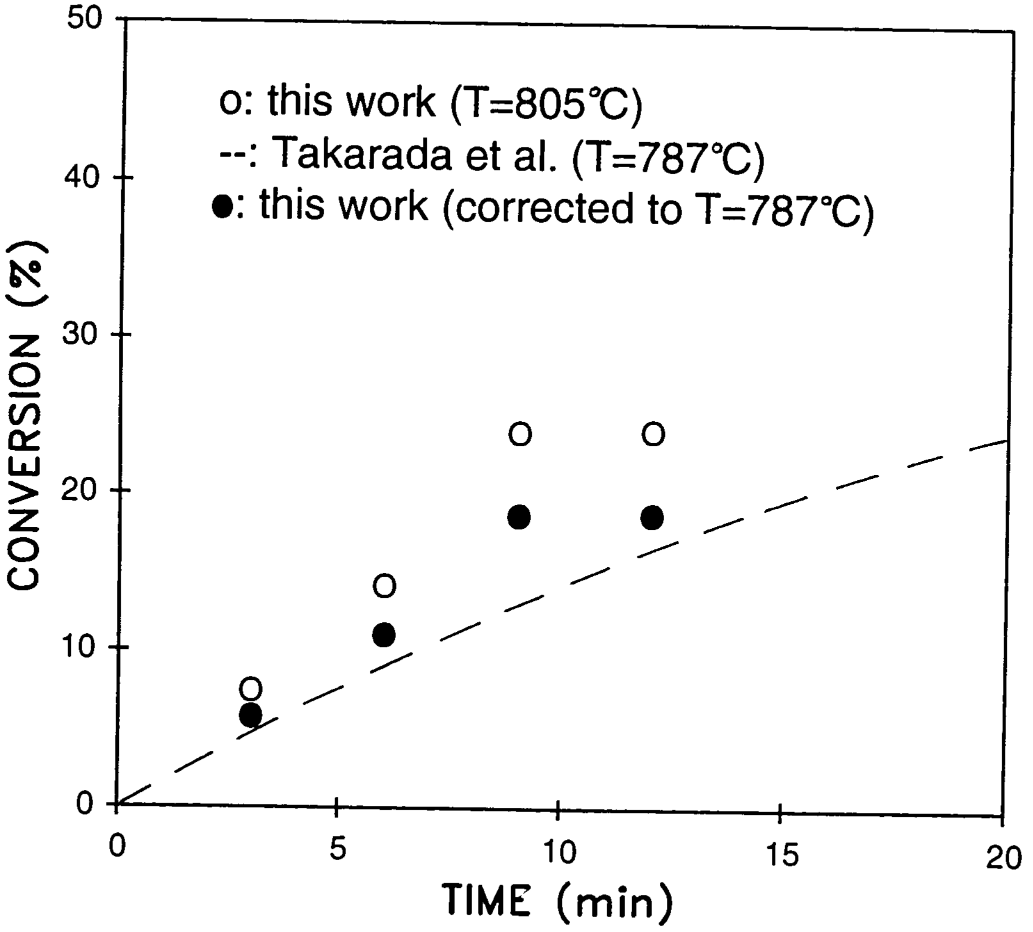


Figure 4-33 Gasification behaviour of Yallourn coal with steam: comparison with results of Takarata et al.(1985)

Chapter 5

EVALUATION OF THE PRESENT INVESTIGATION

This chapter summarizes the major findings and their significance. The study was primarily concerned with the relation between gasification reactivity and various processes of pre-treatment of Bowmans coal, including demineralization, washing and catalyst addition by cation-exchange. Effort has also been made to obtain knowledge of theoretical aspects of gasification, such as: reactivities of lignite towards CO_2 and steam, gasification kinetics, reaction mechanism, the influence of inherent inorganic matter and the catalytic effects of various alkali and alkaline-earth metals which were added to the demineralized coal. The present study is evaluated in the following key areas:

- reactivity of Bowmans coal compared with other coals
- kinetics and mechanisms of coal gasification
- characteristics and beneficiation of Bowmans coal
- the role of inherent and artificially added inorganics in gasification

5.1 Reactivity of Bowmans Coal Compared with Other Coals

The main factors influencing the reactivity of Bowmans coal with different gasifying agents, i.e. carbon dioxide and steam, are examined. The reactivity of Bowmans coal towards CO_2 or H_2O was found to be higher than most Australian coals (Ye et al. 1993). It is essential to understand how the reactivity is related to the properties of a coal.

The reactivities of a wide range of coals with CO_2 and H_2O have been widely studied (Hippo et al. 1979, Hashimoto et al. 1986, Kasaoka et al. 1986, and Miura et al. 1989, 1990). The previous results show no universal trend but depend largely on coal rank and the experimental conditions used. Many investigators have presented their own correlations of reactivity with properties (Kasaoka et al. 1986, and Miura et al. 1989, 1990). Since coal has extremely complex composition and structure, numerous experimental and theoretical efforts have been made to examine coal reactivity by relating it to important coal properties such as coal rank, porosity, surface area, oxygen content, moisture holding capacity and total mineral content. The published results generally agree that the main factors affecting reactivity are chemical and physical structure and the catalytic effect of inorganic constituents. The correlation between coal reactivity and fixed carbon content of the parent coal is quite good for C>80% (daf), but is widely scattered for C<80% (Hashimoto et al. 1986, Tomita et al. 1989). Although the inherent mineral matter is commonly recognized as catalysing gasification, the total ash content shows poor correlation with reactivity.

The reactivities of Bowmans coal towards carbon dioxide and steam, obtained from the present study, have been compared with typical data from other investigations using a wide range of different coals (Takarada, et al. 1985 Hashimoto et al. 1986 and Miura et al. 1989). To simplify the comparison, the reactivity of a particular coal in gas *i* (i.e. CO_2 or H_2O) is characterized by its reactivity index, R_i, which is defined by:

$$R_i = \frac{\Delta X}{\Delta t}\Big|_{X=0.5} = \frac{0.5}{\tau_{0.5}} \qquad (5.1)$$

where $\tau_{0.5}$ denotes the time required to reach a 50% of fixed carbon conversion. Reactivity index was introduced by Takarada (1985) and has been accepted by many researchers (Miura et al. 1989).

Figure 5.1 shows the relationship between the reactivity index for steam (R_{H2O}) and fixed carbon content of the parent coal for 35 coals (data taken from Takarada et al. 1985). It clearly shows that lower rank coals (C<78%) have high reactivities, but that the values are widely spread. There is no definitive correlation between R_{H2O} and the coal rank for lower rank coals. Coals with carbon contents >78% have low reactivities. Other investigators have reported the same trend of coal reactivity with %C, e.g. Miura et al. (1989) found a similar trend to ***Figure 5.1***. Bowmans coal was found to have a higher R_{H2O} value than other coals. Yallourn coal, however, has a very low carbon content, while its reactivity is also very low. The carbon conversion of Yallourn coal did not reach $X=50\%$ under the current experimental conditions, so its R_{H2O} value was estimated by extrapolation. ***Figure 5.1*** indicates that the value from this study is very close to that determined by Takarada et al. (1985). In other words, our experimental data on the gasification of Yallourn coal are in a good agreement with the observations of other investigators.

A comparison of CO_2 reactivities between Bowmans coal and other coals was also made. Typical experimental data were taken from several investigations (Hippo and Walker 1975, Kasaoka et al. 1983, Takarada et al. 1985, Hashimoto and Miura 1989). To ensure that the comparison is consistent, the CO_2 reactivities of this study (R_m) were converted to values at T=900°C. ***Figure 5.2*** shows the relationship between the CO_2 reactivity and the carbon content for 63 coals. The result is similar to that of the steam reactivity. The R_{CO2} values vary widely for low-rank coals (C<80%, daf), while, the R_{CO2} values of the high rank coals are low and decrease with increasing carbon content. The reactivity of Bowmans coal is very high compared to other coals. Other investigators have also observed a similar relation between reactivity and coal rank. Kwon et al. (1988) compared the reactivities of different coals with CO_2. They found a good correlation between the gasification rate and coal rank for all the coals used (carbon contents ranged from 70 to 94%, daf). They attributed the high reactivity of low rank coal to the high concentration of macro and meso pores present.

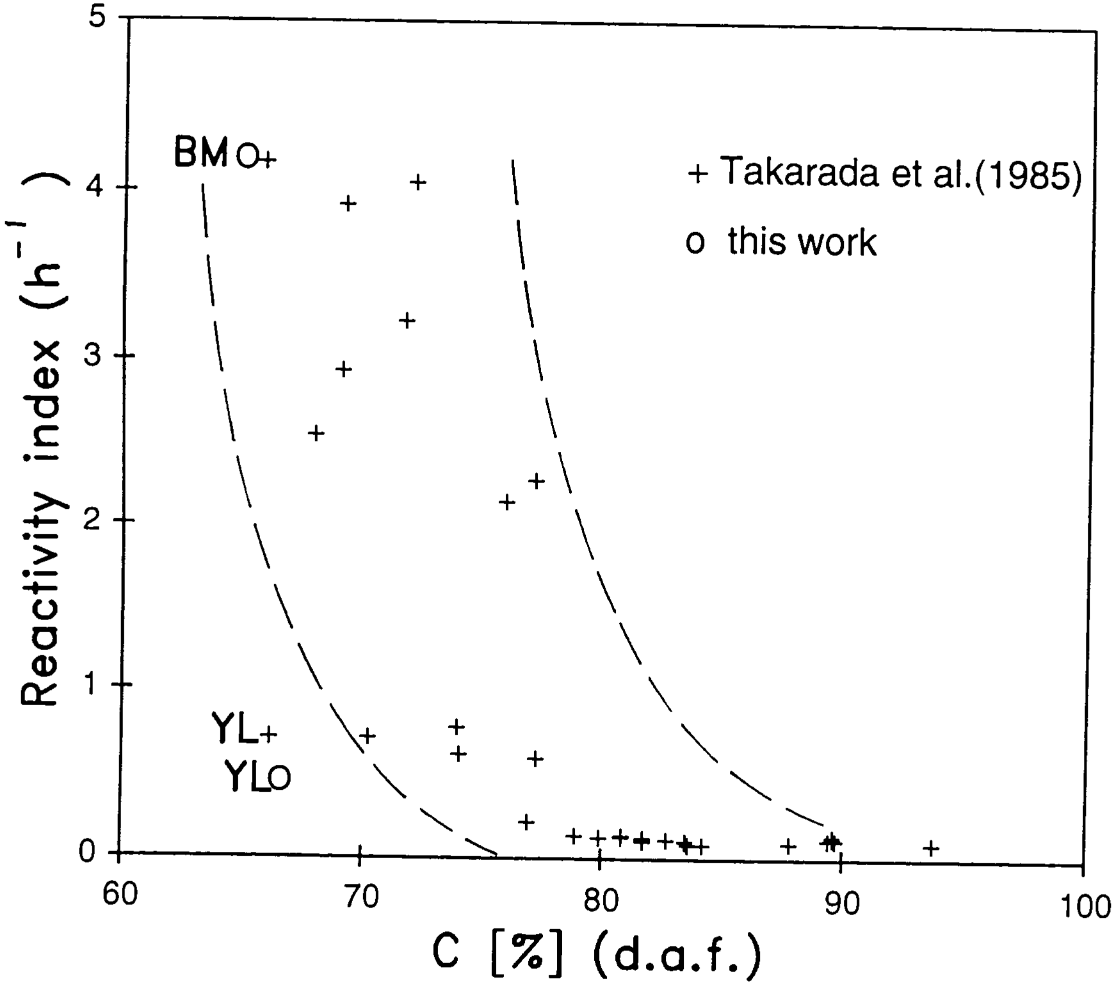


Figure 5-1 Relationship between steam gasification rate and carbon content, % C, in coal at T=750°C and P=1 atm.
(BM for Bowmans coal, YL for Yallourn coal)

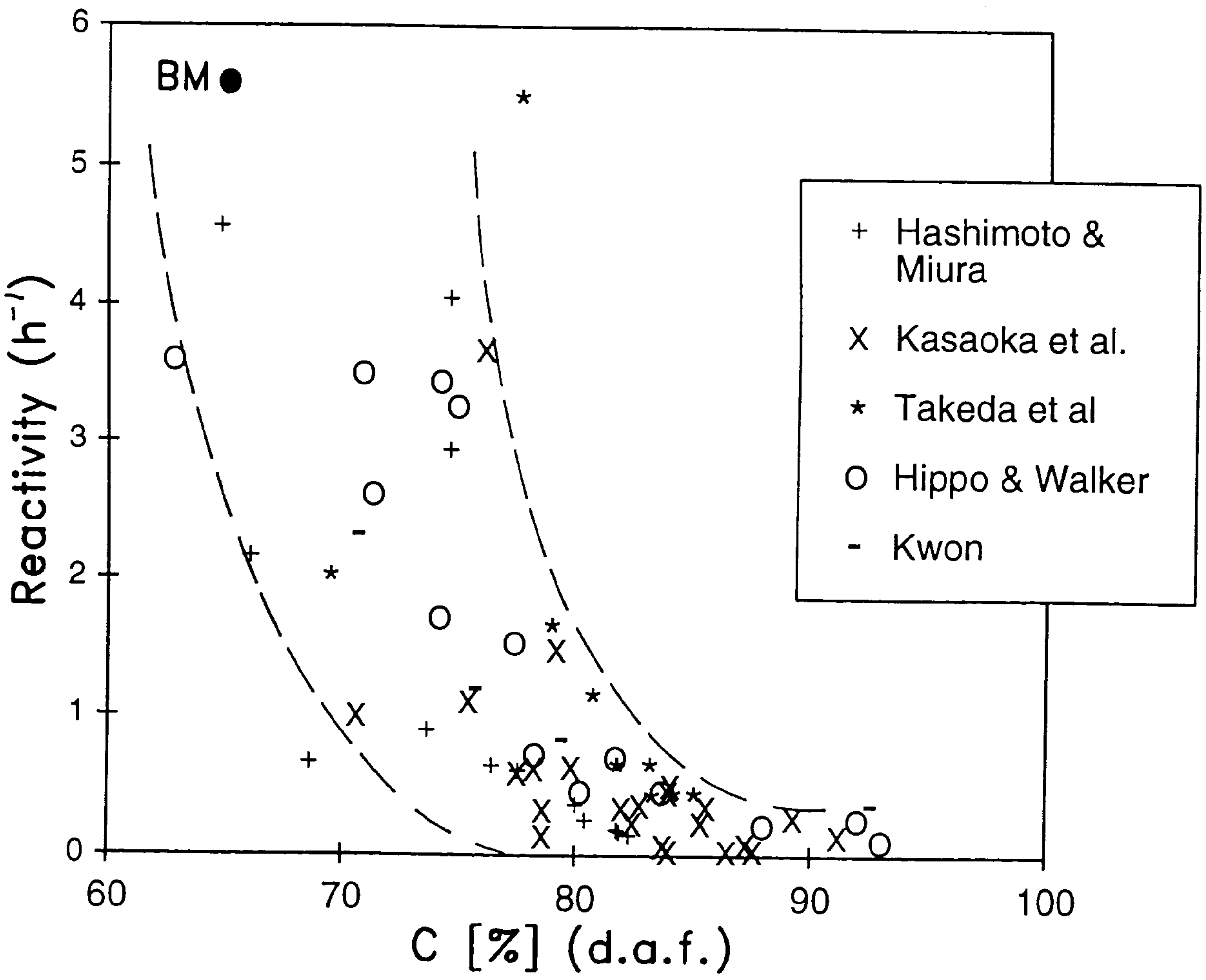


Figure 5.2 Relationship between carbon dioxide gasification reactivity and carbon content % C in coal at T=900℃ and P=1 atm. (BM: Bowmans coal in the present study)

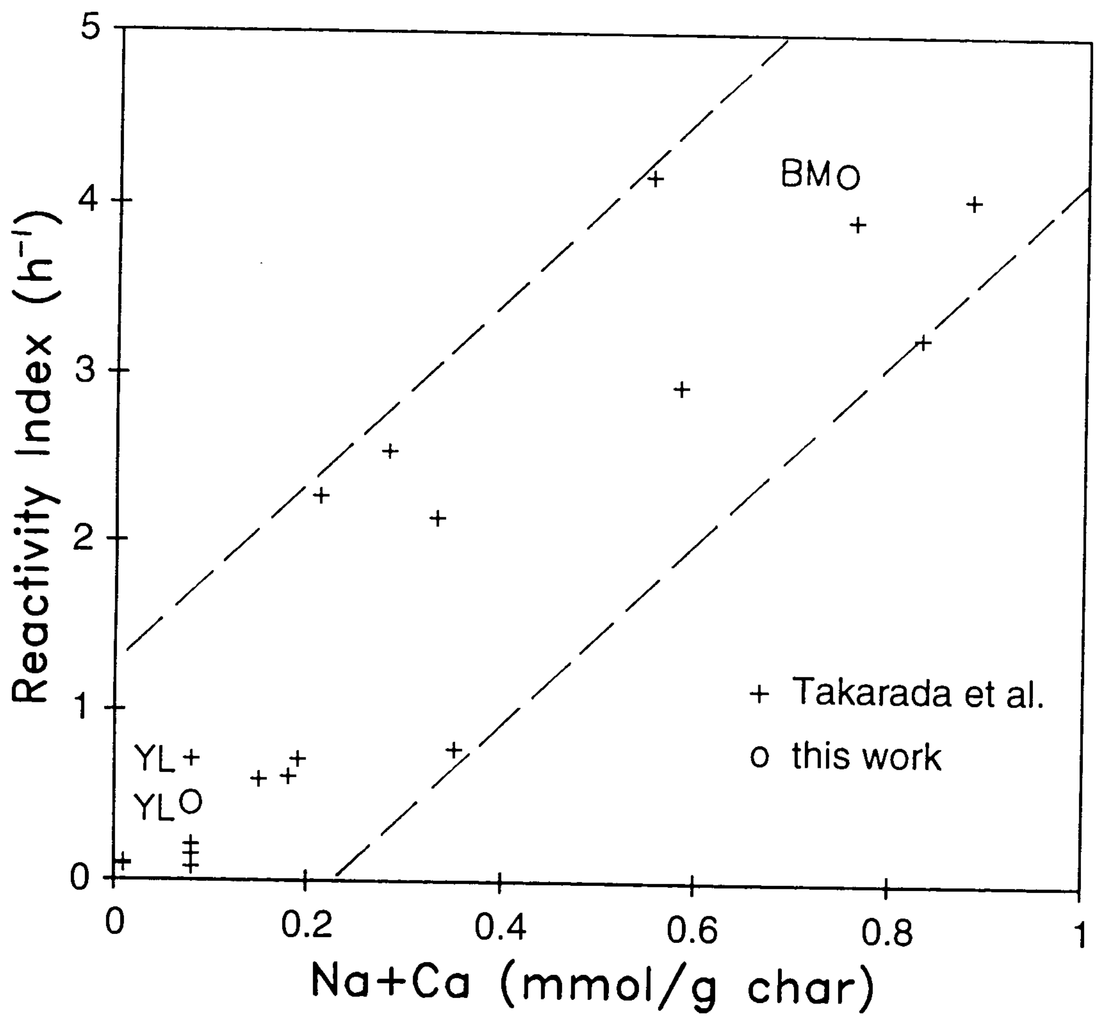


Figure5-3. Relationship between H2O reactivity and leached Na+Ca from coal (BM: Bowmans coal, YL: Yallourn coal, T=750°C).

Table 5-1 Comparison of reactivities and properties of Bowmans coal and Yallourn coal

Property	Bowmans	Yallourn
Proximate analysis (% db):		
Moisture (% as received)	56	64
Fixed carbon (d.b.)	39.5	54.5
Volatile matter (d.b.)	47.5	44.2
Ash (d.b.)	12	1.3
Ultimate analysis (% daf):		
C	65	66.7
H	5.1	4.8
O	23.6	24.8[+]
N	0.45	0.62
S	4.9	0.19
Cl	1.5	0.11
Acid extractable inorganics (%):		
Na (mmol/g d.b. basis)	1.6	0.09[+]
Ca (mmol/g d.b. basis)	0.45	0.12[+]
Physical and chemical properties:		
Porosity (%)	30.9[*]	42.4[*]
Surface area (m^2/g)	196[*]	268[*]
Oxygen-containing functional group(meq/g)	2.93[*]	6.42[*]
Carboxylic functional groups (meq/g)	1.97[*]	2.21[+]
Phenolic functional groups (meq/g)	1.00[*]	3.72[+]
Measured reactivity:		
Steam reactivity (h^{-1}, at 750°C)	4.2	0.46
Steam reactivity of demin. coal (h^{-1}, at 750°C)	0.10	0.11[T]
$Ca(Ac)_2$-cata. H_2O reactivity (h^{-1}, at 800°C)	4.6	3.8[T]
Carbon dioxide reactivity (h^{-1}, at 900°C)	5.6	1.2[K]

Note: [+] data from Schafer (1972), [*] data from Readett et al.(1986), [K] data from Kwon et al. (1988), [T] data from Ohtsuka and Tomita (1986).

The Correlation Between Coal Reactivity and Cation Content

Figure 5.3 shows the reactivity, R_{H2O}, against the sum of the exchangeable sodium and calcium content for 20 coals. A reasonable correlation is observed, indicating that reactivity towards steam is strongly accelerated by the presence of the sodium and calcium in the coal. ***Figure 5.3*** also indicates that there is substantial scatter in the data for all the coals used. A possible explanation is that the inherent alkali and alkaline-earth metals may associate with the coal structure in different ways. As has been mentioned in **Section 4.2.11** and **Section 4.3.9**, alkali and alkaline-earth carboxylates exhibit a substantial catalytic effect on gasification. However, metals which are present in the form of minerals show less catalytic effect. This correlation does not consider the chemical form of the metals present. It should be noted that the method used for cation content measurement in the present investigation is somewhat different from that used by Takarada et al. (1985). In the present study, Na and Ca were leached by treating the raw coal with HCl acid. Takarada et al. (1985) determined the Na and Ca content by treating the raw coal with ammonium acetate. Although the high reactivity of low-rank coal can be attributed to the presence of alkali metals, the total amount of the exchangeable cations in a coal does not have a direct relationship with the coal rank and the concentration of oxygen-containing functional group in the coal.

Based on the above discussion, it can be concluded that the gasification rate strongly depends on the coal type and there is a general trend for low-rank coals to have high reactivity. Furthermore, the amount of exchangeable cation is found to have a good correlation with reactivity.

Questions may be asked to what extent other properties such as oxygen content, porosity, surface area and amount of carboxylic groups contribute to the high reactivity of low-rank coal. It is well known that gasification behaviour is influenced by these factors to different degrees

(Kata et al. 1981, Kasaoka et al. 1986 and 1987). Increasing the values of these parameters generally causes an increase in gasification rate. To estimate the role of these parameters in the gasification of coal, a detailed comparison has been made between Bowmans and Yallourn coal. Studies have been widely carried out on the various aspects of Yallourn coal. Here, typical data (Ohtsuka and Tomita 1986, Readett et al. 1986, and Kwon et al. 1988) are taken from the literature for the comparison.

Table 5.1 compares the CO_2 and H_2O reactivities and important properties of Bowmans and Yallourn coals. It is seen that Yallourn coal has higher porosity and surface area and oxygen-containing functional groups and carboxylic functional groups than Bowmans coal. Bowmans coal has total Na and Ca content approximately 10 times higher than Yallourn coal, and the reactivity of raw Bowmans coal with steam and carbon dioxide is approximately 10 times higher than that of Yallourn coal. The R_{H2O} values are 4.2 and 0.46 for Bowmans coal and Yallourn coal, respectively. This strongly suggests that coal properties such as oxygen content, porosity, surface area and the amount of carboxylic functional groups are not controlling factors for reactivity of low-rank coal. The gasification rates of lignite with CO_2 and H_2O mainly depend on the presence of the exchangeable cations in the coal. After treating both coals with HCl to eliminate the catalytic effect of the inherent inorganics, the reactivity of Bowmans coal with steam is reduced from 4.2 to 0.10, which is almost equal to that for demineralized Yallourn coal (0.11).

Calcium acetate was added to both demineralized Bowmans and Yallourn coals at approximate same level by cation-exchange. The gasification rates of the Ca-catalysed coals were found to be much higher than those of the demineralized coal samples, viz 4.6 and 3.8 for Bowmans and Yallourn coals, respectively at 800°C. With temperature correction using E_a=133 kJ/mol, the reactivity values are 2.2 and 1.8 for Bowmans and Yallourn coals respectively at 750°C. With the presence of calcium, the gasification rate of Yallourn coal with steam is approximately 4 times higher than that for the non-catalytic coal samples. It is interesting to find that the R_{H2O}

values of the $Ca(Ac)_2$-catalysed samples are almost equal for these two coals. The slightly higher R_{H2O} value for Bowmans coal can be attributed to the experimental error. The reactivity of Yallourn coal can be increased as high as that of Bowmans coal by adding the same amount of active cations into the coals. The reason is that Yallourn coal contains similar concentration of carboxyl functional groups.

The experimental and theoretical results, obtained in the present investigation, confirm the following conclusion: in the kinetic regime (temperature < 1000°C), the gasification reactivity of lignite depends mainly on the concentration of the active sites. Alkali and alkaline-earth metals, present in the form of carboxylates provide the basic active sites. The reactivity of coal can be changed by increasing (e.g. by addition of alkali cations) or reducing (e.g. demineralization) the number of the active sites. Other parameters such as oxygen content, pore structure, moisture holding capacity, the amount of carboxylic functional groups and the total minerals content do not directly correlate the reactivity. The low reactivity of high-rank coal can be attributed to the low concentration of active sites. High rank coals have low concentrations of oxygen-containing functional groups and alkali contents. The inherent alkali compounds of high rank coal do not exhibit catalytic effect due to the poor connection between these cations and the coal structure.

5.2 Kinetics of Lignite Gasification

The current experimental data on steam and carbon dioxide gasification have been used to test several kinetic models. Comparison of the results indicates that models which assume that chemical reaction is the rate controlling step describe the process of steam and carbon-dioxide gasification well. Although Shrinking-Core and Homogeneous models have widely been used for coal gasification (Kwon et al. 1986), it is not generally appreciated why these two completely different models are so close in describing the gasification process. Since the Homogeneous model assumes that the reaction occurs throughout the whole particle, while the

Shrinking-Core model assumes that reaction takes place on the reacting surface of the unreacted-core, by changing particle size, the differences between these two models can be brought out. Studies which indicated that both models can be used to describe the same gasification process neglected the influence of particle size. The present results indicate that these two models can not suit the same gasification process! The results supporting the application of the two models for one particular gasification process were drawn from limited data obtained under the investigators' particular experiment conditions.

The present results indicate that gasification of a salty lignite is a catalytic reaction. Mathematical models based on the pore structure are not suitable for gasification of highly reactive coals catalysed by inherent or added inorganic constituents. The most convenient models used for describing coal gasification are only suitable for demineralized lignite at a fundamental level, unless they are modified to consider the catalytic effect of ash. Unfortunately, at present, no results have been reported for gasification modelling in which the catalytic effect of ash has been correlated.

5.3 The Characteristics and Beneficiation of Salty Bowmans Coal

South Australian lignites contain high concentrations of inorganic constituents which significantly affect their utilization. For example, the sodium content causes agglomeration of ash and defluidization in a fluidized-bed gasifier. Complete removal of these inorganic constituents from the raw coal would be costly on an industrial scale. Effective utilization of these coals must consider the influence of the ash content. Water washing, which may significantly reduce the total ash content, seems to provide an attractive method for the beneficiation of these high-ash coals. However, little information is available in the literature on the influence of water-leaching on reactivity.

Approximately 50% of the total inorganics of Bowmans coal is present in water-soluble form and can be removed by water washing. The present result shows that 83% of the total sodium of the coal can be removed by water washing. Approximately 85% of the total minerals, and 98% of the total alkali and alkaline-earth elements such as Na, K and Ca, can be removed by acid-washing. The major inorganic constituent which remaining in the acid-washed coal is silicon which is known to be inactive for gasification. The major metal elements present in raw Bowmans coal are: Na, Mg, Ca, Fe, K, Al and Si. Among them, calcium, potassium and magnesium were determined to be present as carboxylates. Sodium and iron were determined to be partly present as carboxylates and partly as minerals.

The results from this investigation show that water-leaching is an attractive method for the effective utilization of high ash content low-rank coals like Bowmans coal by gasification, because this process can remove 50% of total ash with only slight effect on the reactivity towards CO_2 and H_2O. Water-washed coal seems to be an ideal feedstock for a fluidized-bed gasifier because 83% of total sodium, the major cause of agglomeration and defluidization, is removed while the reactivity remains high. Ash agglomeration and the defluidization are critical operational problems in a fluidized bed gasifier. By using water-treated coal, the potential difficulties can be avoided. The treatment of the raw coal with acid could eliminate the problems by removing virtually all of the sodium, but the reactivity is greatly decreased. Acid-washing would be very costly and is probably unjustifiable for industrial scale utilization. Water-treatment provides a satisfactory balance between coal reactivity and the potential operational problems in the utilization of this coal.

5.4 The Role of Inherent Minerals

The role of inherent inorganic impurities in gasification has been the subject of numerous investigations. The inorganic constituent of coal consists of two major groups: humic salts and minerals. These two groups play different roles in the gasification of a coal. The effect of the inorganic constituents on gasification varies with coal rank. For lignite, the rates of steam and carbon dioxide gasification decrease by several orders of magnitude on removal of the inherent inorganics. For bituminous coal, reactivity can increases (about 1.5 times) in the absence of the inherent minerals (Garcia and Radovic 1986). For high rank coal, the removal of the minerals does not seem to affect their reactivity significantly. For most coals, calcium and sodium are the most abundant inherent active elements in coal. Solid evidence (Murray 1971, Higgins and Allardice, 1986, van Heek et al. 1989, and results from the present study) suggests that, as the major cationic inorganic constituent of lignite, most calcium is presented as carboxylates. Sodium, potassium and iron are partly present as carboxylates and partly as minerals. The total quantity of ash shows a poor correlation with the reactivity of the coal and only the active metal elements catalyse coal gasification.

The results from the present investigation show that reactivity may be greatly reduced by the removal of the inherent inorganic constituents. The high gasification rate of Bowmans coal is due to the presence of high concentrations of alkalis. This is in agreement with most of the publications on the effect of ash on gasification. Furthermore, the present results indicate that metals exhibit poor activities unless they are present in the form of carboxylates. Sodium, the most abundant alkali element of Bowmans coal and the also major source of the potential operational difficulties, has been found to be mainly presented as minerals. Only 13% of the total sodium is present as carboxylates. The organically-bound Na was found to have the main catalytic effect on gasification. Other inherent cations, such as calcium, also make a considerable contribution to the high reactivity. The present results show that most of the inherent calcium was present as carboxylates. Although most of the inherent iron are water-insoluble, the role of the inherent Fe in the gasification is unknown due to the lack of information on its chemical form. Iron is reported to only exhibit catalytic activity in its metallic form. In summary, regarding the role of the inherent inorganic impurities in the gasification of Bowmans coal, it appears that sodium and calcium carboxylates make the major contribution to the catalytic activities; other elements like K, Mg, Al and Si have less importance due to either their small quantity or the inactivity.

5.5 Catalytic Gasification of Bowmans Coal

Many studies have been performed on the catalytic gasification of coal with H_2O and CO_2 using various alkali and alkaline-earth salts. Numerous results have indicated that the salts of alkaline, alkaline-earth and some transition metals greatly catalyse coal gasification. The reported results of the catalytic activities of some salts were found to be confusing. For example, the results reported on the catalytic activity of NaCl in gasification were sometimes in conflict. Lang (1986) reported that NaCl was a poor catalyst for steam gasification. Other investigations (Zhang et al. 1986) indicated that NaCl does have a significant catalytic effect.

The present work deals with steam and carbon dioxide gasification of Bowmans coal using NaCl, $CaCl_2$, KCl, $NiCl_2$, NaAc, $Ca(Ac)_2$, $Ni(Ac)_2$, Na_2SO_4, Na_2CO_3 and NaOH as catalytic agents with the aim of obtaining the further knowledge of the catalytic activities of these salts in the gasification of Bowmans coal. The mechanisms and kinetics of catalysed-gasification have been discussed. The results from the present study have the following implications.

***On the activities of additives*:**

The present results show that alkali and alkaline-earth salts, added to coal by ion-exchange, are excellent catalysts for the gasification of Bowmans coal with carbon dioxide and steam. The relation between the gasification rate and the catalyst loading is found to vary depending on the nature of the salts used. The weak acid salts of the sodium and calcium exhibit a strong catalytic effect. The gasification rates of Bowmans coal with carbon dioxide and steam increase linearly with increasing NaAc and $Ca(Ac)_2$ loading from 0.04 to 2.5 mmol/g. Nickel, which has been reported to significantly catalyse the gasification of Yallourn coal with steam and carbon dioxide at low temperature (from 500 to 750°C), has less catalytic activity than Na, Ca and K under the current experimental conditions. The acetate salts of such metals have strong catalytic activities; in contrast, the chloride salts of these metals have less activity.

The present results provide useful information on the catalytic activities of various salts. The conclusions drawn from this work are supported by other investigations. With the addition of a small amounts of additives, the course of gasification may totally change. In the presence of a catalyst, the reaction temperature can be reduced. A low gasification temperature may avoid potential operational difficulties such as slagging and high temperature corrosion.

On the Mechanism of Catalysed-gasification:

The results obtained from the present study provide an explanation of the catalytic activities of some metals. Regarding the catalytic effect of alkalis on gasification, it indicates that, alkali cations are poor catalysts unless they connect the carboxylic functional groups to form active sites on the surface of the coal. The correlation between the activities of cations and the properties of a coal has been studied. Most investigators agree that low rank coals are more sensitive to catalysts than high rank coals. Some workers attributed this to the low porosity and surface area in the high rank coals compared to low rank coals. The differences in the porosity and surface between low rank coal and high rank coal do have some influence on the catalytic activity, for example, a coal with high porosity promotes the adsorption of cations. The present study indicate that the catalytic activity of alkali and alkaline-earth cations also depends on the properties of the coal - a sufficient amount of oxygen-containing groups, specially carboxyl groups, in the coal is the key factor which controls the activity of any added cations.

These results confirm the active site theory that explains the behaviour of the catalysed-gasification. The basic argument of the active site theory is that cations associated with carboxyl groups to form the active sites on the surface of coal. Gasification reaction takes place on these active sites. The rate of the reaction is proportional to the population of the sites. Compared with bituminous coal and anthracite, lignite contains high concentration of carboxyl groups which provide the possibility of ion-exchange with cations to form active sites.

The catalytic effect of the added cations on gasification is also influenced by other factors (e.g. pyrolysis, heat treatment of coal, and the method of catalyst loading). Their influence can also be explained by the active site theory. Wingmans et al. (1983) found that the catalytic activities of alkali carbonates is influenced by heat treatment. The rate of the catalytic gasification of a coal sample which had been pyrolysed in nitrogen before, was much lower than that of the coal without prior heat treatment. He attributed this to the loss of carboxyl groups due to the heat treatment. It is known that the carboxylic and other oxygen-containing functional groups begin to decompose at 400°C and the decomposition of these groups complete at 600°C (Murray 1973). Other investigators (Yokoyama et al. 1979, Mins et al. 1980, and Wigmans et al. 1981) also found that the catalytic activity of alkali salts is affected by the oxygen content of the coal and the reactivity of the alkali-catalysed coal can be correlated with the oxygen content of the coal. The present results show that heat-treated Bowmans coal is not sensitive to the catalyst loading because of loss of carboxylic function groups. The added alkali salts, which exhibit a strong catalytic effect on the gasification of normal coal samples, do not have any catalytic activity in the heat-treated coal samples. This confirms that alkalis are poor catalysts for gasification unless they connect the carboxylic functional groups.

The catalytic activity of cation is also affected by the method of catalyst loading. Many studies have indicated that the physical mixing of the alkali salts is less efficient than the cation-exchange. In order to obtain a high concentration of carboxylate in the coal, catalyst is added to coal by the impregnation method. The low catalytic activity of catalysts, added to a coal by the method of physical mixing, is generally recognized as being due to the poor dispersion of the metals in the coal. In general, the conclusions of this discussion are: the nature and amount of the oxygen-containing functional groups in a coal determine the catalytic activity of added cations. In the absence of oxygen-containing functional groups, alkalis are poor catalysts. The selection of a catalyst for gasification should be based on two considerations: the activity of the selected cation, and the possibility for the added cation to connect the carboxyl functional groups of coal.

Chapter 6.

CONCLUSION

The gasification of Bowmans, and to a lesser extent Yallourn, coal with carbon dioxide and steam was studied experimentally as well as theoretically. The reactivity of Bowmans coal towards CO_2 and H_2O was determined under varied experimental conditions aimed at obtaining information on the gasification kinetics. Experimentally-obtained kinetic parameters were compared to those of other coals reported in the literature. The transformations of the inorganics in raw Bowmans coal during water-leaching and acid-washing were studied to examine the characteristics of the inherent minerals. Gasification was also carried out on pre-treated coal samples to determine the role of the inherent inorganic impurities in the gasification process. Factors which influence or control the gasification rate were discussed. The catalytic effects of various salts on the gasification of Bowmans coal were examined by impregnating the coal with solutions of different concentrations. Various alkali and alkaline-earth salts were used as catalysts. The kinetics and mechanisms of the gasification of lignite with CO_2 and H_2O were examined. From the results and discussions presented in earlier chapters, the following conclusions are drawn:

1 In comparison with other Australian and overseas coals, the gasification rates of Bowmans coal with steam and carbon dioxide are very high. Generally, the reactivity

7 of high rank coal can be correlated by the carbon content. Low-rank coal has high but widely spread reactivity, while high rank coal has low reactivity. The reactivity of low-rank coal is well correlated by its inherent Na and Ca content.

2 Bowmans coal is more reactive than other Australian coals. Its high reactivity is mainly attributed to the presence of active inorganics in the structure of the coal.

3 Gasification rates of Bowmans coal with CO_2 and H_2O are greatly reduced by treating the raw coal with HCl. Water-washing only slightly affects the reactivity.

4 The gasification rates of raw Bowmans coal with carbon dioxide and steam are found to be much higher than those of the acid-washed samples. When cations, washed from the raw coal, are added back to the deashed coal, its reactivity is increased to the same level as that of the raw coal. The rate of steam gasification is higher than that of carbon dioxide under the current experiment conditions.

5 Particle size does not significantly affect the rate of gasification of Bowmans coal with carbon dioxide and steam. The contribution of the external surface to the gasification rate is small. Reaction mainly takes place at the pore surface.

6 Both the Homogeneous and Shrinking-Core models for descriptions of the gasification process were examined. The Homogeneous model best describes CO_2 gasification of low-rank Bowmans coal in this work because it accounts for particle size variation. The experimentally obtained activation energies of the C-CO_2 and C-H_2O reactions are within the range of previously reported values for lignites.

7 Active site theory provides a satisfactory explanation for the gasification behaviour of low-rank coal. It assumes that reaction mainly occurs at active sites. Cations such as Ca

and Na associated with carboxylic functional groups form active sites on the surface of the coal. The gasification rate of coal is proportional to the concentration of the active sites.

8 Ion-exchange provides a useful method for loading catalysts onto a coal. The adsorption of various cations on coal is found to show a linear relationship with the concentration of the solution. The desired amount of the cations can be added to a coal by impregnating the coal with a solution of correct concentration. The order of cation adsorption on coal is: K ~ Fe^{2+} ~ Fe^{3+} > Mg > Na > Ca.

9 The rate of gasification of Bowmans coal with carbon dioxide and steam can be greatly enhanced by adding active metals such as Na, Ca, K and to a lesser extent Ni to the coal by ion-exchange. The gasification rates of the alkali-catalysed coal samples are found to be several orders of magnitude higher than those of non-catalysed ones.

10 Anions of added catalytic agents are found to have a significant influence on resultant catalytic activities of the cations. Alkali salts of weak acid exhibit a strong catalytic effect on coal gasification; in contrast, alkali salts of strong acids have less catalytic effect. For all the sodium salts used in this investigation, the sequence of catalytic activity is: NaAc ~ NaOH ~ Na_2CO_3 > Na_2SO_4 > NaCl.

11 Water-leaching, which removes 83% of the inherent sodium and approximately 50% of the total mineral content, only slightly affects the gasification of Bowmans coal with steam and carbon dioxide. Water-washing provides an attractive method of using such a high ash coal. After water-washing, the coal remains highly reactive, while, the removal of the inherent sodium avoids agglomeration and defluidization in a fluid-bed gasifier.

12 Sodium, the most abundant active metal in the raw coal, is not the only source of catalytic effect. Inherent calcium also makes a considerable contribution to the high reactivity.

13 Acetate salts of alkali and alkaline-earth metals show a strong catalytic effect on steam and carbon dioxide gasification; in contrast, chloride salts of these metals are found to have much lower activities. This indicates that cations associated with carboxyl groups are active, while physically absorbed cations are far less active.

14 The gasification reactivity of coal samples which were impregnated with a mixture of Na/Ca was found to be significantly lower than the sum of gasification reactivities when with impregnated with each of these elements at the same concentration level. The effect of different metals reported by others has not been found in this study.

15 For the NaAc and $Ca(Ac)_2$ catalysed steam gasification reactions, the reaction rates are found to increase linearly with increase in catalyst loading. For the $Ni(Ac)_2$ catalysed gasification reactions, the reactivity is found to approach saturation, and lose its catalytic efficiency quickly with the progress of reaction. For the gasification reactions catalysed by chloride salts, the reactivity increase with increasing catalyst loading, but no linear relation was found between the reactivity and catalyst loading.

16 Nickel has been found to be more suitable for the catalytic gasification of coal with steam rather than with carbon dioxide.

17 Under the current experimental conditions, with catalyst loading by impregnation of the coal in 0.1M solutions, the catalytic activities for steam gasification are found to be

ranked as: NaAc ~ $Ca(Ac)_2$ > $Ni(Ac)_2$ > $CaCl_2$ > NaCl ~ KCl > $NiCl_2$. The catalytic activities for carbon dioxide gasification is: NaOH ~ NaAc ~ $Ca(Ac)_2$ ~ KAc ~ Na_2CO_3 > Na_2SO_4 > $Ni(Ac)_2$ > NaCl.

18 Heat-treated coal samples are not amenable to catalyst loading by impregnation. For the heat-treated coal samples, impregnation with NaAc and $Ca(Ac)_2$, does not catalyse the gasification reaction. Alkali-catalysed, preheated, demineralized Bowmans coal has the same low reactivity as non-catalysed, deashed coal sample. This indicates that oxygen-containing functional groups play an important role in catalytic gasification.

19 The gasification rates of Bowmans coal with carbon dioxide and steam are much higher than those of Yallourn coal. Measured gasification rates of Yallourn coal in the present study are in good agreement with the results reported by other investigators.

20 The reactivity of lignites is dominated by the quantity and quality of the inherent inorganic impurities. Other properties, such as porosity, surface area, moisture holding capacity and amount of carboxyl or other oxygen-containing functional groups, seem to be less important.

21 The Single Particle Furnace, constructed in the present investigation, was found to be effective for simulating gasification behaviour of single particles under fluidised-bed conditions.

NOMENCLATURE

A	constant for equation 4.2.26
A	area [cm^2]
A_l	ash content [g]
A_o	initial ash content [g/g dry coal]
a	gasification kinetic parameter for equation 2.3.3
a'	gasification kinetic parameter for equation 2.3.4
B	constant for equation 4.2.26
B	alkali index
b	stoichiometric coefficient
b	gasification kinetic parameter for equation 2.3.3
b'	gasification kinetic parameter for equation 2.3.4
C	fixed carbon content [g/g dry coal]
C	constant for equation 4.2.26
C_s	solid (reactant) concentration [kmol/m^3]
C_g	reactant concentration [kmol/m^3]
C_o	initial fixed carbon content [g/g dry coal]
C_p	concentration of product gas [kmol/m^3]
D	bulk diffusivity [cm^2/s]
d	diameter [mm]
d_p	particle diameter [m]
E_a	activation energy [kJ/mol]
E_{CO2}	carbon dioxide gasification activation energy [kJ/mol]
E_{H2O}	steam gasification activation energy [kJ/mol]
f_L	reactivity factor for equation for equation 2.5.11

$f(c_c)$	intrinsic reactivity for equation 2.5.12
K	equilibrium constant
k	reaction rate constant [min^{-1}]
k_1	reaction rate constant [min^{-1}]
k_2	reaction rate constant [min^{-1}]
k_3	reaction rate constant [min^{-1}]
k_f	gas film transfer coefficient [cm/s]
k_g	mass transfer coefficient [cm/s]
k^o	reaction rate constant [min^{-1}]
k_o	preexponential factor [s^{-1}]
k_s	solid-gas reaction rate constant [s^{-1}]
k'	reaction constant [s^{-1}]
M_s	mass of carbon
M_{A1}	ash content [g]
M_{C1}	fixed carbon content [g]
M_{V1}	volatile matter content [g]
n	reaction order respect total carbon content
n	activity constant of inorganics
P	pressure [kPa]
P_{H2}	hydrogen pressure [kPa]
P_{H2O}	steam pressure [kPa]
P_{CO2}	carbon dioxide pressure [kPa]
p^*	partial pressure
R_d	desorption rate
R_o	particle radius [mm]
R_p	pellet radius [mm]
R_{CO2}	carbon dioxide reactivity index [h^{-1}]
R_{H2O}	steam reactivity index [h^{-1}]

R	universal gas constant [kJ/mol]
R_o	initial particle radius [mm]
R_m	reactivity [h^{-1}]
r	radius [mm]
r	reaction rate [$min.^{-1}$]
r_i	grain radius [mm]
r_o	initial grain radius [mm]
Sc	Schmidt number,$\mu/\rho D$
S_x	external surface area [m^2]
S_o	surface area [m^2]
S	pore surface area [m^2]
T	temperature [K]
T_a	reaction temperature [K]
T_i	indicating temperature [K]
T_R	reference temperature [K]
T_s	surface temperature [K]
t	reaction time [min.]
t^*	reduced reaction time [dimensionless]
V	volatile evolved from coal [g/g dry coal]
v	velocity of gas flow [m/s]
V_l	volatile matter [g]
V_o	initial volatile content [g/g dry coal]
V_p	volume of particle [m^3]
X	fractional carbon conversion [%]
X_T	total mass conversion of coal [%]
X_v	volatile matter conversion [%]
τ	reaction time [min]
$\tau_{0.5}$	reaction time to achieve 50% carbon conversion [min]

ρ	density of coal [kg/m^3]
ρ_p	density of particle [kg/m^3]
ρ_s	density of particle reactant [kg/m^3]
θ	effectiveness factor
ε	bed voidage
μ	viscosity [m^2/s]
δ	diameter of pore [Å]
φ	diffusion parameter for equations 4.2.16
φ	structure parameter for equation 2.5.13

REFERENCES

A.I.E., Energy 83, Canberra,*National Conference Publication*, 1983, 83(2), p145

Adanez, J., Miranda, J., and Gavilan, J.-M. (1985), Kinetics of a lignite-char gasification by CO_2. *Fuel*, Vol 64, p801

Adanez, J. and de Diego, L., (1990). Mineral matter effects on the reactivity of char during gasification. *Fuel Processing Technology*, Vol 24, p198.

Adschiri, T. and Furusawa, T. (1986), Relation between CO_2-reactivity of coal char and BET surface area. *Fuel*, Vol, 65, p927

Adschiri, T., Shiraha, T., Kojima, T. and Furusawa, T., (1986). Prediction of CO_2 gasification rate of char in fluidised bed gasifier. *Fuel*, Vol 65, p1688.

Adschiri, T., Nozaki, T., Furusawa, T. and Zhu, Z.-B., (1991). Characterization of coal char gasification rate. *AIChE Journal*, Vol 37, p897

Agarwal, A. K., and Sears, J. T., (1980). *Ind. Eng. Chem. Pro. Des. Dev.*

Agnew, J.B. (1986). *SENRAC* report. University of Adelaide.

Agnew, J.B. (1989). *SENRAC* report. University of Adelaide.

Agnew, J.B. and Ye, D.P., (1992). Problems of temperature measurement in the gas-solid reaction systems. *CHEMECA'92*

Ahmed, S. and Back, M.H., (1985). *Carbon*, Vol 23, 513.

Asami, K. and Ohtsuka, Y., (1990). Gasification of low rank coals with chlorine-free iron catalyst from ferric chloride. *Pittsburgh Coal Conference*, proceeding. p357.

Balci, S., Dogu, G. and Dogu, T., (1987). Structural variation and a deactivation model for gasification of coal. *Ind. Eng. Chem. Res.* Vol 26, p1454.

Baronian, J. and Quast, K.B., (1989). South Australian low rank coal ash study. South Australia Institute of Technology, School of Metallurgy.

Barrett, D., (1984). Gasification of char in fluidized bed systems. End Grant Report 270, University of New South Wales.

Bastick, M., Perrot, J.-M. and Weber, J., (1986). General characteristics of coal gasification. *International Chemical Engineering*, Vol 26, p243.

Beesting, M., Hartwell, R.R. and Wilkinson, H.C., (1977). Coal rank and coke reactivity. *Fuel*, Vol 56, p319.

Binford, J. S., Jr, and Eyring, H., (1956). *J. Phys. Chem.* 60, p486

Bhatia, S. K., and Perlmutter, D., (1981). A random pore model for fluid-solid reactions: (2) Diffusion and transport effects. *AIChE. J.* 27. p247.

Blackwood, J. D. and Ingeme, A. G., (1960). *Aust. J. Chem.* 13, 194

Blake, T. R., Herline, W. E., and Schneyer, G. P., (1979). Numerical simulation of coal gasification process. *National meeting of the AIChE*, Boston, MA.

Brooks, J. D., Duie, R.A. and Sternhell, S., (1958). *Appl. Sci. J.* 9.

Bruno, G., Carvani, L. and Passoni, G., (1986). Pressure influence on potassium catalysed char steam gasification. *Fuel*, Vol 65, p1386.

Bruno, G., Carvani, L. and Passoni, G., (1986). Correlation between potassium losses and mineral matter composition in catalytic cola steam gasification. *Fuel*, Vol 65, p1473

Causton, P. and McEnanay, B., (1985). *Carbon* Vol 64, p1447.

Chin, G., Kimura, S., Tone, S. and Otake, T., (1983). Gasification of coal char with steam (part 2). Pore structure and reactivity. Intern. Chem. Eng. Vol 23, p113.

Chin, G., Liu, G.F. and Dong Q.S. (1987), New approach for gasification of coal char. *Fuel*, Vol 66, p869

Colle, K.S., Kim, K. and Wold, A., (1983). Nickel-catalysed carbon gasification: crystallographic and magnetic studies. *Fuel*, Vol 62, p155.

Cooper, B.R. and Ellingson, W.A., (1983). "The science and technology of coal and coal utilization" Chapter 4 & 5.

Douchanov, D. and Angelova, G. (1983). Effect of catalysis and inlet gas on coal gasification. *Fuel*, Vol 62, p231.

Dryden, I.G.C., (1963). "Chemistry of coal utilization", Suppl. Vol. (Ed. Lowry), John Wiley, New York.

Dunne, D.J., (1988). Upgrading South Australian lignite by high-temperature pre-treatment. Ph.D thesis. The University of Adelaide

Dunne, D.J. and Agnew, J.B., (1990). Thermal upgrading of low-grade, low-rank South Australian coal. *Energy Sources*, Vol. 14, p 169-181.

Durie, R.A. "The science of Victorian brown coal. structure, properties and consequences for utilisation". Butterworth-Heinemann Ltd. Chapter 6, 7 and 8.

Dutta, S. and Wen, C. Y., (1977). Reactivity of coal and char. 1. In carbon dioxide atmosphere. *Ind. Eng. Chem. Proc. Des. Dev.* 16. p20.

Dutta, S. and Wen, C. Y., (1977). Reactivity of coal and char. 2. In oxygen - nitrogen atmosphere. *Ind. Eng. Chem. Proc. Des. Dev.* 16. p31.

Ehrburger, P., Addoun, A. Addoun, F. and Donnet, J., (1986). carbonization of coals in the presence of alkali hydrogen and carbonates: formation of activated carbon. *Fuel*, Vol 65. p1447.

Ellington, R. T., (1977). "Liquid fuel from coal" Academic Press. New York.

Elliott, M.A. (1981). "Chemistry of coal utilization". Chapter 8, 23, 24, 25. John Wiley & Son, Inc.

Ergun, S. J., (1956). *Phys. Chem.* 60. p480.

Fernandez-Gonzalez, C. Linares-Solano, McEnaney, B. and Salinas-Martinez de Lecea, C. (1986). The characterization of surface properties and steam reactivities of two Spanish coals of high ash content. *Fuel*, Vol 65, p991.

Fernandez-Morales, I., Lopez-Garzo, F.J., Lopez-Peinado, A., Moreno-Castilla, C. and River-a-Utrilla, J., (1985). Study of heat-treated Spanish lignite. *Fuel*, Vol 64, p666.

Ferrero, G.L., Maniatis, K., Buekens, A. and Bridgwater, A.V., (1989). "Pyrolysis and gasification". Commission of the European Communities. Elsevier Applied Science, London.

Formella, K. Sulimma, A., van Heek, K.-H. and Juntgen, H., (1986). Interaction of mineral matter in coal with potassium during gasification. *Fuel*, Vol 65, p1470.

Freund, H., (1985). Gasification of carbon by CO_2: a transient kinetics experiment. *Fuel*, Vol 56, p63.

Freund, H., (1986). Kinetics of carbon gasification by CO_2. *Fuel*, Vol 64, p657.

Froment, G.F. and Bischoff, K.B., (1990). "Chemical reactor analysis and design", John Wiley & Son, Chapter 3.

Fung, D.P.C., (1982). Laboratory gasification of five Canadian coals. *Fuel*, Vol 61, p139.

Fung, D.P.C. and Kim, S.D., (1983). Laboratory gasification study of Canadian coals, 2 Chemical reactivity and coal rank. *Fuel*, Vol 62, p1337

Fung, D.P.C., Faribridge, C. and Aderson, R., (1988), Gasification reactivity of Canadian anthracite and semi-anthracite chars. *Fuel*, Vol 67, p753

Furusawa, T., Kojima, T., Kuramoto, M. and Adschiri, T., (1987). Development of a coal gasification process using circulating fluidized bed solid. Studies on utilization of coal conversion, Report of special research on energy under grant in aid of scientific research of Ministry of Education, Science and Culture, Japan

Gan, H., Nandi, S.P. and Walker, P.L. Jr., (1972). *Fuel*, Vol 51. p272.

Garcia, X. and Radovic, L.R., (1986). Gasification reactivity of Chilean coals. *Fuel*, Vol 65, p292.

Gary, V., (1983). A formula for the mineral matter to ash ratio for low rank coals. *Fuel*, Vol 62, p94.

Gavalas G. R., (1980). A random capillary model with application to char gasification at chemically controlled rates. *AIChE. J.* 26. p577

Given, P.H., and Yarzab, R.F., (1975). Problems and solutions in the use of coal analyses, Tech. Report 1 from coal research section, Pennsylvania State University to the US Department of Energy.

Johnson, J. L., (1979). "Kinetics of coal gasification". John Wiley & Sons, New York.

Gomez-Serrano, V., Sanchez-Iniguez, F., Bernalte-Garcia, A. and Valenzuela-Calahorro, C., (1990). Penetration of Na compounds - catalysts of gasification reaction in activated carbon by heating between 380 and 950°C. *Fuel*, Vol 69, p391.

Gonzalez, A.I., Bermejo, J., Martinez-Alonso, A., Moinelo, S.R. and Tascon, J.M.D., (1990). Reaction of coal mineral matter during coal gasification. *Fuel*, Vol 69, p873.

Goyal, A., Zabransky, R. and Rehmat, A., (1989). Gasification kinetics of Western Kentucky Bituminous coal char. *Ind. Chem. Eng. Res.* Vol 28, p1767.

Guo, C.T. and Zhang, L.M. (1986), Kinetics of coal gasification at elevated pressures. *Fuel* Vol 65, p1364.

Gururajan, V.S., Ye, D.P., Agarwal, P.K. and Agnew, J.B., (1991). Mathematical modelling of a fluidized bed coal gasifier and measurement of kinetics of gasification of Bowmans lignite. *CHEMECA'91.*

Gutierrez, L. and Watkinson, A.P., (1982). Fluidized-bed gasification of some Western Canadian coals. *Fuel*, Vol 61, p133.

Haga, T., Sato, M., Nishiyama, Y., Agarwal, P.K. and Agnew, J.B., (1991). Influence of structural parameters of coal char on K- and Ca-catalyzed steam gasification. *Energy & Fuels*, Vol 5, p317.

Hamilton, R.T., Sams, D. and Shadman, F., (1984). Variation of rate during potassium - catalysed CO_2 gasification of coal char. *Fuel*, Vol 63, p1008.

Hashimoto, K., Miura. K., Xu, J.-J. Watanabe, A. and Masukami, H., (1986). Relationship between the gasification rate of carbon supporting alkali metal salts and the amount of oxygen trapped by metal. *Fuel*, Vol 65, p489.

Hashimoto, K., Miura, K. and Ueda, T., (1986). Gasification rates of various coals measured by a rapid heating method. *World Congree of Chemical Engineering*, Tokyo.

Hashimoto, K., Miura, K. and Ueda, T., (1986). Correlation of gasification rates of various coals measured by a rapid heating method in a steam atmosphere at relatively low temperatures. *Fuel*, Vol 65, p223.

Hastaoglu, M.A., Hassam, M.S. and Berruti, F., (1988). Assessment of catalytic effect of iron on carbon gasification using a gas-solid reaction model. *Fuel*, Vol 67, p1482.

Haynes. W.P., Gasior, S.J. and Forney, A.J., (1974). "Coal gasification" (Ed. L.G. Massey), Advances in Chemistry Series 131, *Amer. Chem. Soc.*, Washington, D.C.

Haynes. H. Jr., (1982). "Diffusion and reaction in porous media-IV". *American Institute of Chemical Engineers.*

Hengel, T. and Walker P.L., (1984). Catalysis of lignite char gasification by exchange calcium and magnesium. *Fuel,* Vol 63, p1214.

Hermann, G. and Huttinger, K.J., (1986). Mechanisms of non-catalysed and iron-catalysed water vapour gasification of carbon. *Fuel,* Vol 65. p1410.

Hippo, E.J., Jenkins, R.G. and Walker, P.L., (1979). Enhancement of lignite char reactivity to steam by cation addition. *Fuel,* Vol 58, p338.

Hirato, H. and Ninomiya, Y., (1987). A basic study on the characteristics of as fusion in high temperature coal gasification. Report of special project research on energy. p117.

Holstein, W.L. and Boudart, M. (1983), Transition metal and metal oxide catalysed gasification of carbon by oxygen, water, and carbon dioxide. *Fuel,* Vol 62, p162.

Holstein, W.L., (1983). Design of laboratory reactor for the measurement of catalytic carbon and coal gasification kinetics. *Fuel,* Vol 62, p259.

Huhn, F., Klein, J. and Juntgen, H., (1983). Investigations on the alkali-catalysed steam gasification of coal: kinetics and interactions of alkali catalyst with carbon. *Fuel,* Vol 62, p196.

Huttinger, K.J., (1983). Fundamental problems in iron-catalysed coal gasification - a survey. *Fuel,* Vol 62, p166.

Huttinger, K.J. and Minges, R., (1986). The influence of the catalyst precursor anion in catalysis of water vapour gasification of carbon by potassium. 1. Activation of the catalyst precursors. *Fuel,* Vol 65, p1112.

Huttinger, K.J. and Minges, R., (1986). The influence of the catalyst precursor anion in catalysis of water vapour gasification of carbon by potassium. 2 catalytic activity as influenced by activation and deactivation reactions. *Fuel,* Vol 65, p1122.

Huttinger, K.J. and Krauss, W., (1982). Catalytic activity of coal minerals in water vapour gasification of coal. *Fuel,* Vol 61, p291.

Jensen, G.A,, (1975). The kinetics of gasification of carbon contained in coal minerals at atmospheric pressure. *Ind. Eng. Chem., Process Des. Dev.* Vol 14, p308.

Juntgen, H., (1983). Application of catalysts to coal gasification process. Incentives and perspectives. *Fuel*, Vol 62, p234.

Johnson, J. L., (1975). Relationship between the gasification reactivities of coal char and the physical and the chemical properties of coal and coal char. *American Chemical Society, Division of Fuel Chemistry Coal Gasification Symposium*, Chicago, IL.

Johnson, J. L., (1979). "Kinetics of coal gasification". John Wiley & Sons, New York.

Johnson, J. L., (1981). "Fundamentals of coal gasification, chemistry of coal utilization". Wiley-Interscience, New York.

Johnstone, J. F., Chen, C. Y., and Scott, D. S., (1952). *Ind. Eng. Chem.* 44, p1564.

Joly, J.P., Cazorla-Amoros, D., Charcosset, H., Linares-Solano, A., Marcilio, N.R., Martinez-Alonso and Salinas-Martinez de Lecea, C., (1990). The state of calcium as a char gasification catalyst - a temperature-programmed reaction study. *Fuel*, Vol 69, p878.

Kasaoka, S. Sakata, Y. and Tong, S., (1983). *J. Fuel Soc. Japan* Vol 62, p335.

Kasaoka, S. Sakata, Y. and Tong, C., (1985). Kinetic evaluation of the reactivity of various coal chars for gasification with carbon dioxide in comparison with steam. *International Chemical Engineering*, Vol 25, p160

Kasaoka, S. and Sakata, Y., (1987). Fundamental study on the development of a gasification process for various coals. Report of special project research on energy, p147.

Katta, S. and Keairns, D., (1981). Study of kinetics of carbon gasification reactions. *Ind. Eng. Chem. Fundam.* 20, p6.

Katta, S. and Keairns, D., (1986). Effect of time/temperature history on char Reactivity. *The Canadian Journal of Chemical Engineering*, Vol 64, p994

Kapteijin, F. and Moulijn, A., (1983). Kinetics of the potassium carbonate-catalysed CO_2 gasification of active carbon. *Fuel*, Vol 62 p211.

Kapteijin, F., Peer, O. and Moulijn, A., (1986). Kinetics of the alkali carbonate catalysed gasification of carbon. 1. CO_2 gasification. *Fuel*, Vol 65 p1371.

Kayembe, N. and Pulsifer, A.H., (1967). Kinetics and catalysis of the reaction of coal char and steam. *Fuel*, Vol 55, p211.

Keller, J., (1990). Diversification of feedstocks and products: recent trends in the development of solid fuel gasification using the Texaco and the HTW process. *Fuel Processing Technology*, Vol 24, p247.

Khan, M. R. and Jekins, R.G., (1986). Influence of added calcium compounds on swelling, plastic, and pyrolysis behaviour of coal devolatilization at elevated pressure. *Fuel*, Vol 65, p1203

Khan, M. R., (1987). Significance of char active surface area for appraising the reactivity of low- and high- temperature chars. *Fuel*, Vol 66, p1626

King, W., (1981). Coal gasification. *Fuel*, Vol 60, p803.

Klei, H.E., Sahagian, J. and Sundstrom, D.W., (1975). Kinetics of the active carbon-steam reaction. *Ind. Chem. Eng., Process Des. Dev.*, Vol 14, p470.

Knight, A.T. and Segeant, G., (1982). Reactivity of Australian coal-derived chars to carbon dioxide. *Fuel*, Vol 61, p145

Knight, A.T. and Segeant, G., (1982). Studies of the reactivity of chars derived from Australian coals in carbon dioxide - influence of inorganic impurities and internal pore structures. *CHEMECA'82*, Sydney, 24-26 August.

Koenig, P.C., Squires, R.G. and Laurendeau, N.M., (1986). Char gasification rate by carbon dioxide: Further evidence for a two-site model. *Fuel*, Vol 65. p412.

Kopsel, R., Zabawski, H., (1990). Catalytic effect of ash components in low rank coal gasification. 1 Gasification with carbon dioxide. *Fuel*, Vol 69, p275.

Kopsel, R., Zabawski, H., (1990). Catalytic effect of ash components in low rank coal gasification. 2 Gasification with steam. *Fuel*, Vol 69, p282.

van Krevelen, D.W., (1982). Development of coal research - a review. *Fuel*, Vol 61, p786.

Kuhn, L. and Plogmann, H., (1983). Reaction of catalysts with mineral matter during coal gasification. *Fuel*, Vol 62, p205.

Kunii, D. and Levespiel, O., (1969). "Fluidization Engineering", John Wiley and Sons Inc. Chapter 7.

Kwon, T.W., Kim, S.D. and Fung,P.C., (1988). Reaction kinetics of char-CO_2 gasification. *Fuel*, Vol 67, p530.

Kwon, T.W., Kim, J.R., Kim, S.D. and Park, W.H., (1989). Catalytic steam gasification of lignite char. *Fuel*, Vol 68, p416.

Kyotani, T., Aang, Z.G., Hayashi, S. and Tomita, A., (1988). *Energy & Fuels*, Vol 2, p136

Lang, R.J. and Neavel, R.C., (1982). Behaviour of calcium as a steam gasification catalyst. *Fuel*, Vol 61, p620.

Lang, R.J., (1986). Anion effects in alkali-catalysed steam gasification. *Fuel*, Vol 65, p1324.

Laurendeau, N. M., (1978). Heterogeneous kinetics of coal char gasification and combustion. *Prog. Energy Combust. Sci.* 4. p221-270.

Lee, S., Angus, J.C., Edwards, R.V. and Gardner, N.C., (1984). Noncatalytic coal char gasification. *AIChE Journal* Vol 30, p583.

Leonhardt, P., Sulimma, A., van Heek, K.-H. and Juntgen(u..), H., (1983). Steam gasification of German hard coal using alkaline catalysts. *Fuel*, Vol 62, p201.

Levenspiel, O., (1979). "Chemical reaction engineering", chapter 12. John Wiley & Son Inc. New York.

Linares-Solano, A., Salinas-Martinez de Lecea, C., Rodriguez-Reinoso, F. and Almela-Alarcon, M., (1986). *Fuel*, 1986, Vol 65, p1345.

Linares-Solano, A., Mahajian, O.P. and Walker, P.L., (1979). Reactivity of heat-treated coals in steam. *Fuel*, Vol 58, p327.

Linares-Solano, A., Hippo, E.J., and Walker, P.L., (1986). Catalytic activity of calcium for lignite char gasification in various atmospheres. *Fuel*, Vol 65, p776.

Linder, B. and Simonsson, D., (1981). Comparison of structure models for gas-solid reactions in porous solids undergoing structural changes. *Chem. Eng. Scie.* Vol 36, p1519.

Liu, Z.-L. and Zhu, H.-H., (1986). Steam gasification of coal char using alkali and alkaline-earth metal catalysts. *Fuel*, Vol 65, p1334.

Long, F. J. and Sykes, K. W., (1948). *Proc. R. Soc.* A193, p337.

Mahajian, O. Yarzab, R. and Walker, P., (1979). Unification of coal-char gasification reaction mechanisms. *Fuel*, Vol 57, p643.

Mahajian, O. and Walker, P., (1979). Effect of inorganic matter removal from coals and chars on their surface area. *Fuel*, Vol 58, p333.

Matsui, I., Kunii, D. and Furusawa, T., (1987). Study of char gasification by carbon dioxide. 1. kinetic study by thermogravimetric analysis. *Ind. Eng. Chem. Res.* Vol 26, p91.

Matsui, I., Kojima, T., Kunii, D. and Furusawa, T., (1987). Study of char gasification by carbon dioxide. 2. continuous gasification in fluidized bed. *Ind. Eng. Chem. Res.* Vol 26, p95.

Matsukata, M. and Morita, Y., (1987). Catalytic gasification of carbonaceous on potassium catalyst. Report of special project research on energy. p111

Manzoori, A.R. and Plastow, K.M., (1988). Gasification of South Australian salty coal using High Temperature Winkler process. Australian Coal Science Conference 1988, University of Adelaide.

Manzoori, A.R. (1990). Role of inorganic matter in agglomeration and defluidisation during the circulating fluid bed combustion of low-rank coal. Ph.D thesis. The University of Adelaide.

McKee, D.W., (1983). Mechanisms of the alkali metal catalysed gasification of carbon. *Fuel*, Vol 62, p170.

McKee, D.W., Spiro, C., Kosky, P. and Lamby, E.J., (1983). Catalysis of coal char gasification by alkali metal salts. *Fuel*, Vol 62, p217.

Meijer, R. Muhlen, H.J., Kapteijn, F. and Mouliji, J.A., (1990). Burn-off behaviour in catalysed CO_2 gasification of bituminous coal char: A comparison of TGA and fixed-bed reactor. *Pittsburgh Coal Conference*, proceeding. p338.

Meijer, R. Weeda, M., Kapteijn, F. and Mouliji, J.A., (1990). Catalyst loss and retention during alkali catalysed carbon gasification in CO_2. *Pittsburgh Coal Conference*, proceeding. p362.

Meyers, R.A., (1982). "Coal structure". Academic Press, Inc. (London). Chapter 5.

Miller, R.N., Yarzab, R.F. and Given, P., (1979). Determination of the mineral-matter content of coals by low-temperature ashing. *Fuel*, Vol 58, p4.

Mims, C.A. and Pabst, J.K., (1983). Role of surface salt complexes in alkali-catalysed carbon gasification. *Fuel*, Vol 62, p176.

Miura, K., Aimi, M., Naito, T. and Hashimoto, K., (1986). Steam gasification of carbon: effect of several metals on the rate gasification and the rate of CO and CO_2 formation. ***Fuel***, Vol 65, p407

Miura, K., Hashimoto, K. and Silveston, P.L., (1989). Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity. ***Fuel***, Vol 68, p1461

Miura, K., Makino, M. and Silveston, P.L., (1990). Correlation of gasification reactivity with char properties and pyrolysis conditions using low rank Canadian coals. ***Fuel***, Vol 69. p580

Morgan, M. E., Jenkins, R. G., Jr and Walker, P. L., (1981). Inorganic constituents in American lignite. ***Fuel***, Vol 62 p189.

Muhlen, H. J., (1986). Influence of pretreatment temperature and pressure on char reactivity during hydrogasification. ***Fuel***, Vol 65, p591.

Muhlen, H. J., van Heek, K. H. and Juntgen, H., (1987). *Am. Chem. Soc. Div.* ***Fuel*** *Chem.*, Vol 32(1), p286.

Murray, J.B., (1973). Changes in state of combination of inorganic constituents during carbonization of Victory Brown coal. ***Fuel***, Vol 52, p105.

Neogi, D., Chang, C.C., Walawender, W.P. and Fan, L.T., (1986). Study of coal gasification in an experimental fluidized bed reactor. *AIChE*, Vol 32, p17.

Nishiyama, Y. and Tamai, Y., (1979). Gasification of coals treated with non-aqueous solvents. 2. Effect of liquid ammonia treatment on gasification with hydrogen. ***Fuel***, Vol, p559.

Nishiyama, Y. and Tomita, Y., (1979). Gasification of coals treated with non-aqueous solvents. 4. Reactivity of coal treated with liquid ammonia. ***Fuel***, Vol 58, p366.

Nishiyama, Y., (1986). Catalytic behaviour of iron and nickel in coal gasification. ***Fuel***, Vol 65, p1404.

Nishiyama, Y. and Haga, T., (1987). Studies on the catalysis of coal gasification. Report of project research on energy, 1986, Japan.

Nishiyama, Y., Haga, T., Terada, K., Amaya, M. and Nogi, K., (1990). Product selectivity in catalytic gasification of carbon with steam. *Pittsburgh Coal Conference*, proceeding. p365.

Ohtsuka, Y. and Tomia, A., (1986). Calcium catalysed steam gasification of Yallourn brown coal. *Fuel*, Vol 65. p1653.

Ohtsuka, Y., Kuroda, Y., Tamai, Y. and Tomita, A., (1986). Chemical form of iron catalysts during the CO_2-gasification of carbon. *Fuel*, Vol 65, p1476.

Ohtsuka, Y. and Asami, K., (1990). Steam gasification of high sulphur coal with calcium hydroxide. *Pittsburgh Coal Conference*, proceeding, p353.

Otto, K., Bartosiewicz, L., and Shelef, M., (1979). Catalysis of carbon - steam gasification by as components from two lignites. *Fuel*, Vol 58, p85.

Padhye, A.R., (1988). Evaluation of mechanistic model for coal gasification, Final Technical Report, West Virginia University DE-AC21-82MC19168.

Paulson, L.E. and Ellman, R.C., (1979) Reduction of sodium in lignite by ion exchange. Technical Information Center, U.S. Dept. of Energy.

Petersen, E. E., (1957) *AIChE. J.* 3. p433.

Prasad, K.H. Prasad, P. and Subbarao, Y. (1990). Reactivity of a high ash Indian coal (Mamuguru, Godavari Valley) towards CO_2. *Fuel*, Vol 69 p1517

Purdy, M.J., Felder, R.M. and Ferrell, J.K., (1981). Coal gasification in a pilot scale fluidized bed reactor. 1. Gasification of a devolatilized bituminous coal. *Ind. Eng. Chem. Process. Des. Dve.* Vol 20, p675.

Quast, K.B., Hall, S.F. and Readett, D.J., (1990). Characterisation of the interaction of lignite with water - part 3: effect of ion exchange. S.A. Institute of School of Metallurgy. Technology, School of Metallurgy.

Quast, K.B., Pescott, E. and Readett, D., (1990). The particle removal of soluble salt from Bowmans coal and its effect on combustion. *CHEMECA'90*, p331

Radovic, L., Walker, P. and Jenkins, R.G., (1983). Effect of lignite pyrolysis conditions on calcium oxide dispersion and subsequent char reactivity. *Fuel*, Vol 62, p209.

Radovic, L., and Walker, P., (1984). *Fuel Proc. Technol.* Vol 8, p149.

Radovic, L., and Walker, P. and Jenkins, R.G., (1984). *Fuel* Vol 63, p1208.

Raghunathan, K. and Yang, R.Y.K., (1989). Unification of coal gasification data and its application. *Ind. Eng. Chem. Res.* 1989, 28, 518-523

Readett, D.J., (1983). Beneficiation of Wakefield lignite: with particular reference to the reduction of the sodium content. S.A. Institute of School of Metallurgy. Technology, School of Metallurgy.

Readett, D.J., (1984). Beneficiation of Wakefield lignite: with particular reference to the reduction of the sodium content. Stage 2. S.A. Institute of School of Metallurgy. Technology, School of Metallurgy.

Readett, D.J., and Quast, K.B., (1985). South Australian lignites - lignite/water system. Report to SENRAC.

Readett, D.J., and Quast, K.B., (1986). Mechanical Dewatering of S.A. lignites - a preliminary study. South Australia Institute of Technology, School of Mining and Metallurgy.

Readett, D.J., Hall, S.F., Quast K.B. and Ketteridge, I.B., (1986). Beneficiation of Bowmans lignite-optimization of Sodium reduction. CHEMCA 86, Adelaide, p325.

Readett, D.J. Quast, K.B. and Kettridge, I.B., (1986). Characterization of the interaction of lignite with water. *CHEMECA'86*, p330

Readett, D.J. Quast, K.B., (1987). Minerals and inorganics associated with S.A. lignites. South Australia Institute of Technology, Report to SENRAC.

Readett, D.J. and Quast, K.B., (1989). Beneficiation of Bowmans coal lignite; water leaching of soluble salt. *CHEMECA'89*, p456.

Readett, D.J. and Quast, K.B., (1991). Beneficiation of Bowmans lignite: part 3- effect of initial moisture content on water leaching of soluble salts. *CHEMECA'91*, Newcastle, p295

Riley, R.K. and Judd, M.R., (1987). The measurement of char-steam gasification kinetics for the design of a fluidised bed coal gasifier which contains a drafe tube. *Chem. Eng. Comm.* Vol 62, p151

Ruan, X.Q., Wu, Y.Q. Liu, Z.L. and Li, S.F. (1987), Effect of catalysis of gasification of Datong coal char. *Fuel*, Vol 66, p568

Rusianova, N.D., Maksimova, V.S. and Butakova, V.I., (1990). Structure and reactivity of coals. *Fuel*, Vol 69, p1448.

Saber, J. M., Falconer, J. L. and Brown, L. F., (1986). Interaction of potassium carbonates with surface oxides of carbon. *Fuel* Vol 65, p1356.

Saffer, M., Ocampo, A. and Laguerie, C., (1988). Gasification of coal in a fluidized bed in the presence of water vapor and oxygen; an experimental study and a first attempt at modeling the reactor. *International Chemical Engineering*, Vol 28, p47.

Sakawa, M. Sakurai, Y. and Hara, Y., (1982). Influence of coal characteristics on CO_2 gasification. *Fuel*, Vol 62, p717

Sato, S., Morita, M., Hashimoto, T., Ikezoe, M., Chiba, K. and Tagaya, H., (1989). Activity enhancement of iron ores as a catalyst for direct coal liquefaction. *Fuel*, Vol 68, p622.

Schafer, H.N.S., (1979). *Fuel*, Vol 58, p673.

Schafer, H.N.S., (1980). *Fuel*, Vol 59, p295.

Schafer, H.N.S., (1984). Determination of Carboxyl groups in low rank coals . *Fuel*, Vol 63, p723.

Schafer, H.N.S. and Wornat, M.J., (1990). Determination of Carboxyl groups in Yallourn brown coal. *Fuel*, Vol 69, p1456.

Schmal, M., Monteiro, J.L. and Toscanl, H., (1983). Gasification of high ash content coal with steam in a semibath fluidized bed reactor. *Ind. Eng. Chem. Des. Dev.* Vol 22, p563.

Schumacher, W., Muhlen, H.-J., van Heek, K.H. and Juntgen, H. (1986). Kinetics of K-catalysed steam and CO_2 gasification in the presence of product gases. *Fuel*, Vol 65, p1360.

Schwartz, C.W., (1982). Combined cycle coal gasification. *Energy Progress.* Vol 2. p207

Serio, M.A., Solomon, P.R. and Bassilakis, R., (1990). The effect of minerals on coal reactivity. *Pittsburgy Coal Conference*, proceeding. p341.

Shah, Y.T., (1981). "Reaction Engineering in Direct Coal Liquefaction". Addison-Wesley Publishing Company.

Shedden, I.W., (1986). Power generation by combined cycle from South Australian lignite using a high temperature Winkler gasifier. *CHEMECA'86*, Adelaide, p313

Shishido, M., Mashiko, T., Adschiri, T. and Arai, K., (1991). The gasification reactivity of residual coal chars from supercritical fluid extraction of coal. *Fuel*, Vol 70, p539.

Simons, G. A., and Finson, M.L., (1979). The structure of coal char, Part I. Pore branching . *Combust. Sci. Tech.* Vol 19, p217

Simons, G. A., (1979). Char gsification, Part I. Transport Model. *Combust. Sci. Tech.* 19, p227

Smith, I.W. and Tyler, R. J., (1974). The reactivity of porous brown coal char carbon to oxygen between 630 and 1812°K. *Combust. Sci. Tech.* 9. p87.

Smith, I.W., (1978). The intrinsic reactivity of carbon to oxygen. *Fuel,* Vol 57 p409.

Smith, J.G., Smith, I.W. and Tylor R.J., (1990). Intrinsic reactivity and structure development of petroleum coke during gasification in O_2, CO_2 and H_2O. *Pittsburgh Coal Conference Proceedings.* p293.

Smoot, L.D. and Pratt, D.T., (1979). "Pulverized-coal combustion and gasification". Plenum Press, New York. Chapter 7 & 9.

Smoot, L.D., and Smith, P.J., (1985). "Coal combustion and gasification". Plenum Press, New York.

Spiro, C.L., Mckee, D.W. Kosky, P.G. and Lamby, E.J., (1983). Catalytic CO_2-gasification of graphite versus coal char. *Fuel,* Vol 62, p183.

Spiro, C.L., Mckee, D.W. Kosky, P.G., Lamby, E.J., and Maylotte, D.H., (1983). Significant parameters in the catalysed CO_2-gasification of coal chars. *Fuel,* Vol 62, p323.

Standish, N. and Tanjung, A.F.A., (1988). Gasification of single wood charcoal particle in CO_2. *Fuel,* Vol 67, p666.

Suzuki, T., Mishima, M., Takahashi, T. and Watanabe, Y., (1985). Catalytic steam gasification of Yallourn coal using sodium hydridotetracarbonyl ferrate. *Fuel,* Vol 64, p661.

Suzuki, T., Mishima, M., Anzai, I., Yamauchi, A. and Watanabe, Y., (1986). *J. Fuel Soc., Japan,* Vol 65, p123.

Suzuki, T., Inoue, K. and Watanabe, Y., (1989). Steam pulsed gasification of Na_2CO_3 or $Fe(NO_3)_3$ loaded Yallourn coal char. *Fuel,* Vol 68, p626.

Takarada, T., Tamai, Y. and Tomita, A., (1985). Reactivities of 34 coal under steam gasification. *Fuel,* Vol 64, p1438.

Tomkow, K., Jankowska, A., Czechowski, F. and Siemieniewska, T. (1977). *Fuel*, Vol 56, p101.

Tomita, A., Mahajan, O. P. and Walker, P. L. Jr, (1977). Reactivity of heat-treated coals in hydrogen. *Fuel*, Vol 56.

Tomita, A., Tano, T., Oikawa, Y. and Tamai, Y., (1979). Gasification of coals treated with non-aqueous solvents. 5. Properties of coal treated with liquid ammonia. *Fuel*, Vol 58, p609.

Tomita, A., Tano, T., Oikawa, Y. and Tamai, Y., (1979). Gasification of coals treated with non-aqueous solvents. 6. Catalytic steam gasification at atmospheric pressure. *Fuel*, Vol 58, p614.

Tomita, A., Ohtsuka, Y. and Tamai, Y., (1983). Low temperature gasification of brown coal catalysed by nickel. *Fuel*, Vol 62, p150.

Tomita, A., Ohtsuka, Y., Takarada, T. and Tamai, Y., (1987). A study on effective catalysts for the gasification of brown coal. Studies on utilization of coal through conversion. Report of project research on energy 1986, Japan.

Tsai, S.C.,(1982). "Fundamentals of coal beneficiation and utilization". Elsevier Scientific Publishing Company. New York.

Tyler, R.J. and Schafer, H.N., (1980). *Fuel* Vol 59 p302

van Krevelen, D. W., (1961). "Coal", Elsevier, Amsterdam.

van Heek, K, and Muhlen, H.-J., (1985). Aspects of coal properties and constitution important for gasification. *Fuel*, Vol 64, p1405.

Verra, M.J. and Bell, A.T., (1978). Effect of alkali metal catalysts on gasification of coal char. *Fuel*, 57, p194

Walker, P.L., Shelef, M. and Anderson, R. T. (1968). "Catalysis of carbon gasification, chemistry and physics of carbon". Marcel Dekkler, New York.

Walker, P.L., (1981). Structure of coals and their conversion to gases fuels. *Fuel*, Vol 60, p801.

Walker, P.L., Matsumoto, S., Hanzawa, T., Muira, T. and Ismail, M.K., (1983). Catalysis of gasification of coal-derived cokes and chars. *Fuel*, Vol 62, p140.

Weeda, M., Tromp, P.J.J. and Moulijn, J.A., (1990). High temperature gasification reactivity of coal under severely product inhibited conditions. *Fuel Processing Technology*, Vol 24, p269.

Wen, C.Y. and Cuang, T. Z., (1978). Entrained coal gasification modeling. West Virginia University, Morgantion, WV.

Wigmans, T., Haringa, H. and Moulijn, J.A., (1983). Nature, activity and stability of active sites during alkali metal carbonate-catalysed gasification reactions of coal char. *Fuel*, Vol 62, p185.

Wigmans, T., Doorn, J. and Moulijn, J.A., (1983). Temperature-programmed desorption study of Na_2CO_3-containing activated carbon. *Fuel*, Vol 62, p190.

Wildegger-Gaissmaier, A.E., (1988). Drying and devolatilization of South Australian Bowmans coal. Ph.D thesis. University of Adelaide.

Wright, A. (1992). Transformation of sodium of Bowmans coal during devolatilization. Department of Chemical Engineering. The University of Adelaide.

Xie, K.C., Li, C.Z. and Ling, D.Q., (1990). Reaction kinetics of the CO_2 pressurized gasification of Chinese coals/chars: using DTA technology. *Pittsburgh coal conference precedings*, p441.

Yuh, S.J. and Wolf, E.E., (1983). FTIR studies of potassium catalyst-treated gasified coal chars and carbons. *Fuel*, Vol 62, p252.

Yuh, S.J. and Wolf, E., (1984). Kinetics and FT-i.r. studies of sodium-catalysed steam gasification of coal chars. *Fuel*, Vol 63, p1604.

Ye, D.P., Agnew, J.B. and Agarwal, P.K., (1993). Gasification of Bowmans coal with CO_2 and H_2O: Kinetic studies. *CHEMECA'93*, Oct. Melbourne.

Ye, D.P., Agnew, J.B. and Agarwal, P.K., (1993). Catalytic gasification of Bowmans with steam. *CHEMECA'93*, Oct. Melbourne.

Ye, D.P., Zhang, D.K. and Agnew, J.B., (1993). The reactivities of lignites towards CO_2 and H_2O. *The Australia Symposium on Combustion*, Nov. Newcastle.

Appendix A

TEMPERATURE MEASUREMENT AND CALIBRATION OF REACTOR

Summary

Accurate measurement of reaction-zone temperature is an essential prerequisite for establishing a meaningful correlation of experimental reaction data. As direct measurement is not possible for the present reactor, an appropriate method must be advised for indirect measurement. Detailed description about the temperature measurement was given as a paper which was present in CHEMECA'92 (Agnew & Ye 1992). The reaction temperature was analysed by putting a mobile thermocouple into the quartz tube. The "true" reaction temperature can been obtained by integrating the inside temperature of the total cross area of the reactor. This method of analysis was confirmed by the experimental data.

Thermocouple Set-Up and Measurement

Chemical reaction rate highly depends on temperature. Temperature measurement is an important consideration in the present gasification kinetic study. It is known that C-CO_2 and C-H_2O reactions are very sensitive to temperature. The correlation between reaction rate and temperature is:

$$\frac{dk}{k}=\frac{Ea}{R}\cdot\frac{dT}{T}$$

The overall rate of coal gasification may change from chemical reaction control stage to diffusion or mass transfer control with increasing the reaction temperature. Accurate measurement of reaction temperature is important to study gasification kinetics.

The diagram of reaction system and thermocouple set-up are shown in ***Figures A-1*** and *A-2*. Three thermocouples are used to measure the temperatures of the reaction system. Reacting gas is introduced from the bottom of the steel tube into the fluid-bed heater. It goes through the sand bath while heated by external electrical rods to the desired temperature, finally reaches the vertical quartz tube reactor. Coal particles were introduced into the quartz tube reactor, a metal screen was placed at the bottom of quartz tube to prevent coal particles from falling into the fluid bed. Three thermocouples, named thermocouple *1*, *2* and *3* (correspond to the temperatures T_1, T_2 and T_3, respectively) are located at different places of the reactor to determine the temperatures of the reactor and fluid bed.

As it is not possible to locate a thermocouple in the reaction zone during the reaction period, the indirect measure of the reaction temperature is obtained from a thermocouple (T_3) located on the surface of the metal tube. To check the suitability of this location, another thermocouple (T_2) was inserted through a small hole drilled in the metal wall and located in the centre of pipe. A third, movable thermocouple (T_1) was temporarily inserted down into the reaction zone of the quartz tube for tests in the absence of coal particles.

In a typical test, for T_3 at 700°C, T_1 is 800°C and T_2 is 840°C. The tested results indicated that T_2 is approximately 40°C higher than T_1 when the system temperature increased to 800°C; and the temperature of the outside surface of the steel tube, T_3, is approximately 100 °C lower than T_1. Compared to T_2 and T_3, T_1 is more close to the real reaction temperature. During the reaction, coal particles move randomly through the reaction zone, so the area-mean temperature are calculated from the profiles. ***Figure A-3*** shows the distribution of temperature in the quartz tube within a limited region. It is seen that there is significant difference of temperatures between the centre and edge of the tube. T_1 and T_2 provide instantaneous indication of the reaction temperature. T_1(mean) values were calibrated against T_2 and T_3 readings for use in reaction runs.

Suppose in a section area of quartz tube under certain distance above the bottom screen. *T* is the temperature, *r* is the radius of selected circle

$$T_m = \frac{4\pi r \int_{r_2}^{r_1} F(t)dt}{\pi(r_2^2 - r_1^2)}$$

here T_m represents the average temperature. *F(t)* represent the individual temperature value, it is the function of radius. An average temperature value (T_{ave}), which covers the total cross area, is obtained by integrating the above equation from 0 to *R*:

$$T_{ave} = \frac{4\pi r \int_{0}^{R} F(t)dr}{\pi R^2}$$

It should be noted that the gasification temperature is the coal particle temperature during the reaction. It is very difficult, probably impossible, to measure the surface temperature of coal particles. Therefore, we assume the environmental temperature is the reaction temperature. In a fluid-bed reactor coal particles keep moving and circulating, it is difficult to follow the movement of coal particles. It is assumed the coal particles uniformly distribute in the quartz tube. T_{ave} is the reasonable value in representing the real reaction temperature.

In the present experimental system, the reaction temperature measured is very sensitive to the velocity of the flow gas during the gasification. The thermocouple 1 (T_1) can not be placed in the quartz tube when reaction is in progress. To ensure the reaction temperature is strictly controlled. A temperature controller was used to provide an auto-control of T_2. Using the corrected temperature, the activation energy for CO_2 gasification of Bowmans coal was determined to be 91kJ/mol, compared with 74.5 kJ/mol using uncorrected temperature - a significant difference.

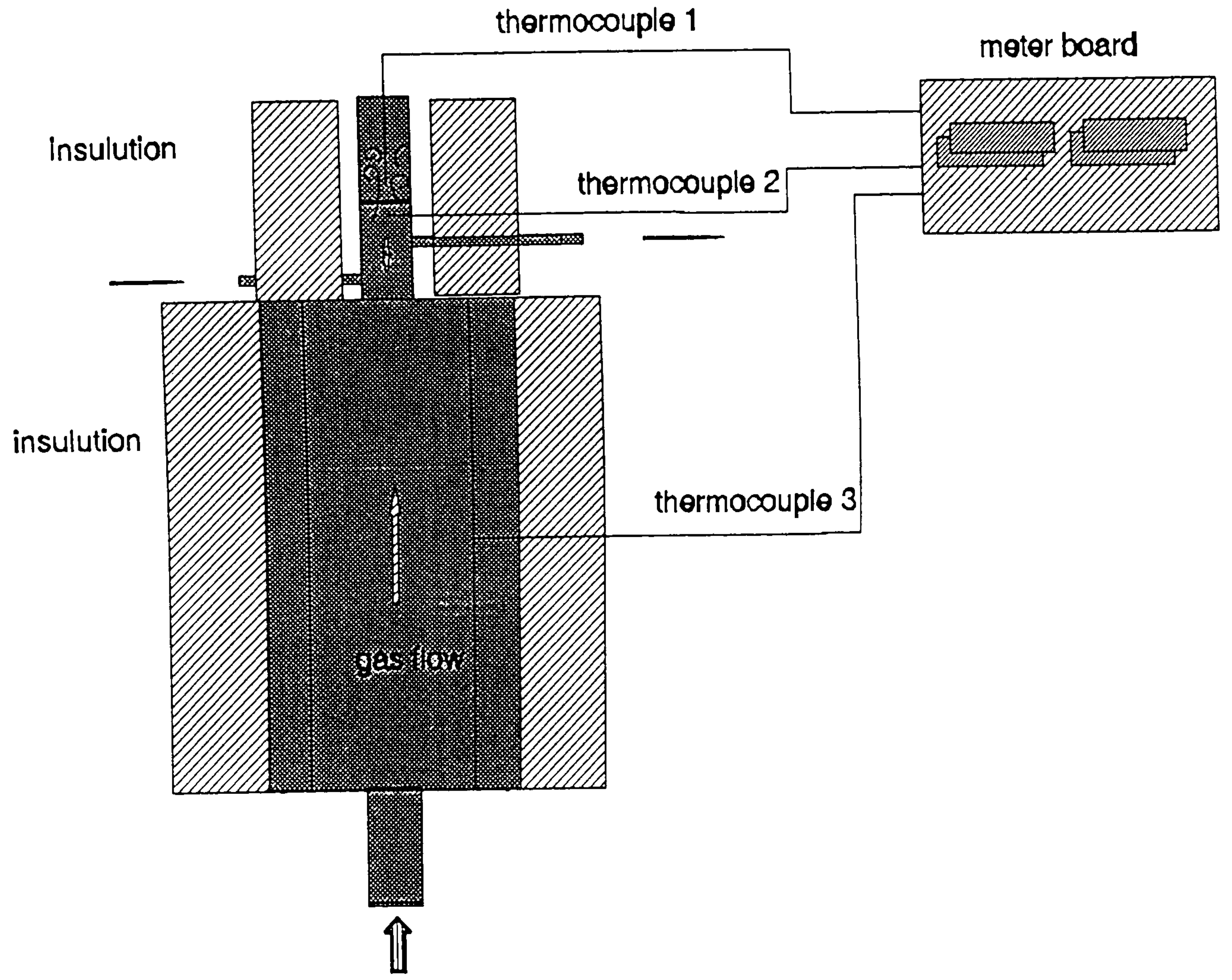


Figure A-1 Temperature measurement for reaction system

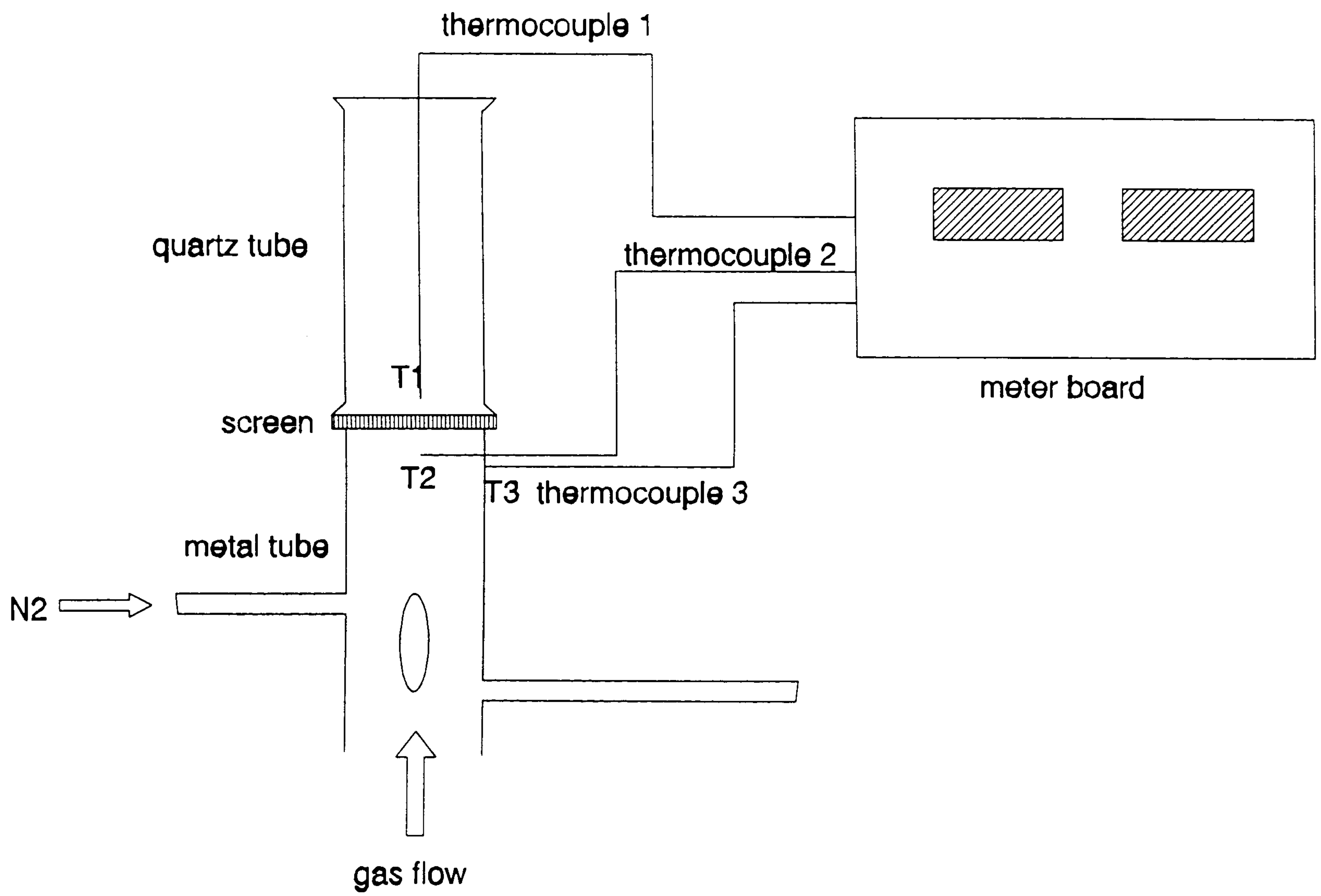


Figure A-2 Temperature measurement for reaction system

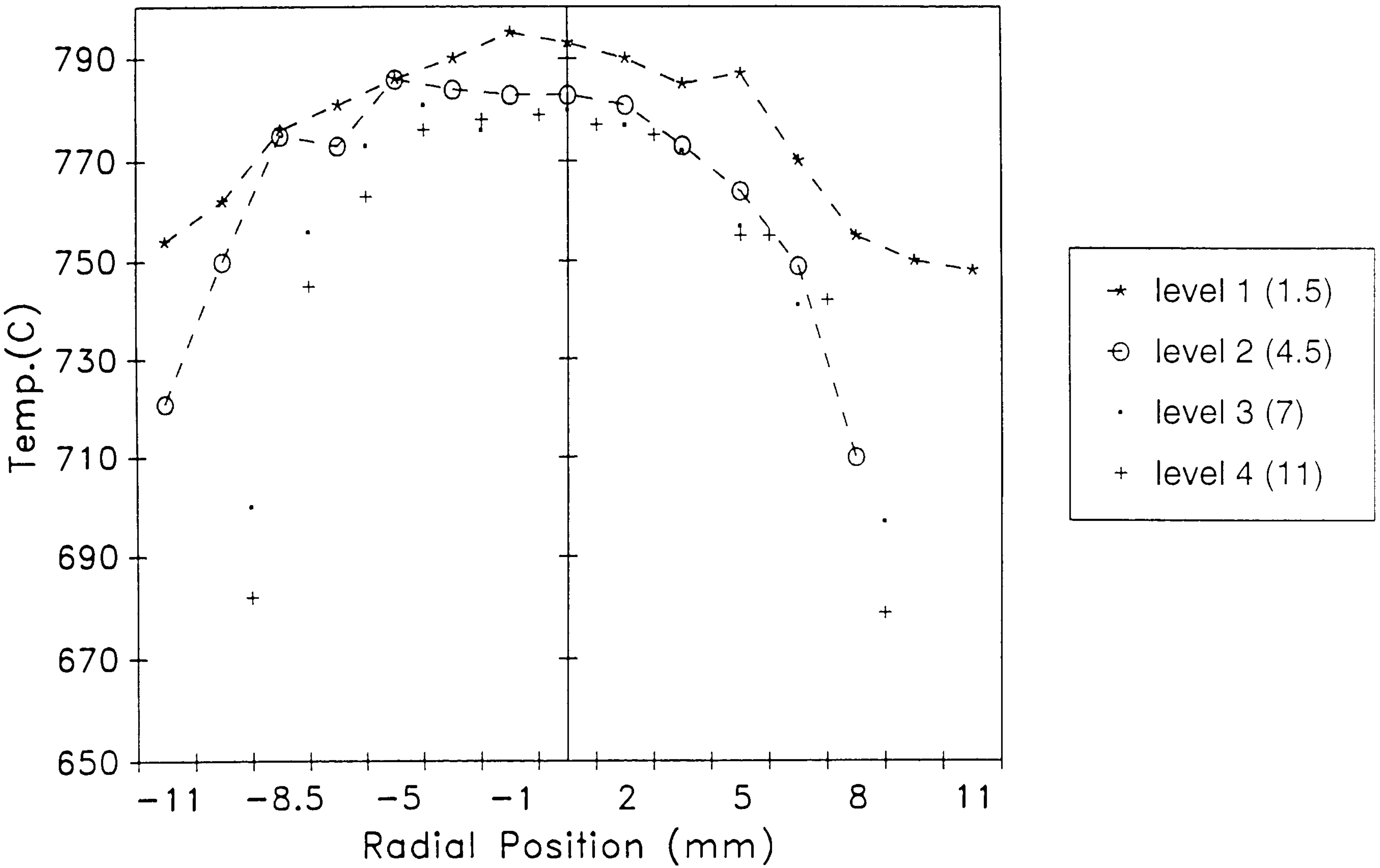


Figure A-3 Temperature distribution in quartz tube reactor.
level 1 (1.5) represent distance 1.5 mm above the metal screen

APPENDIX B

CALCULATION OF CARBON CONVERSION

In the present study, the gasification rate is defined as the function of the fixed carbon conversion of coal, X, and the reaction time t. The fractional fixed carbon conversion, X, is obtained by measuring the ash and carbon contents of the reacted coal in comparison to that of the unreacted coal sample. Assume the total mass of the coal sample used for the reaction is M (g):

The total mass of the raw coal is:

$$M_1 = M_{v1} + M_{c1} + M_{A1} \tag{B1}$$

$$M_1 = M_1 (V_1 + C_1 + A1) \tag{B2}$$

where M_1 is the total mass of the raw coal sample, the M_{v1} is the mass of the volatile matter, M_{c1} is the mass of the fixed carbon, and M_{A1} is the mass of ash. V_1, C_1 and A_1 are the fractions of the volatile matter, fixed carbon and ash content of raw coal.

Assume the total mass of the reacted coal sample is M_2, then:

The total mass of the reacted coal sample is:

$$M_2 = M_{v2} + M_{c2} + M_{A2} \tag{B3}$$

$$M_2 = M_2 (V_2 + C_2 + A2) \tag{B4}$$

where M_{v2}, M_{c2}, and M_{A2} are the mass of the volatile matter, fixed carbon, and ash of the reacted coal sample, respectively. V_2, C_2 and A_2 are the fractions of the volatile matter, fixed carbon and ash contents of the reacted coal sample, respectively.

During the gasification, the overall mass balance for the coal sample is:

The fractional conversion of the total coal sample is:

$$conversion = \frac{mass\,of\,initial\,coal - mass\,of\,final\,coal}{mass\,of\,final\,coal} \tag{B5}$$

$$X_T = \frac{M_1 - M_2}{M_1} \tag{B6}$$

The fractional conversion of the volatile matter of coal is:

$$X_v = \frac{M_1 \cdot V_1 - M_2 \cdot V_2}{M_1} \cdot V_1 \tag{B7}$$

The fractional conversion of the fixed carbon is:

$$X_c = \frac{M_1 \cdot C_1 - M_2 \cdot C_2}{M_1} \cdot C_1 \tag{B8}$$

where X_T, X_v and X_c are the fractional conversions of the total mass, volatile matter, and fixed carbon of the coal, respectively.

As the ash is not available for the reaction, the amount of ash is constant during the reaction.

The mass balance of ash of the coal sample during the reaction is:

$$M_1 \cdot A_1 = M_2 \cdot A_2 \tag{B9}$$

$$M_2 = M_1 \cdot \frac{A_1}{A_2} \tag{B10}$$

Equation (10) is used for the fractional conversion calculation, the equations (6), (7) and (8) are expressed as:

$$X_v = 1 - \frac{A_1}{A_2} \cdot \frac{V_2}{V_1} \tag{B11}$$

$$X_c = 1 - \frac{A_1}{A_2} \cdot \frac{C_2}{C_1} \tag{B12}$$

It is known that devolatilization occurs almost simultaneous under relevant temperature conditions and results in the evolution of volatile matter. The reaction between fixed carbon and reactant gases was much slower than pyrolysis. The conversion of fixed carbon is taken to indicate the degree of coal gasification.

Appendix C

RAW EXPERIMENTAL DATA

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: NaCl-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9119	9859	9470	9144	52.6	44.1	3.3	0
0	10827	11660	11233	10858	51.2	45.1	3.8	0
0	11129	11892	11486	11158	53.2	43.0	3.8	0
0	7700	8348	8013	7726	51.7	44.2	4.1	0
5	10716	11221	11169	10747	10.3	83.5	6.2	-14.8
5	11703	12053	12010	11727	12.3	80.7	7.0	2.0
5	7479	7871	7831	7503	10.2	83.4	6.4	-12.0
8	11054	11523	11477	11086	9.9	83.4	6.7	-5.6
8	9454	9795	9756	9477	11.5	81.7	6.8	-2.3
8	9000	9415	9373	9029	10.3	82.7	7.1	0.5
12	11266	11610	11580	11289	8.7	84.6	6.7	-7.5
12	10406	10829	10790	10435	9.1	84.1	6.8	-5.5
12	10964	11313	11268	10987	13.1	80.5	6.4	-7.1
15	11397	11798	11766	11431	8.2	83.6	8.3	14.0
15	9014	9371	9335	9045	10.2	81.1	8.6	19.8
15	9901	10193	10163	9924	10.4	81.7	7.9	11.6

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 852°C

Particle size: 1.6~2.4 mm

Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
1	11206	11682	11625	11303	12.0	61.6	20.4	3.6
1	10748	11125	11082	10836	11.4	65.3	23.3	19.1
1	10407	10839	10789	10503	11.6	66.2	22.2	13.8
1	11209	11668	11611	11309	12.4	65.8	21.8	12.6
1	10402	10669	10633	10458	13.5	65.5	21.0	9.6
1	11201	11572	11529	11273	11.6	69.0	19.4	-2.9
2	12060	12207	12183	12094	16.3	60.5	23.1	24.3
2	10410	10773	10732	10487	11.6	67.1	21.3	8.7
2	11207	11366	11337	11240	18.2	61.0	20.8	15.0
2	10745	11032	10998	10808	11.9	66.2	22.0	12.7
2	11625	11946	11906	11693	12.5	66.4	21.2	12.7
3	11612	11960	11920	11701	11.5	62.9	25.6	28.8
3	12060	12165	12139	12085	24.8	51.4	23.8	37.3
3	10410	10601	10571	10455	15.7	60.7	23.6	25.4
3	11208	11556	11515	11298	11.8	62.4	25.9	30.2
3	10753	11193	11142	10863	11.6	63.4	25.0	26.6
4	12056	12600	12542	12192	10.7	64.3	25.0	25.4
4	11205	11695	11643	11313	10.6	67.3	22.0	11.6
4	10405	10847	10803	10509	10.0	60.5	23.5	18.2
4	10748	11236	11185	10858	10.5	67.0	22.5	13.0
4	10459	10622	10584	10490	17.8	61.6	20.4	12.3
4	9944	10078	10046	9971	23.9	56.0	20.1	19.6
5	10753	11017	10985	10822	12.1	61.7	26.1	31.7

5	10408	10741	10699	10500	12.6	59.8	27.6	37.4
5	10746	11267	11209	10887	11.1	61.8	27.1	33.9
5	11588	12053	12002	11733	11.0	57.8	31.2	46.3
5	12068	12673	12602	12214	11.7	64.1	24.1	23.1
6	11594	11868	11832	11669	13.1	59.9	27.4	37.1
6	11558	11911	11875	11650	10.2	63.7	26.1	29.2
6	12060	12436	12393	12163	11.4	61.2	27.4	35.4
6	11209	11591	11549	11308	11.0	63.1	25.9	29.5
6	11202	11570	11525	11318	12.2	56.2	31.5	48.4
8	10409	10906	10855	10553	10.3	60.8	29.8	39.3
8	10748	11179	11130	10858	11.4	63.1	25.5	28.5
8	11594	11991	11945	11712	11.6	58.7	29.7	42.9
8	11562	11647	11628	11598	22.5	35.3	42.4	75.8
10	12058	12181	12158	12098	18.7	48.8	32.5	56.6
10	11204	11395	11368	11260	14.1	56.5	29.3	44.2
10	10406	10789	10742	10532	12.0	55.1	32.9	51.6
10	10746	10974	10941	10830	14.0	49.1	36.8	61.4
10	11592	11829	11797	11676	13.1	51.5	35.4	68.8
10	12060	12247	12218	12136	15.5	43.9	40.6	68.8

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 803°C

Particle size: 1.6~2.4 mm

Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	11198	11768	11695	11325	12.8	64.9	22.2	15.7
2	11179	11416	11372	11219	16.1	66.1	17.8	-7.2
2	11456	11843	11787	11527	14.5	67.2	18.3	-6.0
2	12016	12246	12207	12057	17.0	65.2	17.8	-5.9
4	10459	10611	10584	10490	17.8	61.8	20.4	12.3
4	9944	10173	10136	9964	23.4	56.0	20.1	19.6
8	11570	11891	11854	11656	11.5	61.7	26.7	33.4
8	10380	10652	10611	1045	15.1	58.5	26.5	36.1
8	10684	10921	10883	10739	16.0	60.8	23.2	24.3
8	12890	13225	13178	12978	14.0	59.7	26.3	34.2
10	10709	11133	11078	10817	13.0	61.6	25.5	30.1
10	11194	11547	11497	11300	14.2	55.8	30.0	46.2
10	12044	12515	12457	12193	12.3	56.1	31.6	48.7
10	11514	11826	11782	11593	14.1	60.6	25.3	30.8
10	11463	11826	11777	11556	13.7	60.7	25.5	35.2
10	11582	12070	12010	11689	12.3	65.8	21.9	31.6
12	10380	10793	10735	10503	14.0	56.2	29.8	45.4
12	10380	10686	10645	10476	13.4	55.2	31.4	49.1
12	10674	10855	10825	10726	14.4	47.6	37.9	63.7
12	10376	10546	10510	10459	17.3	31.5	51.2	82.2
12	10680	10960	10917	10787	15.4	46.5	38.2	64.8
14	12045	12342	12297	12145	15.2	51.2	33.7	56.0
14	10675	11012	10965	10762	13.9	60.2	25.8	32.5
14	11197	11429	11394	11264	15.1	56.0	28.9	43.9

14	11182	11550	11502	11304	13.0	53.8	33.2	53.1
14	12017	12265	12225	12085	16.1	56.5	27.4	40.4
16	11499	11751	11711	11590	15.9	48.0	36.1	61.5
16	12045	12169	12141	12096	23.1	37.2	39.7	72.8
16	11193	11294	11271	11223	22.7	47.5	29.7	53.7
16	11503	11649	11620	11578	19.3	29.0	83.8	83.3

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 891°C

Particle size: 1.6~2.4 mm

Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	10674	10897	10861	10733	14.6	58.4	26.9	37.2
2	11815	12054	12017	11848	15.5	70.7	13.8	0.0
2	11933	12196	12160	11973	13.6	71.0	15.2	4.6
0.5	11823	12068	12034	11853	13.1	69.9	11.6	-
0.5	11954	12273	12223	11990	15.7	73.0	11.3	-
0.5	10357	10648	10606	10398	14.3	71.5	14.1	-
3	10339	10487	10461	10373	17.6	59.5	23.0	39.9
3	9819	9983	9957	9860	15.9	59.2	25.0	39.8
3	11961	12033	12019	11980	19.0	54.2	26.4	45.0
3	11186	11453	11413	11256	15.0	58.8	26.2	13.8
3	12031	12254	12220	12102	15.2	52.9	31.8	35.1
3	11483	11727	11693	11554	13.9	57.0	29.1	43.4
4	11579	11849	11814	11664	13.0	55.6	31.5	48.9
4	6435	6616	6595	6480	11.6	63.5	24.9	52.3
4	6183	6412	6380	6237	14.0	62.6	23.6	38.5
4	6132	6257	6239	6167	15.0	64	26.4	52.2
5	9795	9986	9954	9850	16.8	54.5	28.8	56.1
5	11902	12234	12191	11976	13.0	65.4	21.7	30.1
5	11793	11905	11880	11833	22.3	41.9	35.7	67.4
5	10309	10480	10454	10358	15.2	56.1	26.7	51.0
6	9834	9985	9956	9878	19.2	51.7	29.1	58.8
6	11970	12188	12164	12033	11.0	60.0	28.9	51.7
6	6456	6677	6648	6512	13.1	61.5	25.5	43.6
6	11943	12099	12082	12003	10.9	50.7	38.5	69.4

DEVOLITILIZATION EXPERIMENTS

Temperature: 853°C

Particle size: 1.6~2.4 mm

Condition: devolatilization of water-leached coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	Vol. matt. co nversion
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(% d.b.)
0.5	12055	12528	12465	12414	13.0	68.8	18.3	83.6
0.5	10400	10829	10773	10476	12.0	70.0	17.9	84.5
0.5	12824	13164	13122	12873	12.4	69.4	14.41	80.1
0.5	12929	13372	13313	13003	13.3	70.0	16.7	81.5
0.5	11076	11670	11614	11196	13.6	72.6	13.7	74.9
0.5	10113	10643	10573	10185	13.2	68.6	19.19	77.5
2	10551	11009	10950	10613	10.7	75.2	13.5	81.7
2	10017	10443	10399	10072	10.3	77.8	12.9	81.5
2	10735	11154	11107	10791	9.3	77.0	13.7	84.3
2	10806	11445	11378	10914	8.6	74.1	17.3	88.4
3	12020	12709	12647	12124	9.0	86.2	15.1	77.5
4	11145	11747	11696	11258	8.6	83.8	17.5	88.7
4	11603	12098	12052	11712	9.3	69.1	21.6	90.4
4	12062	12558	12511	12155	9.7	71.1	19.1	88.3
4	12055	12441	12402	12132	10.1	70.0	20.0	88.3
5	10648	11281	11227	10754	8.5	71.3	19.9	90.1
6	13964	13523	13482	13143	8.6	74.6	17.2	87.9
6	10611	11137	11079	11682	9.0	77.2	13.8	84.9
6	10717	11056	11024	10763	9.4	77.0	13.6	83.9
6	10410	10791	10754	10489	10.0	69.6	20.7	88.9
6	11207	11642	11600	11300	9.7	69.0	21.4	89.5
6	10400	10806	10767	10483	9.6	70.4	20.0	88.5
7	10686	11144	11099	10762	9.8	74.6	16.6	86.3
7	11022	11220	11189	11075	11.7	73.0	14.3	86.5

7	10745	11006	10891	10801	9.6	67.0	21.5	89.7
7	11711	12107	12073	11790	8.6	71.5	20.0	90.0
8	12966	13404	13365	13092	8.9	76.3	14.8	85.7
8	10079	10502	10462	10155	9.5	72.5	18.0	85.0
8	11109	11670	11614	11196	8.4	76.8	15.8	87.8
8	10754	11280	11236	10872	8.4	69.6	22.0	91.2
10	11600	11021	11969	11693	10.2	67.6	22.2	89.9
10	10586	10891	10859	10634	10.5	73.9	15.6	84.5
12	10761	11267	11221	10877	9.1	68.0	22.9	90.8
12	13027	11.411	13379	13092	8.3	74.8	16.9	88.6
14	10042	10478	10437	10016	9.4	75.9	14.7	85.2

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 809°C

Particle size: 1.6~2.4 mm

Condition: gasification of acid-washed Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
3	10721	11426	11380	10751	6.5	89.3	4.2	12.4
3	10182	10844	10798	10206	7.0	89.5	3.5	-5.0
3	11236	12175	12110	11270	6.9	89.5	3.6	-1.8
3	11705	12574	12509	11739	7.4	88.6	3.9	7.9
3	8458	9154	9096	8485	8.3	87.8	3.9	6.1
6	9884	10633	10583	9918	6.6	88.8	4.6	19.8
6	10946	11607	11559	10973	7.3	88.6	4.1	10.6
6	10226	10919	10876	10256	6.1	89.5	4.4	16.0
6	11841	12239	12232	11880	9.2	86.2	3.7	0.8
10	10947	11338	11307	10940	8.0	88.7	3.3	-11.0
10	10244	10800	10768	10265	5.8	90.4	3.5	-6.4
10	10734	11542	11480	10762	9.6	86.7	3.8	3.2
10	10231	10776	10739	10257	6.8	88.2	3.7	-1.7
10	11247	12015	11875	11275	8.2	87.8	4.0	10.2
15	11253	11834	11785	11273	8.4	88.0	3.5	-3.7
15	11716	12305	12265	11744	6.8	88.5	4.7	22.1
15	8474	9097	9061	8498	5.7	90.5	3.8	2.1
15	9861	10357	10324	9877	6.7	90.1	3.2	-14.8
18	8459	9217	9180	8490	4.8	91.1	4.1	8.2
18	9865	10483	10438	9889	7.3	88.9	3.8	4.5
18	10206	10807	10778	10226	4.9	91.7	3.4	-0.8
18	10225	10838	10807	10254	5.0	90.4	4.6	19.5
30	10722	11531	11486	10754	5.5	90.5	4.0	5.3

30	11254	12015	11962	11281	7.1	89.4	3.5	-5.1
30	11705	12487	12432	11735	7.0	89.1	3.9	5.3
30	12941	11690	11646	10967	5.8	90.7	3.5	-8.4
30	10154	10544	10335	10163	6.3	89.8	3.8	4.2
40	8474	9097	9061	8498	5.7	90.4	3.8	2.0
40	11315	12184	11765	11521	8.2	91.7	3.5	-3.1
40	11253	11834	11785	11273	8.4	88.0	3.5	03.7
40	9861	10357	10324	9877	6.7	90.1	3.2	-14.7

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 806°C (New system)

Particle size: 1.6~2.4 mm

Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	10902	11497	11412	11079	12.7	69.5	17.9	0
2	11489	12308	12204	11847	12.0	70.2	17.8	4
2	11864	12410	12338	12009	12.8	67.0	20.2	5
2	10083	10552	10483	10166	12.6	69.2	18.2	2
5	10967	11432	11371	11062	13.3	66.4	20.3	5.3
5	10290	10688	10638	10385	11.5	65.1	23.5	19.9
5	89796	95673	95054	91212	10.5	66.3	23.2	17.2
5	85698	88278	87866	86271	16.0	62.2	21.8	17.3
5	10901	11680	11591	11124	11.4	66.7	21.9	11.9
9	11868	12195	12146	11954	15.2	58.3	26.3	35.5
9	10086	10428	10378	10174	14.6	59.6	25.1	33.4
9	10971	11474	11410	11104	12.8	60.7	26.5	33.6
9	10295	10644	10595	10387	14.0	59.7	26.3	34.2
9	89837	95436	94759	91185	12.1	63.9	24.0	22.9
13	85728	91509	90817	87321	12.0	60.5	27.5	36.3
13	10909	11539	11453	11079	13.7	57.3	27.0	36.4
13	10891	11431	11349	11040	15.2	57.2	27.6	39.9
13	11868	12323	12264	11996	12.9	59.0	28.0	39.1
13	10083	10378	10335	10164	14.5	58.1	27.4	38.7
17	10979	11479	11413	11130	13.3	56.6	30.1	45.5
17	10299	10850	10785	10460	11.8	58.9	29.3	41.8
17	89865	95335	94485	91417	15.5	56.1	28.4	42.8
17	11481	11791	11735	11592	17.9	46.1	35.9	62.9
17	11861	12509	12429	12051	12.3	58.3	29.3	42.3

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 765°C (New system)
Particle size: 0.8~1.6 mm
Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	10978	11807	11642	11154	20.0	59.6	20.4	15.6
2	89875	98907	97817	92147	12.1	68.5	19.4	-2.1
2	85786	92024	91323	87057	11.2	68.4	20.4	2.9
2	10893	12449	12218	11202	14.8	65.3	19.9	4.8
2	11480	12315	12189	11673	15.1	64.9	20.0	6.3
5	85819	92576	91699	87337	13.0	64.6	22.5	16.9
5	10982	11596	11514	11122	13.3	63.9	22.8	18.8
5	10308	10795	10727	10420	14.0	63.0	23.0	20.6
5	89915	94754	94063	91152	14.3	60.2	25.6	31.9
5	10899	11423	11359	11286	12.3	65.3	22.4	15.6
8	10070	10494	10433	10190	14.5	57.2	28.4	41.7
8	10990	11551	11475	11125	13.6	62.4	24.0	24.9
8	10307	10870	10800	10452	12.4	61.8	25.8	30.6
8	89948	96422	95579	91462	13.0	63.6	23.4	21.3
10	10301	10738	10683	10420	12.4	59.9	27.6	37.2
10	11866	12334	12262	11994	15.4	57.3	27.3	39.3
10	10070	10586	10517	10218	13.4	57.9	28.7	41.6
10	10897	11368	11305	11018	13.4	60.7	25.9	32.3
10	11486	12011	11931	11627	14.1	59.0	26.9	36.7

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 765°C (New system)

Particle size: 2.4~4.1 mm

Condition: gasification of raw coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
3	10899	11376	11324	10999	11.0	68.2	20.9	5.8
3	11494	12156	12091	11662	9.7	64.8	25.5	26.4
3	11867	12654	12556	12019	12.4	68.4	19.0	-2.7
3	90070	96967	96213	91478	10.9	68.7	20.4	2.7
3	10909	11707	11621	11085	10.8	67.1	22.0	12.1
6	10311	10762	10709	10411	11.8	66.0	22.2	14.0
6	89977	94283	93795	90945	11.3	66.2	22.5	14.8
6	85919	94251	93386	87806	10.4	67.0	22.6	14.4
6	10996	11759	11669	11170	11.8	65.4	22.8	17.1
6	10316	11296	11201	10539	9.8	67.5	22.8	14.2
6	11495	12287	12201	11657	10.9	68.7	20.4	2.7
10	11488	12113	12040	11630	11.7	65.5	22.8	16.8
10	11862	12306	12247	11975	13.3	61.3	25.4	30.1
10	85904	92020	91307	87495	11.7	62.3	26.0	30.7
10	10077	10500	10446	10190	12.7	60.5	26.8	34.9
10	10998	11828	11741	11195	10.5	65.7	23.7	19.9
10	10319	11041	10952	10495	12.3	63.4	24.3	24.5
10	10915	11539	11453	11088	13.8	58.4	27.7	39.1
14	10993	11577	11512	11176	11.0	57.5	31.5	47.1
14	10311	11015	10942	10512	10.3	61.2	28.5	37.8
14	10154	10993	10880	10296	12.1	62.2	25.7	29.9
14	11506	11993	11922	11650	14.5	56.4	29.1	44,0
14	11871	12414	12345	12022	12.8	59.4	27.9	38.3
14	86015	89199	88670	86981	16.6	53.0	30.2	49.4

18	89996	93184	92773	90984	12.9	56.1	31.0	47.6
18	10904	11587	11499	11105	12.9	57.8	29.3	43.0
18	11867	12164	12123	11988	13.9	45.4	40.7	67.7
18	85962	92371	91669	87944	11.0	58.1	30.9	45.6
18	10060	10520	10457	10208	13.7	54.0	32.2	51.5
18	90070	97610	96738	92189	11.6	60.3	28.1	37.9

STEAM GASIFICATION EXPERIMENTS

Temperature: 766°C

Particle size: 1.6~2.4 mm

Condition: gasification raw Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	11267	12093	11980	11436	24.6	54.9	20.5	22.4
2	11720	12780	12648	11926	12.5	68.1	19.4	-1.3
2	8479	9077	8992	8597	14.3	66.0	19.7	3.1
2	8491	9284	9206	8656	9.8	69.3	20.8	3.7
2	9862	10529	10461	9996	10.2	69.7	20.1	-0.3
3	10207	10952	10877	10363	10.1	69.0	21.0	4.8
3	10216	10898	10826	10367	10.6	67.3	22.1	12.1
3	10715	11731	11638	10930	9.2	69.6	21.1	4.7
3	11269	11879	11824	11399	9.1	69.7	21.2	4.9
3	11729	12771	12673	11939	9.3	70.5	20.1	-1.3
5	9857	10312	10234	9976	17.3	56.6	26.1	37.2
5	10230	11056	10943	10423	13.7	63.0	23.3	22.0
5	10216	10598	10532	10311	17.2	57.9	24.9	32.6
5	10708	11400	11294	10890	15.4	58.2	26.4	36.1
5	11265	11901	11807	11441	14.7	57.5	27.7	40.0
5	10941	11674	11609	11101	8.9	69.3	21.8	8.0
5	8499	9041	8986	8637	10.1	64.5	25.4	26.5
7	10212	10769	10684	10375	15.3	55.5	29.2	45.0
7	10709	11295	11220	10868	12.9	60.0	27.1	36.0
7	11721	12310	12222	11885	14.9	57.3	27.8	40.2
7	8486	9084	8994	8647	15.0	58.1	26.8	37.4
7	9860	10375	10299	10018	14.7	54.6	30.7	48.5
7	9866	10310	10266	9982	9.9	64.0	26.1	29.0

8.5	10225	10640	10574	10342	16.1	55.8	28.2	42.7
8.5	10212	10622	10555	10317	16.4	58.0	25.6	34.5
8.5	10707	11136	11053	10835	19.2	50.9	29.9	50.8
8.5	11267	11585	11535	11372	15.7	51.3	33.0	55.0
8.5	11723	12061	12013	11856	14.3	46.4	39.2	65.8
10	11724	11946	11899	11792	21.2	48.0	30.8	55.0
10	10936	11203	11153	11036	18.9	43.7	37.4	66.2
10	8483	8728	8685	8575	17.4	45.2	37.3	65.0
10	10222	10573	10519	10306	15.4	60.5	24.1	27.0
10	11267	11452	11420	11339	17.3	43.9	38.8	67.3
10	10731	11160	11108	10853	12.0	59.5	28.5	39.7

STEAM GASIFICATION EXPERIMENTS

Temperature: 808°C

Particle size: 1.6~2.4 mm

Condition: gasification raw Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
1	11287	12413	12292	11498	10.8	70.5	18.8	-9.1
1	11713	12704	12605	11908	10.0	70.3	19.7	-3.1
1	10875	11659	11582	11029	9.9	70.5	19.7	-3.6
2	10726	11434	11359	10888	10.5	66.6	23.0	16.2
2	11271	11910	11849	11424	9.4	66.6	23.9	19.4
2	11721	12354	12293	11861	9.7	68.2	22.1	10.8
2	10887	11267	11225	10968	10.9	67.8	21.4	8.2
2	8509	9147	9087	8658	9.4	67.2	23.4	16.8
3	10718	11323	11266	10873	9.4	64.9	25.6	26.7
3	11721	12178	12127	11848	11.1	61.0	27.8	36.6
3	10874	11592	11527	11049	9.0	66.6	24.4	20.9
3	9842	10625	10556	10026	8.8	67.8	23.5	16.5
4	8499	8970	8919	8628	10.9	61.8	27.3	34.6
4	9838	10281	10231	9967	11.4	59.5	29.1	40.8
4	10201	10549	10512	10301	10.9	60.5	28.6	38.8
4	10207	10621	10576	10336	10.8	58.1	31.2	46.1
4	10225	10762	10708	10382	10.2	60.6	29.2	40.0
5	10220	10641	10590	10360	12.2	54.6	33.2	52.5
5	10721	10987	10955	10808	12.2	55.3	32.4	50.7
5	11274	11606	11505	11393	12.4	51.7	35.8	58.2
5	11720	11975	11944	11792	12.0	59.6	28.3	39.1
5	10887	11284	11235	11022	12.5	53.4	34.1	54.7
5	9842	10073	10039	9927	14.5	48.7	36.8	61.7

6	8503	8780	8741	8616	14.1	45.0	40.9	68.2
6	10201	10535	10492	10332	13.0	47.8	39.2	64.7
6	10223	10501	10466	10340	12.4	45.3	42.2	68.9
6	11279	11652	11599	11425	14.4	46.7	38.9	65.3

STEAM GASIFICATION EXPERIMENTS

Temperature: 708°C

Particle size: 1.6~2.4 mm

Condition: gasification of raw Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
5	10689	11642	11543	10880	10.3	69.6	20.0	-0.5
5	11291	12218	12123	11476	10.2	69.8	20.0	-1.2
5	11721	12621	12525	11894	10.6	70.2	19.2	-5.8
5	8442	9180	9103	8593	10.5	69.1	20.5	2.4
5	10214	11072	10990	10385	9.6	70.5	19.9	-2.3
5	10229	10914	10856	10369	8.5	70.9	20.5	0.05
10	10877	11595	11516	11037	11.0	66.7	22.3	13.5
10	9845	10527	10458	10005	10.2	66.4	23.4	17.9
10	10211	10856	10788	10364	10.5	65.9	23.6	19.4
10	10229	10880	10811	10386	10.3	73.9	27.4	27.9
10	11725	12247	12184	11853	12.0	63.5	24.4	24.7
10	10878	11459	11396	11013	10.7	66.0	23.3	17.9
15	10671	10902	10858	10766	18.7	39.9	41.4	72.2
15	11290	11676	11626	11416	12.8	54.6	32.5	51.4
15	11719	12273	10218	11876	9.7	61.8	28.5	37.2
15	8446	8754	8712	8558	13.6	49.9	36.5	60.4
15	9841	10276	10221	9972	12.6	57.2	30.2	45.2
15	10216	10677	10628	10346	10.7	61.2	28.1	37.0
15	10680	11214	11152	10816	11.6	62.8	25.5	28.7
15	11211	11746	11682	11353	12.0	61.3	26.7	33.5
20	10874	11292	11245	11015	11.3	55.1	33.7	52.7
20	9847	10127	10094	9965	11.8	46.2	42.1	68.2
20	10671	10832	10807	10755	15.6	32.3	52.1	82.1

20	11214	11652	11603	11356	11.2	56.3	32.5	49.9
20	10202	10442	10407	10306	14.4	42.1	43.5	72.0
20	10233	10628	10582	10364	11.7	55.2	33.1	51.8
25	10228	10467	10438	10334	12.2	43.4	44.4	71.7
25	11732	12023	11977	11846	15.6	45.1	39.3	66.8
25	8454	8722	8677	8561	16.9	43.1	40.0	68.8
25	10883	11241	11185	11000	15.7	51.6	32.7	54.2
25	9845	9937	9920	9881	18.9	42.5	38.6	68.1

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 2.4~4.1mm

Condition: gasification raw Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	11745	12503	12427	11899	10.0	69.7	20.3	0.7
2	8457	9301	9223	8627	9.3	76.6	20.1	-1.8
2	10695	11425	11363	10858	8.5	69.2	22.3	10.1
2	11222	12006	11942	11386	8.1	71.0	20.8	1.3
2	11733	12546	12475	11901	8.8	70.6	20.6	1.0
2	11674	12352	12269	11814	12.3	67.0	20.7	6.4
2	8415	9258	9178	8578	9.5	71.2	19.3	-6.4
2	10900	11784	11702	11083	9.3	70.0	20.7	2.0
2	9724	10616	10531	9905	9.4	70.3	20.3	-0.37
3	10177	10857	10794	10330	9.2	68.3	22.5	12.3
3	10241	11020	10955	10408	8.4	70.1	21.5	5.5
3	10649	11485	11407	10827	9.3	69.4	21.3	5.7
3	11181	11931	11858	11355	9.7	67.1	23.8	16.6
4	10685	11102	11056	10787	11.2	64.5	24.3	23.3
4	11222	11807	11745	11370	10.6	64.1	25.3	26.8
4	9785	10403	10350	9940	8.7	66.3	25.0	23.3
4	10185	10740	10693	10337	8.4	64.2	27.4	32.2
4	10238	10796	10747	10377	8.7	66.5	24.9	22.6
4	9725	10497	10434	9911	8.8	67.7	24.1	18.8
6	10894	11274	11227	11019	12.4	54.7	32.9	51.8
6	9850	10334	10284	9988	10.3	61.2	28.5	37.8
6	10206	10655	10607	10359	10.5	55.4	34.1	53.0
6	8444	8914	8865	8596	10.3	57.4	32.4	48.7

6	10913	11367	11323	11060	9.6	58.0	32.4	48.3
6	9765	10201	10158	9907	9.9	57.6	32.5	48.7
8	10237	10597	10560	10371	10.5	52.4	37.0	59.0
8	10691	10936	10905	10791	12.6	44.2	43.1	70.3
8	11221	11465	11435	11329	12.6	43.1	44.2	71.8
8	10183	10486	10455	10305	10.0	49.9	40.1	64.0
8	10238	10501	10471	10354	11.3	45.5	44.1	70.8
8	10897	11066	11043	10962	13.7	48.0	38.3	63.8
10	11737	11911	11882	11826	16.4	32.3	51.3	81.8
10	8453	8578	8555	8526	18.2	23.1	58.7	88.6
10	10899	11085	11057	11001	14.8	30.6	54.6	83.8
10	10642	10813	10786	10725	17.5	33.7	48.7	80.0
10	11675	11892	11864	11774	13.0	41.6	45.4	73.5

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 2.4~4.1mm

Condition: gasification of acid-washed Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
15	11344	11924	11894	11367	5.1	91.2	4.0	5.2
15	8141	8630	8601	8157	6.0	90.7	3.3	-7.8
15	10663	11302	11259	10687	6.6	89.3	4.1	8.2
15	11339	11978	11939	11362	6.2	90.1	3.7	5.7
15	10644	11258	11228	10667	5.0	91.3	3.7	3.3
22	10645	11248	11206	10675	6.9	88.5	4.6	15.8
30	10738	11486	11437	10765	6.5	88.9	3.6	3.3
30	9872	10405	10376	9897	5.6	89.7	4.7	25.1
30	10713	11308	11277	10735	5.1	91.8	3.6	-0.9
30	9503	10048	10024	9524	4.5	91.6	3.9	6.9
45	9503	10101	10072	9530	4.9	90.7	4.5	11.2
45	10201	10795	10765	10223	5.1	91.2	3.7	3.2
45	11339	11853	11820	11362	6.4	89.1	4.5	22.3
45	9865	10380	10341	9887	7.6	88.3	4.2	17.0
52	8121	8615	8587	8140	5.7	90.5	3.8	7.0
60	10295	10749	10708	10317	9.0	86.2	4.8	29.6
60	10266	10769	10740	10288	5.8	89.8	4.4	20.9
60	8121	8613	8584	8143	6.0	89.5	4.5	21.6
60	10060	10559	10538	10085	4.3	90.7	5.0	29.4

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 2.4~4.1mm

Condition: gasification of water-washed Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
5	10187	10785	10730	10265	9.2	77.8	13.0	13.4
5	11320	11810	11765	11386	9.1	77.4	13.5	17.2
5	8071	8604	8549	8141	10.3	76.7	13.0	15.0
5	10701	11252	11204	10774	8.7	78.1	13.2	14.5
5	9485	9969	9929	9553	8.2	77.7	14.1	21.1
10	10702	11140	11093	10770	10.6	73.8	15.6	31.7
10	9866	10298	10250	9928	11.0	74.7	14.3	24.0
10	10514	10905	10874	10572	7.8	77.3	14.9	25.2
10	8044	8453	8421	8109	7.8	76.4	15.8	30.4
10	11313	11634	11598	11371	11.3	70.7	18.0	43.4
15	11318	11600	11574	11371	9.3	72.0	18.7	44.6
15	8069	8366	8338	8126	9.2	71.7	19.1	46.2
15	10155	10454	10428	10213	8.4	72.1	19.4	46.4
15	9862	10198	10169	9918	8.6	74.7	16.7	35.7
15	8026	8364	8328	8078	10.8	73.7	15.5	31.4
20	9488	9704	9673	9528	14.6	67.4	18.0	45.6
20	10583	10830	10800	10637	12.2	66.0	21.8	56.3
20	9960	10283	10242	10019	12.8	68.8	18.4	46.6
20	10185	10462	10433	10238	10.4	70.6	19.0	46.4
20	10700	10982	10958	10756	8.7	71.7	19.6	47.1
20	10155	10413	10380	10205	12.6	67.6	19.8	50.6
25	9861	10059	10031	9900	14.1	16.0	19.9	52.3
25	9486	9709	9686	9535	10.0	68.0	22.1	55.7

25	11315	11524	11502	11360	10.4	68.1	21.5	54.1
25	10702	10942	10910	10752	13.3	65.8	20.9	54.6
25	9863	10139	10101	9916	13.8	67.0	19.2	49.5

STEAM GASIFICATION EXPERIMENTS

Temperature: 780°C

Particle size: 2.0~3.2mm

Condition: gasification of water-washed Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
5	11255	12016	11902	11274	15.0	82.5	2.6	0
5	10605	11306	11234	10624	10.3	86.9	2.7	0
5	11399	12182	12091	11421	11.6	85.5	2.8	0
5	10580	11236	11136	10597	15.2	82.3	2.5	0
5	10239	10712	10643	10250	14.6	83.0	2.5	0
5	11041	11695	11625	11059	10.8	86.5	2.7	0
5	11256	12051	11972	11278	9.9	87.2	2.8	0
5	10228	10955	10880	10249	11.4	86.9	2.8	0
10	11402	11802	11760	11414	10.5	86.3	3.2	9.5
10	11559	12219	12147	11578	6.7	90.4	2.9	0
10	11039	11400	11370	11050	8.5	88.4	3.1	4.2
10	11400	11999	11932	11416	11.1	86.1	2.7	0
10	11259	11659	11604	11271	14.0	83.1	3.0	7.7
10	11503	12053	11991	11519	11.3	85.7	3.0	4.9
10	11392	12276	12190	11419	9.8	87.3	3.0	1.6
15	11040	12118	12010	11071	10.0	87.2	2.9	7.7
15	10251	10788	10739	10267	9.2	87.8	3.0	3.1
15	11255	11771	11726	11273	8.7	87.8	3.5	17.1
15	11538	11991	11955	11554	8.0	88.4	3.6	18.2
15	11524	12014	11951	11538	13.0	84.1	2.9	3.4
15	10561	11169	11095	10580	12.2	84.8	3.0	8.2
15	10491	11063	10986	10508	13.4	83.6	3.0	7.6
15	11039	11585	11524	11057	11.3	85.4	3.3	14.7

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 2.0~3.2mm

Condition: gasification of water-washed Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
3	8221	8552	8517	8231	10.6	86.3	3.1	12.0
3	9131	9392	9355	9138	14.0	83.4	2.7	0
3	10843	11257	11206	10855	12.2	84.7	3.1	8.4
6	9144	9478	9431	9155	14.1	82.6	3.3	19.9
6	7733	7968	7929	7740	16.5	80.4	3.2	18.4
6	7049	7334	7306	7061	9.8	85.9	4.2	35.2
9	11134	11360	11321	11142	17.2	79.5	3.3	23.8
9	7720	7900	7873	7726	14.9	81.7	3.4	23.8
9	8220	8534	8499	8232	11.1	85.2	3.7	25.7
12	10224	10419	10392	10232	13.8	82.1	4.1	36.6
12	7049	7353	7324	7062	9.6	86.1	4.2	35.0
12	9082	9320	9293	9090	11.3	85.1	3.6	24.5

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: NaCl-catalysed gasification of Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
5	10078	10551	10512	10116	8.4	83.4	8.1	15.0
5	7921	8560	8493	7970	10.5	81.2	7.5	9.9
5	11232	11723	11681	11278	8.4	82.2	9.3	26.9
5	9147	9679	9629	9190	9.5	82.6	7.9	13.6
10	9751	10198	10172	9792	5.9	84.8	9.2	23.9
10	11262	11786	11744	11312	7.9	82.5	9.5	28.5
10	10617	11057	11027	10651	6.7	85.6	7.7	7.6
10	9409	9915	9879	9452	7.1	84.2	8.7	19.4
15	10079	10524	10490	10125	7.6	81.9	10.4	37.7
15	9758	10214	10178	9800	7.9	83.1	9.0	23.8
15	10086	10404	10374	10124	9.2	78.8	11.9	45.4
15	7924	8244	8218	7960	8.3	80.4	11.2	40.5
20	11258	11524	11504	11293	7.3	79.6	13.1	49.8
20	10638	10847	10823	10671	11.3	72.8	15.8	61.8
20	9415	9772	9742	9454	8.4	80.6	10.9	38.7
20	9748	10111	10084	9788	7.2	81.9	10.9	37.5

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: NaAc-catalysed gasification of Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
2	9150	9662	9628	9252	6.6	73.5	19.8	24.1
2	11273	11877	11801	11368	12.6	71.6	15.8	7.2
2	10625	11199	11140	10720	10.3	73.3	16.4	8.6
2	9417	9920	9870	9504	10.1	72.7	17.3	13.9
3	10077	10467	10421	10155	12.0	68.0	20.0	30.2
3	7922	8301	8266	8001	9.4	69.8	20.7	31.1
3	11231	11605	11567	11312	10.4	67.9	21.7	36.0
3	9424	9787	9730	9450	9.3	70.5	20.2	28.6
4	11231	11571	11535	11311	10.6	65.8	23.6	42.7
4	9152	9452	9414	9228	12.6	61.9	25.4	50.1
4	11281	11493	11461	11334	15.0	59.7	25.3	51.7
4	10632	10917	10877	10697	14.0	62.9	23.0	44.0
5	11230	11442	11415	11292	12.8	58.0	29.2	59.3
5	9149	9432	9400	9234	11.5	58.0	30.0	60.0
5	11264	11508	11475	11329	13.2	60.1	26.7	53.9
5	9754	10018	9983	9825	12.9	59.9	27.1	54.8
6	10616	10761	10733	10663	19.3	48.8	31.9	68.7
6	9411	9623	9591	9481	15.3	51.7	32.9	67.9
6	9748	9901	9876	9797	16.2	51.3	32.5	67.7
6	10082	10293	10261	10144	14.9	55.6	29.4	61.4
6	7922	8126	8098	7986	13.7	54.8	31.3	64.2
7	7918	8005	7983	7949	25.6	38.6	35.8	77.5

STEAM GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: $Ca(Cl)_2$-catalysed gasification of Bowmans coal

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
10	11232	11730	11706	11266	4.7	88.5	6.7	-5.0
10	9153	9660	9631	9192	5.7	86.6	7.6	8.9
10	10089	10501	10471	10119	7.2	85.6	7.2	4.5
20	11286	11591	11570	11313	6.8	84.5	8.6	21.3
20	10637	11134	11093	10676	8.3	83.9	7.7	13.4
20	9428	9814	9786	9459	7.3	84.7	8.0	15.2
20	9759	10093	10070	9786	6.7	85.3	8.0	14.5
30	7927	8361	8342	7967	4.3	86.4	9.3	25.5
30	11234	11640	11626	11267	3.3	88.7	8.0	10.8
30	9154	9549	9528	9184	5.4	87.0	7.6	8.4

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2CO_3-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9485	10583	10054	9653	48.2	36.5	15.3	0
0	10845	12114	11509	11034	47.7	37.4	15.0	0
0	9854	11202	10563	10079	47.4	35.9	16.7	0
0	7720	8638	8206	7877	47.1	35.8	17.1	0
3	9076	9492	9403	9186	21.3	52.1	26.6	18.4
3	11662	12143	12036	11795	22.3	50.2	27.5	24.0
3	7680	8287	8095	7825	31.7	44.5	23.9	22.5
3	10684	11171	11055	10813	23.7	49.7	26.6	22.0
5	11096	11478	11403	11214	19.7	49.5	30.8	33.1
5	10674	11107	11020	10803	20.1	50.1	29.8	29.8
5	9077	9508	9429	9213	18.3	50.1	31.7	34.0
5	11672	12088	12001	11797	20.9	49.0	30.1	32.1
7	7702	8266	8163	7877	18.4	50.6	32.1	32.1
7	11078	11574	11449	11236	25.2	43.1	31.7	43.3
7	9523	10039	9952	9699	16.9	49.0	34.2	40.2
7	10790	11220	11220	10931	20.4	46.8	32.9	40.6
10	10210	10643	10562	10367	18.6	45.2	36.3	48.0
10	10816	11192	11118	10946	19.5	45.9	34.6	44.6
10	9911	10306	10230	10050	19.2	45.7	35.2	54.1
10	11075	11538	11430	11238	23.2	41.4	35.4	51.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2CO_3-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9485	10583	10054	9653	48.2	36.5	15.3	0
0	10845	12114	11509	11034	47.7	37.4	15.0	0
0	9854	11202	10563	10079	47.4	35.9	16.7	0
0	7720	8638	8206	7877	47.1	35.8	17.1	0
3	9076	9492	9403	9186	21.3	52.1	26.6	18.4
3	11662	12143	12036	11795	22.3	50.2	27.5	24.0
3	7680	8287	8095	7825	31.7	44.5	23.9	22.5
3	10684	11171	11055	10813	23.7	49.7	26.6	22.0
5	11096	11478	11403	11214	19.7	49.5	30.8	33.1
5	10674	11107	11020	10803	20.1	50.1	29.8	29.8
5	9077	9508	9429	9213	18.3	50.1	31.7	34.0
5	11672	12088	12001	11797	20.9	49.0	30.1	32.1
7	7702	8266	8163	7877	18.4	50.6	32.1	32.1
7	11078	11574	11449	11236	25.2	43.1	31.7	43.3
7	9523	10039	9952	9699	16.9	49.0	34.2	40.2
7	10790	11220	11220	10931	20.4	46.8	32.9	40.6
10	10210	10643	10562	10367	18.6	45.2	36.3	48.0
10	10816	11192	11118	10946	19.5	45.9	34.6	44.6
10	9911	10306	10230	10050	19.2	45.7	35.2	54.1
10	11075	11538	11430	11238	23.2	41.4	35.4	51.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2CO_3-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9485	10583	10054	9653	48.2	36.5	15.3	0
0	10845	12114	11509	11034	47.7	37.4	15.0	0
0	9854	11202	10563	10079	47.4	35.9	16.7	0
0	7720	8638	8206	7877	47.1	35.8	17.1	0
3	9076	9492	9403	9186	21.3	52.1	26.6	18.4
3	11662	12143	12036	11795	22.3	50.2	27.5	24.0
3	7680	8287	8095	7825	31.7	44.5	23.9	22.5
3	10684	11171	11055	10813	23.7	49.7	26.6	22.0
5	11096	11478	11403	11214	19.7	49.5	30.8	33.1
5	10674	11107	11020	10803	20.1	50.1	29.8	29.8
5	9077	9508	9429	9213	18.3	50.1	31.7	34.0
5	11672	12088	12001	11797	20.9	49.0	30.1	32.1
7	7702	8266	8163	7877	18.4	50.6	32.1	32.1
7	11078	11574	11449	11236	25.2	43.1	31.7	43.3
7	9523	10039	9952	9699	16.9	49.0	34.2	40.2
7	10790	11220	11220	10931	20.4	46.8	32.9	40.6
10	10210	10643	10562	10367	18.6	45.2	36.3	48.0
10	10816	11192	11118	10946	19.5	45.9	34.6	44.6
10	9911	10306	10230	10050	19.2	45.7	35.2	54.1
10	11075	11538	11430	11238	23.2	41.4	35.4	51.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2CO_3-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9485	10583	10054	9653	48.2	36.5	15.3	0
0	10845	12114	11509	11034	47.7	37.4	15.0	0
0	9854	11202	10563	10079	47.4	35.9	16.7	0
0	7720	8638	8206	7877	47.1	35.8	17.1	0
3	9076	9492	9403	9186	21.3	52.1	26.6	18.4
3	11662	12143	12036	11795	22.3	50.2	27.5	24.0
3	7680	8287	8095	7825	31.7	44.5	23.9	22.5
3	10684	11171	11055	10813	23.7	49.7	26.6	22.0
5	11096	11478	11403	11214	19.7	49.5	30.8	33.1
5	10674	11107	11020	10803	20.1	50.1	29.8	29.8
5	9077	9508	9429	9213	18.3	50.1	31.7	34.0
5	11672	12088	12001	11797	20.9	49.0	30.1	32.1
7	7702	8266	8163	7877	18.4	50.6	32.1	32.1
7	11078	11574	11449	11236	25.2	43.1	31.7	43.3
7	9523	10039	9952	9699	16.9	49.0	34.2	40.2
7	10790	11220	11220	10931	20.4	46.8	32.9	40.6
10	10210	10643	10562	10367	18.6	45.2	36.3	48.0
10	10816	11192	11118	10946	19.5	45.9	34.6	44.6
10	9911	10306	10230	10050	19.2	45.7	35.2	54.1
10	11075	11538	11430	11238	23.2	41.4	35.4	51.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2CO_3-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	9485	10583	10054	9653	48.2	36.5	15.3	0
0	10845	12114	11509	11034	47.7	37.4	15.0	0
0	9854	11202	10563	10079	47.4	35.9	16.7	0
0	7720	8638	8206	7877	47.1	35.8	17.1	0
3	9076	9492	9403	9186	21.3	52.1	26.6	18.4
3	11662	12143	12036	11795	22.3	50.2	27.5	24.0
3	7680	8287	8095	7825	31.7	44.5	23.9	22.5
3	10684	11171	11055	10813	23.7	49.7	26.6	22.0
5	11096	11478	11403	11214	19.7	49.5	30.8	33.1
5	10674	11107	11020	10803	20.1	50.1	29.8	29.8
5	9077	9508	9429	9213	18.3	50.1	31.7	34.0
5	11672	12088	12001	11797	20.9	49.0	30.1	32.1
7	7702	8266	8163	7877	18.4	50.6	32.1	32.1
7	11078	11574	11449	11236	25.2	43.1	31.7	43.3
7	9523	10039	9952	9699	16.9	49.0	34.2	40.2
7	10790	11220	11220	10931	20.4	46.8	32.9	40.6
10	10210	10643	10562	10367	18.6	45.2	36.3	48.0
10	10816	11192	11118	10946	19.5	45.9	34.6	44.6
10	9911	10306	10230	10050	19.2	45.7	35.2	54.1
10	11075	11538	11430	11238	23.2	41.4	35.4	51.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: Na_2SO_4-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	10692	11341	11000	10729	52.6	41.7	5.7	0
0	11680	12432	12040	11724	52.2	42.0	5.8	0
0	10588	11355	10954	10633	52.3	41.9	5.8	0
5	11681	12229	12156	11758	13.4	72.7	13.9	28.0
5	7559	7971	7862	7611	26.5	60.9	12.7	33.8
5	10701	11060	10982	10748	21.8	65.3	13.0	30.6
5	10971	11492	11408	11044	16.2	69.8	14.1	31.6
7	10697	11123	11056	10758	15.7	70.0	14.3	32.7
7	9453	9880	9816	9521	15.0	69.1	15.9	40.1
7	11686	12134	12065	11759	15.4	68.3	16.3	42.2
7	10509	10809	10751	10560	19.2	63.8	17.0	48.2
10	10994	11379	11309	11050	18.2	67.3	17.3	36.3
10	10533	10852	10756	10578	30.2	55.8	18.6	45.0
10	7544	7869	7807	7600	19.2	63.6	17.2	49.0
10	9442	9669	9618	9481	22.6	60.6	16.9	50.6
14	9033	9274	9197	9075	32.0	50.8	17.3	59.4
14	9908	10078	10029	9940	28.8	52.6	18.6	61.1
14	9021	9328	9228	9069	32.7	51.8	15.5	54.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C

Particle size: 1.6~2.4mm

Condition: NaOH-catalysed gasification of Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	10715	11511	11123	10822	48.7	37.9	13.4	0
0	11690	12516	12113	11799	48.8	38.1	13.1	0
0	9446	10177	9821	9542	48.6	38.3	13.0	0
0	10950	11737	11356	11056	48.4	38.1	13.5	0
3	11660	12264	12183	11803	13.5	62.8	23.8	8.1
3	10458	10840	10795	10555	11.9	62.7	25.4	14.1
3	11680	12098	12036	11780	14.8	61.3	23.9	10.5
3	10953	11348	11286	11048	15.7	60.2	24.2	13.3
5	10687	11198	11128	10824	13.7	59.5	26.8	22.6
5	10952	11477	11399	11101	14.8	56.8	28.4	30.5
5	10702	11025	10976	10791	15.1	57.3	27.7	27.8
5	7513	7750	7712	7583	16.1	54.4	29.5	35.9
7	9432	9808	9748	9540	16.1	55.1	28.9	33.7
7	9018	9487	9420	9161	14.3	55.2	30.6	37.2
7	10441	10717	10671	10528	16.6	51.8	31.5	42.7
7	9013	9204	9168	9075	18.8	48.6	32.6	48.0
10	7519	7813	7773	7622	13.7	51.4	34.9	48.7
10	9907	10130	10098	9994	14.2	46.5	39.3	58.7
10	9448	9654	9618	9535	17.4	40.1	42.6	67.3

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C (pyrolysed coal sample)

Particle size: 1.6~2.4mm

Condition: $Ca(Ac)_2$-catalysed gasification of The Heat-Treated Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	10635	11440	11309	10675	16.3	78.7	5.1	0
0	9405	10084	9964	9438	17.7	77.4	4.9	0
0	10350	11255	11100	10389	17.1	78.6	4.3	0
0	8989	9663	9549	9023	17.0	79.0	5.1	0
0	9901	10411	10319	9926	18.1	77.1	4.9	0
7	11260	11612	11584	11282	8.0	85.7	6.4	16.5
7	10630	11049	11009	10654	9.4	85.0	5.6	5.4
7	8995	9294	9269	9014	8.3	85.4	6.3	16.6
7	11638	12264	12218	11672	7.3	87.2	5.5	1.2
10	11623	12202	12162	11660	6.9	86.6	6.5	17.2
10	8951	9484	9437	8984	9.0	84.9	6.1	14.0
10	11061	11390	11363	11080	8.0	86.1	5.9	9.6
10	11269	11973	11925	11307	6.8	87.7	5.5	0.9
13	11042	11680	11634	11080	7.1	87.0	5.9	8.9
13	9367	9754	9724	9391	7.8	86.1	6.1	12.0
13	9433	9711	9690	9450	7.8	86.3	5.9	9.9
13	11404	12143	12096	11447	6.4	87.9	5.8	5.6
16	11405	12094	12050	11443	6.3	88.1	1.3	
16	10280	10597	10577	10300	6.2	87.4	6.4	15.4
16	10373	10768	10744	10396	6.0	88.0	6.1	9.1
16	11051	11849	11799	11100	6.3	87.6	6.1	11.1

CARBON DIOXIDE GASIFICATION EXPERIMENTS

Temperature: 756°C (pyrolysed coal sample)

Particle size: 1.6~2.4mm

Condition: NaAc-catalysed gasification of Heat-treated Bowmans coal (0.3M)

Time	Cruc. wt	Cruc. + sampl. wt.	Cruc. + devo. sampl. wt	Cruc. + comb. sampl. wt	V.M.	F.C.	Ash	X
(min.)	(mg)	(mg)	(mg)	(mg)	(% d.b.)	(% d.b.)	(% d.b.)	(%)
0	11404	12224	12088	11427	16.6	81.2	2.2	0
0	9891	10543	10431	9912	17.2	79.6	3.2	0
0	10290	11120	10982	10313	16.7	80.6	2.8	0
0	8983	9699	9580	9009	16.7	79.6	3.7	0
0	9374	9979	9878	9395	16.7	79.9	3.4	0
6	10361	10939	10903	10383	6.2	90.1	3.7	4.2
6	11265	11967	11923	11293	6.3	89.9	3.9	8.4
6	10389	10738	10712	10403	7.5	88.7	3.8	7.9
6	11699	11996	11972	11711	8.2	88.0	3.8	7.9
7	11272	12074	12012	11301	7.7	88.7	3.7	4.2
7	8993	9395	9361	9008	8.5	87.7	3.8	8.2
7	10633	11183	11183	10653	8.1	88.4	3.6	2.7
10	11047	11482	11452	11063	6.8	89.5	3.7	4.4

ADDENDUM

Error Analysis

A detailed error analysis of experimental data was conducted for the gasification of Bowmans coal in this work, and was detailed in a separate report by Ye and Agnew (1990).

Generally speaking, in the present investigation, the gasification conversion calculated is strongly influenced by errors associated with operational procedures and the method of analysis. In this work, the sources of error include: variations in mineral matter content of coal samples, temperature variations, gas flow variations. The major contributor of errors is the variability in inorganic matter content of coal. The present results indicated that the gasification conversion is sensitive to the proximate analysis of the reacted coal samples. A small variation in ash content can result in a significant difference in the calculated conversions, particularly at high conversion levels.

Precise analysis of errors was carried out for a series of raw data. Under a specific condition, the maximum error, σ, is determined. Experimental data accepted were only limited within $\bar{u}$ - σ and $\bar{u} + \sigma$. Where $\bar{u}$ is the average conversion value. The experimental data which has greater errors than the maximum was neglected.

Usually, four or five repeat runs were conducted for each set of conditions and the average value was taken. Experimental data points, which are plotted on most figures in this thesis, are average values. Following figures show the difference of these plots.

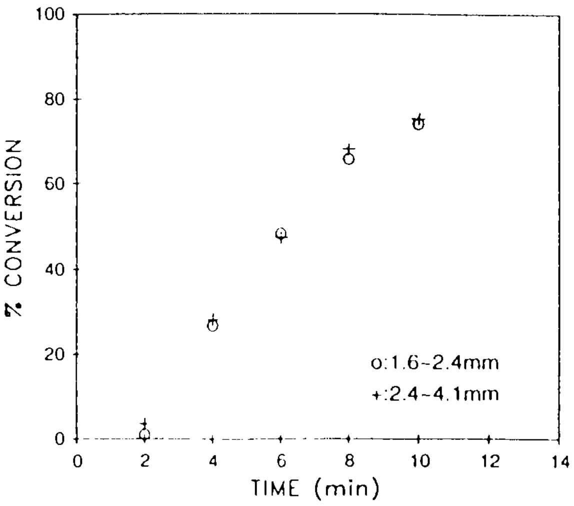


Figure 4.24

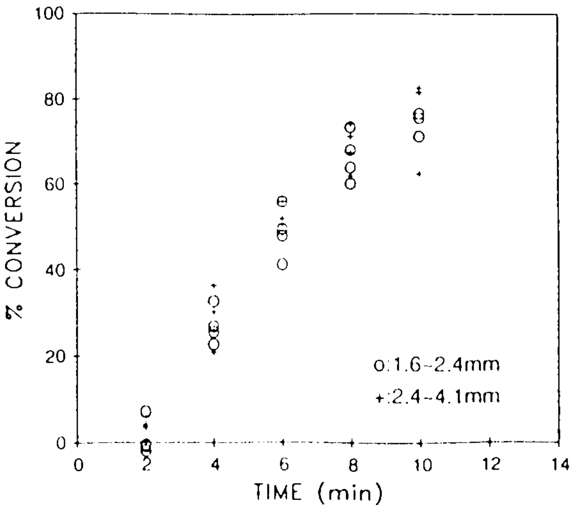


Figure 4.24A

Page 138 In the present study, the "active sites" is defined as the organic groups associated with active cations. The concentrations of oxygen-containing functional groups of coal is given *Table 5-1*. Catalyst loading can be regarded as the index of "active sites".

Bowmans coal contains high concentrations of Na and Ca which act as catalysts. Comparing to the role of Na and Ca in gasification, changing surface has less influence on the reaction rate. For the lignite gasification, surface area or pore surface is not the rate-controlling factor at low temperature (<900°C). Therefore, in this work, measurement of surface area was not conducted, and the emphasis was given to the inherent minerals. The surface areas of raw Bowmans and Yallourn coals was given in *Table 5-1*.

Page 103 As shown in ***Figure 4-3***, comparing to other coals, the calculated apparent activation energy (*E*) of Bowmans coal is low and the reaction rate is high. The high reactivity of Bowmans coal is due to the presence of high inherent Na and Ca contents in raw coal. The presence of Na and Ca increases the population of active sites. Since preexponential factor (*A*) is the frequency of effective collision and is proportional to the total number of active sites, increasing the number of active sites should increase the preexponential factor of reaction. Apparently, the presence of active metal reduces the *energy barrier* (activation energy) of carbon-gas reactions and makes carbon atoms easily react with gas reactants, compared with non-catalysed carbon gasification. Therefore, for Bowmans coal, the high populations of Na and Ca increase the *A* value by increasing active sites, and reduce activation energy (*E*) of the gasification reactions.

Page 165 Bowmans coal contains high concentration of minerals. The level off of conversion occuring at longer times (>8min), shown in ***Figure 4-24***, is possibly due to other physical influence, e.g. ash layer mass resistance.

Page 169 The importance of ***Figure 4-28*** is that it indicates the low reactivity of the acid-washed Bowmans coal. Since conversion is very sensitive to ash content of reacted coal sample, therefore, the non-linearity relation could be due to small experimental error and uneven distribution of minerals in samples.

Page 177 The present results indicate that both Na and Ca are strong catalysts for gasification. Since Na and Ca have similar catalytic activities, therefore the two sets of experimental data are very close, as indicated by the single conversion curve.

Page 83 Si exists in coal in different chemical forms. It associates with some inorganics forming inorganic complex. Part of the complexes can be acid-leached or even water-leached depending on the their chemical form.

Page 76.A vertical quartz-tube reactor was used for gasification experiment (***Figures 3-1 & 3-2***). The major parts of the reaction system are the stainless steel fluid bed heater and the quartz-tube reactor. The fluid bed is filled with approximately 0.8 mm diameter sand as bed particles. Sands with other particle sizes could also be filled depending on the gas velocity demanded. Reactant gases pass through the fluid-bed sand bath and reach the quartz-tube reactor. The steel tube fluid bed is heated by four heating elements. Since fluid bed is well known for its high heat transfer efficiency and even distribution of temperature in bed, in this system, the fluid bed is used to heat reactant gases. It should be noted that, although most investigators use fluid bed as reaction zone to investigate fluid-bed gasification of coal, in the present investigation, the fluid bed is not reaction zone. Bed material (sands) only acts as heat carrier to heat gases passing through the fluid bed. Gasification occurs only in the vertical quartz-tube reactor on top of fluid bed. A metal screen was placed at the bottom of the quartz tube to prevent coal particles falling into fluid bed.