Development of a Continuous Low Temperature Catalytic Coal Gasification Process for Production of FT Suitable Synthesis Gas

SYNOPSIS: Catalytic coal gasification using K₂CO₃ is an efficient way to gasify coal to FT suitable synthesis gas. This study reports the development of a continuous catalytic gasification process to gasify low rank coals and lignite to produce FT suitable synthesis gas in a single direct step using K₂CO₃ as a catalyst and a mixture of Steam and CO₂ as gasifying agent. A small 0.2 g/min laboratory scale continuous catalytic gasification unit was developed and experiments were carried out at 700 °C with pure steam and a mixture of steam and CO₂. Synthesis gas with H₂/CO= 1, 2, and 3 was produced by changing the steam/CO₂ ratio of the gasifying agent. Experimentally observed gas composition was compared with the calculated values obtained by using thermodynamic equilibrium conditions and a good match was obtained.

1. INTRODUCTION
For indirect production of liquids/chemicals from coal, FT synthesis process is a primary process. The FT-suitable synthesis gas is produced by a two step process; coal gasification process followed by water gas shift process to adjust the H₂/CO ratio of synthesis gas. High temperature gasification is a primary conversion route to produce synthesis gas (H₂ and CO) from coal. Gasification is an endothermic reaction and requires temperature above 1000 °C to achieve acceptable rates for commercial application. However, at such high temperature synthesis gas composition is primarily decided by thermodynamic equilibrium rather than kinetics, product gas has low H₂/CO (0.5~0.7) and a down-stream low temperature water gas shift reactor is necessary to adjust the H₂/CO to produce FT-suitable synthesis gas. From thermodynamic equilibrium consideration, H₂/CO ratio of synthesis gas increases with decreasing temperature. Catalytic gasification of coal is an attractive way to achieve commercially acceptable reaction rates at low temperature. Lowering of gasification temperature also leads to production of FT suitable synthesis gas with high H₂/CO ratio directly in a single step. Development of such a process is technologically attractive.

In this study, we report the development of a laboratory scale continuous catalytic coal gasification experimental unit. Coal was gasified in a steam and CO₂ mixed environment as a gasifying agent at 700 °C with K₂CO₃ as a catalyst. Effect of ratio of steam to CO₂ on composition of the gas produced was investigated. It was found that synthesis gas with H₂/CO=1, 2, 3 can be produce at 700 °C in a single step and the produced gas composition can be predicted by thermodynamic equilibrium.

2. EXPERIMENTAL
Adaro (AD) coal from Indonesia was selected for the investigation. The elemental analysis of Adaro coal is: C=71.2%, H= 5.2%, N= 1.13%, O (by diff) = 19.4; Ash- 2.9 %. A schematic diagram of the experimental set up is shown in Figure 1.

About 25 g coal is physically mixed with 25 g K₂CO₃ and loaded in the top feeder hopper. The coal particles were in 0.5~1 mm size range. Coal+K₂CO₃ sample was fed to the gasifier from the top at 0.2 g/min rate in about 400 cc/min N₂ flow as carrier gas. The reactor had two stages; upper for gasification of coal and lower for tar cracking. Both stages operate in fluidized bed state. Char and K₂CO₃ act as the bed material for gasifier stage while K₂CO₃ and 5% alumina act as bed material in the lower tar cracking stage. Coal fed from the feeder into the upper gasifier stage is pyrolysed to produce char, tar and pyrolysis gases. A mixture of steam/CO₂ and N₂ was supplied from the bottom of the upper stage to act as gasifying agent as well as fluidizing agent. Char is gasified with steam/CO₂ by K₂CO₃ as catalyst. Synthesis gas produced containing tar, pyrolysisis gases together with excess steam/CO₂ flow to the lower tar cracking stage. A certain amount of K₂CO₃ was preloaded in the lower tar cracking stage to catalytically crack the tar produced. The synthesis gas was then cooled using double ice cooled tar traps and two thimble filter units. The composition of the cleaned gas was analyzed using mass spectrometer. The results are tabulated in Table 1.
gases was measured by an online micro gas chromatograph (Agilent 3000A). The total gas flow rate at the outlet was measured by a digital flow meter and also every 3 min by a film flow meter.

The temperature of gasifier and tar cracker was maintained at 700±5 °C. Experiments were carried out for 100 % steam, 70% steam+30% CO₂, 50% steam+ 50% CO₂, (on volume basis) and steam to coal (as carbon) ratio of 5. A coal gasifier simulation code was written in Fortran90 to obtain gas composition, cold gas efficiency, and thermal efficiency based on thermodynamic equilibrium, mass balance and energy balance.

3. RESULTS AND DISCUSSION

Figure 2(a, b, c) show the composition profile of the evolved gases from catalytic gasification of Adaro coal at 700 °C with H₂O/CO₂=100/0, 70/30, 50/50 respectively.

At H₂O/CO₂=100/0, produced gas contained mainly H₂ and very little CO. As H₂O/CO₂ changed to 70/30, and 50/50, H₂ decreased and CO increased. These results show that synthesis gas with H₂/CO ratio from 1~3 can be produced by gasification of coal in a single step by changing the steam/CO₂ ratio of the gasifying agent. Synthesis gas with H₂/CO=1, 2 and 3 can be used as feedstock for FT synthesis process to produce DME, methanol, methane and other chemicals. The production profile of all the gases in the three cases was smooth and suggests that there is not any serious back pressure development in the system. All the experiments were carried out continuously where coal and K₂CO₃ was fed from top by a feeder at 0.2 g/min. Mixture of ash and K₂CO₃ was removed from the bottom and the withdrawal rate was controlled by a feeder.

Figure 3 shows a plot between carbon recovery fraction and gasification time. The fraction on y-axis is the ratio of moles of Carbon in out gases to Carbon in as solid carbon in coal. A ratio of less than 1 suggests carbon conversion is less than 100% while more than 1 means carbon from K₂CO₃ decomposition also appears as CO₂. A ratio of 1 is just when carbon in is equal to carbon out and the time taken to reach this state is the residence time or gasification time necessary. This time is about 40 min similar to that obtained from a TGA experiment.

Figure 2. Gas evolution profiles of catalytic gasification of Adaro at 700 °C (a) 100% Steam, (b) 70/30 % Steam/CO₂, (c) 50/50 % Steam/CO₂.

Figure 3. Carbon recovery fraction (C_{out}/C_{in}) with gasification time.

It is important to investigate whether the outlet gases are in thermodynamic equilibrium state. Table 1 compares the average experimental gas fractions with the calculated fractions. A good match was obtained confirming that synthesis gas produced by catalytic gasification of coal is in equilibrium state and its composition can be predicted.

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<tr>
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<th>H₂O/CO₂=100/0</th>
<th>H₂O/CO₂=70/30</th>
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4. Conclusions

A continuous catalytic coal gasification experimental setup was developed and nearly 5 h long continuous experiments were successfully carried out. Synthesis gas with H₂/CO suitable for methanol, DME and methane production by FT synthesis was produced in single step. Carbon balance calculation showed that nearly 100% carbon conversion was achieved with 40 min residence time. Comparison of experimentally observed gas composition with the calculated values confirmed that synthesis gas produced by catalytic gasification of coal is in thermodynamic equilibrium state.

References