No. 36 Effect of reaction parameters on gasification rate and $H_2/CO$ ratio of synthesis gas produced by catalytic steam gasification of HyperCoal

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SYNOPSIS: Effect of steam partial pressure on reaction rate and on composition of the gas produced from catalytic steam gasification of HyperCoal has been investigated. The parameters investigated were gasification temperatures 700, and 750 °C, catalyst loading 50 wt %, and steam partial pressure 0.5, 0.1 and 0.02 atm. By changing partial pressure of steam, synthesis gas with desired $H_2/CO$ ratio was obtained. Gasification rates were high. The results showed that synthesis gas suitable for DME, methanol and methane production by FT synthesis process can be produced in a single step at 700 °C by catalytic steam gasification process.

INTRODUCTION

Gasification is a primary conversion route to produce synthesis gas ($H_2$ and CO) from coal. Gasification is an endothermic reaction and requires temperature above 1000 °C to achieve acceptable rates for commercial application. The product gas obtained at such high temperatures usually has low $H_2/CO$ (0.5–0.7). Catalytic gasification of coal has been widely considered as an effective mean to decrease the gasification temperature and control the composition of the product gas. The most favored catalysts are alkali metal salts especially $K_2CO_3$. However, the major drawback in catalytic gasification of coals is the interaction of catalyst with the mineral matter (ash) present in the coals leading to the formation of compounds from which recovery of the catalyst is difficult. To overcome the problem of loss of catalyst, our research group has developed a process to remove mineral matter from coal by solvent extraction. The solvent extracted coal from hereon called HyperCoal (HPC) has less than 500 ppm of ash. Because of its ash-less characteristics, a catalytic gasification process for coal may be developed by using HyperCoal as a feed material leading to low gasification temperature, easy recovery and recycling of catalyst [1,2].

Production of synthesis gas ($H_2/CO$) at such low temperatures would also be an attractive application for HyperCoal. Our previous studies showed that $K_2CO_3$-catalysed steam gasification of HyperCoal contained $H_2$ and CO as the major products gases with little CO and was suitable for $H_2$ production [3].

In this study, effect of steam partial pressure on reaction rate and on composition of the gas produced from catalytic steam gasification of HyperCoal has been investigated. The parameters investigated were gasification temperatures 700, and 750 °C, catalyst loading 50 wt %, and steam partial pressure 0.5, 0.1 and 0.02 atm.

EXPERIMENTAL

A subbituminous coal, Pasir (PAS) from Indonesia was selected for the investigation. HyperCoal production method and gasification procedure has been described in detail elsewhere. Briefly, HyperCoal (HPC) was produced by the solvent extraction of the coal with 1-methylnaphthalene at 360 °C and subsequently separating the extract (HyperCoal) from the solvent. The extraction yield was 51 % for Pasir coal. The properties of the coal and HyperCoal are shown in Table 1. In the present study all samples for catalytic gasification experiments were prepared with 50 % catalyst loading. Catalyst loading was on dry and ash free wt % basis of coal and HPC. Catalyst mixing method has been described in detail elsewhere [3]. Briefly, a desired amount of $K_2CO_3$ was added on the top of a measured sample already loaded into a test crucible as solid particles and stirred with a small spatula until white $K_2CO_3$ disappears by capturing moisture from the air. The particle size of coal and HyperCoal sample was under 75 μm.

The gasification experiments were carried out at 700 and 750 °C and at 0.5, 0.1 and 0.02 atm steam partial pressure. Experiments were carried out in a thermo gravimetric (TG-DTA 2020S, MAC) apparatus. Desired amount of water was pumped by a HPLC pump to a steam generator held at 250 °C. Argon was also passed to the steam generator as a steam carrier gas. By changing the amount of water pumped by the HPLC pump to the steam generator, and the flow rate of argon as the carrier gas, steam partial pressures of 0.5, 0.1 and 0.02 atm were achieved. A 4-way valve at the inlet of the TG-DTA was used to change (Ar+O2) flow to (Ar+steam) flow. The flow lines were kept at 230 °C by using ribbon heaters. The evolved gases flow out together with the purge gas from the side into an ice cooled tar trap to remove tar before injecting to the micro gas chromatograph (Agilent 3000A). The total gas flow rate at the outlet was measured every 3 min by a film flow meter.

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<th>Table 1: Properties of coal and HyperCoal.</th>
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RESULTS AND DISCUSSION

The coal/HPC conversion (X) on dry, ash, catalyst and volatile free basis (daf) was calculated.
Figure 1. Effect of steam partial pressure on rate.

Figure 1 shows the effect of steam partial pressure on gasification rate at 700 and 750 °C. The conversion profiles shown in Figure 1 represent the progress of C-H2O reaction (1). Any change observed in conversion profiles shown in Figure 1 indicates the change in reaction (1). Reaction (2) is more representative of gas composition of the produced gas. The results show that gasification rates decreased with decreasing steam partial pressure. This decrease suggests that lowering of partial pressure slowed down the rate of reaction (1). Figure 2 shows the effect of steam partial pressure on gas composition of the produced gas in mole percent at 700 and 750 °C for HPC with catalyst at 0.5, 0.1 and 0.02 atm partial pressure of steam. Gas composition is primarily determined by reaction (2) which is strongly dependent on the gasification conditions. At 700 °C, H2 decreased from 63 % at 0.5 atm to 55 % at 0.02 atm, CO2 from 33 % at 0.5 atm to 25 % at 0.02 atm while CO increased from 3 % at 0.5 atm to 19 % at 0.02 atm. H2/CO ratio was 21 at 0.5 atm, 9 at 0.1 atm and 3 at 0.02 atm. The results indicate that synthesis gas with H2/CO=2, suitable for DME and methanol production by FT synthesis process may be produced in a single step at 700 °C by catalytic HyperCoal steam gasification process. Rate constants were obtained by inverting this time value. The rate constants thus obtained were plotted against steam partial pressure according to equation

\[ k = k_0 \times P_{H2O}^{n} \]  

Figure 3 shows a plot between ln(p) and ln(k). At 700 and 750 °C, order of reaction with respect to steam was 0.5. This suggests that reaction rate of K2CO3-catalysed steam gasification of char is affected by the steam partial pressure but not to the same extent as in the case of non catalytic steam gasification.

Figure 2. Effect of steam partial pressure on gas composition.

Figure 3. Plot between steam partial pressure and rate.

Conclusions

Effect of partial pressure of steam on gasification rate and on composition of product gas from catalytic steam gasification of HyperCoal at 700 and 750 °C was examined. Gasification rate decreased with decreasing steam partial pressure. Order of reaction with respect to steam was 0.5. By changing partial pressure of steam, H2/CO ratio of the synthesis gas can be controlled in a single step process.

References