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GASIFICATION OF SOUTH AUSTRALIAN LIGNITE

**A thesis submitted for the degree of
Doctor of Philosophy**

by

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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 in 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 (CO₂, Steam, N₂);
- . 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 $\text{NaAc} \sim \text{Ca}(\text{Ac})_2 > \text{Ni}(\text{Ac})_2 > \text{CaCl}_2 > \text{NaCl} > \text{KCl} > \text{NiCl}_2$ for CO_2 gasification and $\text{NaAc} \sim \text{Na}_2\text{CO}_3 \sim \text{NaOH} \sim \text{Ca}(\text{Ac})_2 \sim \text{KAc} > \text{Na}_2\text{SO}_4 > \text{Ni}(\text{Ac})_2 > \text{NaCl}$ 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.

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