

SUBSEQUENT REACTIVITY OF COAL CHAR IN THE PRESENCE OF BIMETALLIC CATALYSTS

D. Tandon and E.J. Hippo

Department of Mechanical Engineering and Energy Processes
Southern Illinois University at Carbondale
Carbondale, IL 62901

INTRODUCTION

Carbon gasification is a heterogeneous reaction between a solid (carbon) and a gaseous (O_2 , CO_2 , H_2O , H_2 , etc.) phase, in which the solid phase is being consumed continuously and the major products of reaction are gases. The process of gasification can be both exo and endothermic. Combustion of coal (carbon) to produce heat is one of the most important reactions; but in carbon gasification process, it is an undesirable reaction.

Commercial application of coal gasification is mainly focused on noncatalytic reactions to produce syngas (CO & H_2) [1]. This reaction is however extremely energy intensive (endothermic). Methane can be produced from coal directly by reacting it with hydrogen, but this is a very slow reaction. The reactivity of all the gasification processes can be increased by the addition of catalyst. Thus, catalytic gasification at lower carbon/steam gasification temperatures for production of CH_4 is required.

Alkali metals, e.g., sodium, potassium and calcium and transition metals, e.g., iron, nickel are found to be good catalyst for carbon gasification. An understanding of reactivity and catalytic effects is important to develop economical gasification processes.

Bimetallic catalysts have addressed some of the limitations of single catalyst gasification [2-8]. Gas production increases with the use of bimetallic catalyst. The catalyst remains active for a longer duration and is more resistant to poisoning. A catalyst that is not deactivated by sulfur would enable the gasification of high sulfur coals. Synergetic effects have been observed by the use of bimetallic catalysts [9].

Carrazza et al. [2] found that when KOH/NiO bimetallic catalyst was used for steam/graphite gasification; the gas was still being produced after 25% graphite conversion and the catalyst was active even after 24

hours of reaction time. These experiments were performed at high temperature and near atmospheric pressure. Thus, the principle products of gasification were CO_2 and H_2 . A potassium/iron system was also found to be a good catalyst for steam/carbon gasification [10].

It is the aim of this study to develop a bimetallic catalyst system that would be active at lower temperatures and higher pressures. These operating conditions shift the equilibrium away from CO formation and towards CH_4 formation.

EXPERIMENTAL

The coal selected for use in this research is from the Illinois Basin Coal Sample Program (IBCSP). It is Herrin No. 6 (IBC 106) coal. This coal has high sulfur content which make it undesirable in direct combustion. Both as received and demineralized coal samples were used in this study. A portion of coal sample was demineralized, details of this process can be found elsewhere [11]. Coal char was prepared by devolatilizing coal in a vertically mounted induction furnace in a nitrogen atmosphere. The chars were prepared by heating the sample at $1000^\circ C$ for one hour.

The catalysts selected for this study are potassium, sodium, nickel, iron, molybdenum and calcium. Catalysts were added to the coal or the char, by incipient moisture technique. Samples were prepared by adding catalyst to the raw coal samples, coal char samples, and in some cases by adding the catalyst to the raw and demineralized coal samples and then charring the coal sample. This provided a comparison between catalyst addition prior to or after charring, and a comparison was made between the efficiency of the process in both cases. Catalyst loadings (based on metal) of 1.0, 2.0, 5.0 and 10.0 wt.% were employed in this study. Bimetallic catalyst systems were prepared by mixing the individual salts in 1:2, 1:1, and 2:1 ratios to obtain the above mentioned loadings.

Gasification of all samples was conducted in an electric furnace (Lindberg). The reactor, was a stainless steel tube (3/4 inch dia. and 2 feet long), mounted vertically in the furnace. A high pressure pump (Eldex A-60-S) was employed to pump water at the rates of 30-60 ml hr⁻¹ gm⁻¹ of coal. Samples were placed in the reactor in a wire mesh bucket. The glass wool at the top of the reactor was used to trap any tarry material that might tend to escape. The system was purged with argon and pressurized with steam. Gas samples were collected at regular time intervals (5, 15, 30, 60, 90, 120, and 180 min.) in gas bags and gas chromatography was performed on each gas bag. Product gas composition and concentration were monitored by gas chromatography. From the gas yield and composition, the carbon conversion in each interval and the accumulated carbon conversion were calculated. The experiments were terminated when the rate of gas production diminished significantly.

Initially, temperature programmed experiments were performed on uncatalyzed demineralized chars at various pressures (0.1 to 5 MPa). At a given pressure, experiments were performed at 1000 K; and the temperature was lowered by 100 K till such temperature where the gas production was negligible.

Various combinations of alkali and alkali-earth metals with transition metals were examined to study the synergetic effects and longer activation periods expected with these combinations. The catalyst systems were prepared by the incipient moisture technique. It was anticipated that alkali and alkali-earth metals, especially at high pressures, should assist in the penetration of transition metals in the coal matrix, and should also keep the transition metals reduced for longer periods of time.

RESULTS AND DISCUSSION

Use of low temperatures and high pressures help in shifting the gasification equilibrium towards methane formation. Addition of catalysts not only increased the rate and amount of carbon conversion but also assisted in production of higher concentrations of methane. At 500°C and 35 atm., a significant amount of methane is produced. All the initial experiments were carried out for two hours. With raw coal without catalyst, 21% carbon conversion was achieved. The primary gases in the product were CO, H₂, CO₂, and small quantities of methane. With 10% potassium low 30% carbon conversions were obtained. With 10% iron high 20% carbon conversions were obtained. The gas in both

the cases was a mixture of CH₄, CO₂, CO, and H₂. With a mixture of 10% potassium and 5% iron, carbon conversion of 37% was achieved. The gas concentration of the product was, primary gases CO₂, CH₄, and small amounts of CO and H₂. When 10% potassium and 10% iron was used the conversion remained the same and there was slight increase in the methane in the product gas. The catalyst system was still active after two hours. Apparently the potassium helps keep iron reduced and thus keeps it active for longer time periods. Other catalysts (both single and bimetallic) systems are under investigation and the results will be reported.

CONCLUSIONS

Steam gasification of coal under high pressures and lower temperatures, with the bimetallic catalyst system. The reaction equilibrium towards methane production. Results indicate a definite increase in the concentration of methane in the gas produced. Various other catalyst mixtures will be tried to study their effects on increasing the gasification rate towards maximum methane formation. The bimetallic catalyst system is active for longer time periods. Alkali metals help keep the transition metals reduced for longer time periods and thus keep them active.

REFERENCES

1. R.Y. Hamilton, D.A. Sams, F. Shadman, Fuel, **63**, 1008, 1984.
2. J. Carrazza, W.T. Tysoe, H. Heinemann and G.A. Somorjai, J. Catal., **96**, 234, 1985
3. J.S. Binford and H. Eyring, J. Am. Chem.Soc., **60**, 486, 1956.
4. R.G. Jenkins, S.P. Nandi, and P.L. Walker, Jr. Fuel, **52**, 288, 1973.
5. E.J. Hippo and P.L. Walker, Jr., Fuel, **54**, 245, 1974.
6. K.J. Huttinger and W.F. Merdes, Carbon, **30**(6), 883, 1992.
7. J.L. Johnson, Fuel Chem. Div. prepr., 170th ACS national meeting, Chicago, IL. Aug. 24-29, 1975.
8. J.W. Patrick and F.H. Shaw, Fuel, **51**, 69, 1972.
9. Y. Nishiyama, Fuel Processing Technology, **29**, 31, 1991.
10. J. Alder, K.J. Huttinger, and R. Minges, Fuel, **63**, 1397, 1984.
11. A. Inaeres-Solano, E.J. Hippo, and P.L. Walker, Jr., Fuel, **65**, 776, 1986