Syngas Production from Lignite Coal Using \( \text{K}_2\text{CO}_3 \) Catalytic Steam Gasification with Controlled Heating Rate in Pyrolysis Step

Dijan Supramono***, Dewi Tristantinia, Agustina Rahayua, Ricky Kristanda Suwignjoa, David Hartono Chendraa

**a Department of Chemical Engineering, Universitas Indonesia, Depok 16424, Indonesia

Abstract

Gasification uses steam increases \( \text{H}_2 \) content in the syngas. Kinetics of gasification process can be improved by using \( \text{K}_2\text{CO}_3 \) catalyst. Controlled heating rate in pyrolysis step determines the pore size of charcoal that affects yield gas and \( \text{H}_2 \) and \( \text{CO} \) content in the syngas. In previous research, pyrolysis step was performed without considering heating rate in pyrolysis step. This experiment was performed by catalytic steam gasification using lignite char from pyrolysis with controlled heating rate intended to produce maximum yield of syngas with mole ratio of \( \text{H}_2/\text{CO} \geq 2 \). Slow heating rate (3°C/min) until 850°C in the pyrolysis step has resulted in largest surface area of char. This study was performed by feeding Indonesian lignite char particles and \( \text{K}_2\text{CO}_3 \) catalyst into a fixed bed reactor with variation of steam/char mole ratio (2.2; 2.9; 4.0) and gasification temperature (750°C, 825°C, and 900°C). Highest ratio of \( \text{H}_2/\text{CO} \) (1.682) was obtained at 750°C and steam/char ratio 2.2. Largest gas yield obtained from this study was 0.504 mol/g of char at 900°C and steam/char mole ratio 2.9. Optimum condition for syngas production was at 750°C and steam/char mole ratio 2.2 with gas yield 0.353 mol/g of char and \( \text{H}_2/\text{CO} \) ratio 1.682.

Keywords: char; steam catalytic gasification; fixed-bed reactor; \( \text{K}_2\text{CO}_3 \)

Nomenclature

---

1. Introduction

The issuance of Indonesian Government Regulation No. 7 year 2012 which stated a ban on the export of raw materials mining aims to increase the value of raw coal Indonesia [1]. This legislation is related to the fulfillment of domestic energy needs particularly of liquid fuels for the transportation sector. Domestic fuel needs may be fulfilled by using synfuel made from Indonesian lignite coal which still has large deposit amounting to 105,200 million tons [2]. It can be produced through two consecutive processes, i.e. lignite coal gasification to produce syngas gas and Fischer Tropsch reaction to produce the synfuel.

Gasification of coal char generally produces synthesis gas (syngas) with \( \text{H}_2/\text{CO} \) mole ratio lower than desired for the Fischer-Tropsch process (mole ratio of \( \text{H}_2/\text{CO} \approx 2 \)) [3]. Series of studies have been done to use syngas in Fischer Tropsch
process catalyzed with Co/Al₂O₃, Co-Re/Al₂O₃ and Co-Fe/Al₂O₃ reach 40-50% conversion [4-6]. Based on the research, syngas with H₂/CO mole ratio 2-2.1 yields highest conversion in synfuel production[7-8].

Therefore, this research aims to obtain optimum condition of Indonesian lignite char to produce high yield syngas with mole ratio of H₂/CO approaching 2, required in the utilization for Fischer Tropsch process. Among several gasification methods, steam gasification increases the concentration ratio of H₂/CO in syngas [3]. Lignite char particles have high reactivity due to their high surface area so they are easily react in the process of gasification [9]. Less ash content in this char results in higher conversion to syngas [10]. Potassium carbonate catalyst has a high reactivity and capability in converting coal into syngas [11]. The addition of the catalyst K₂CO₃ on char feed aims to decrease the activation energy, so optimum gasification process could be conducted in lower temperature. Heating rate used in the char preparation was 3°C/min with final pyrolysis temperature at 850°C. At this pyrolysis condition, char particles had largest pore surface area [12]. Larger surface area of char was predicted to produce high syngas yield. In the present research, gasification was conducted at varied temperatures of 750, 825, and 900°C, which will obtain maximum gas yield and H₂ content in syngas production [13]. In addition, gasification was also conducted at varied steam to char mole ratios (2.2; 2.9; 4.0). Hydrogen content in syngas is predicted to increase by feeding more steam.

2. Methodology

Method of gasification used in this study was steam gasification with the addition of K₂CO₃ catalyst and controlled pyrolysis heating rate. Operating temperature and steam/char ratio were varied to obtain optimum operating conditions to produce syngas with high value of H₂/CO mole ratio and gas yield. This study used a fixed bed reactor and manual steam generator. After going through the gasification reaction, syngas was analyzed using gas chromatography to determine the composition of each component in the syngas. Equipment scheme used in this research is shown in Fig. 1 and 2 below.

![Fig. 1. Equipment scheme of pyrolysis step for char preparation](image)
2.1. Preparation

Coal preparation, tool calibration, leakage test and char preparation were done before the experiment. Coal preparation stage consisted of crushing and sifting the coal. Before being crushed and sifted, coal was dried in the sun light for 10 hours. Coal was crushed roughly on a container with mortar. Then coal particles were sieved to 0.4 mm screen for feed in the pyrolysis reactor (Fig.1). Calibration stage consisted of nitrogen flowmeter and steam generation rate calibration. Leakage test was done by simple method using soap water. This step was conducted in the condition of flowing nitrogen. Coal char preparation was done by coal pyrolysis process. Coal pyrolysis was performed with heating rate and final temperature variation. The char particles used in gasification were those from pyrolysis with heating rate of 3°C/min and final temperature of 850°C. BET analysis was done to calculate out the surface area of coal char produced in pyrolysis process. It shows that the surface area of char particles is 168.6 m²/g of char [12].

2.2. Gasification Stage

Gasification stage was done by feeding 2 grams coal char and 10% K₂CO₃ catalyst in the fixed bed reactor (Fig.2). Before gasification process was started, for a while, nitrogen gas was flowed through syngas outlet line. Then, nitrogen flow was closed and reactor was started to be heated until reaction temperature (750, 825, and 900°C). While heating the reactor, steam inlet line to the reactor was heated at temperature of 150°C. After reaching the reaction temperature, steam generator was heated to particular temperature to control evaporating rate of steam. When the water started boiling, nitrogen was flowed through the steam generator line. At this time, the gasification reaction began to occur. Syngas from the reactor flowed through solid trap and water trap. Then, syngas flowed through the injection port where gas samples was taken.

2.3. Sampling Test Stage

After going through solid trap and water trap, syngas was considered to be clean from impurities (tar and condensed water) and could be analyzed. Analysis of syngas component concentration was performed by gas chromatography-TCD (Thermal Conductivity Detector). Sample analysis was performed offline by gas-tight syringe every 10 minutes for 120 minutes. Peak area resulted from GC was converted into concentration units. Concentration data of syngas components then were processed to calculate the H₂/CO mole ratio.
3. Result and Discussion

3.1. Effect of Temperature on Gasification Reaction Phenomena

Based on Fig. 3(b), it is noted that at 750°C reaction temperature, H₂ reaches its highest concentration at \( t = 80 \) min. At \( t = 80 \) min, the reaction can be considered have reached equilibrium because the concentration difference with the following minute is quite small. Fig. 3(e) shows that at 825°C reaction temperature, H₂ reaches its highest concentration at \( t = 60 \) min. After \( t = 60 \) min, both CO and H₂ concentrations decreased. This phenomena indicates that the reaction is complete before it can run on its equilibrium state. In Fig. 3(g), it is known that H₂ and CO reach its highest concentration at \( t = 30 \) min. After \( t = 30 \) min, both H₂ and CO decreased. It is predicted that concentration drop occurs because the reaction has passed its equilibrium state.

Reaction temperature affects reaction kinetic through Arrhenius equation. Reaction kinetics increases with higher reaction temperature [14]. Thus, reaction with higher temperature will reach its equilibrium faster. Relation between reaction kinetics and reduction rate of bed height can be explained as increasing reaction kinetics results in acceleration of bed height reduction. Therefore, as shown in Fig. 3(e) and Fig. 3(g), the mass required to run the reaction in equilibrium state increased so that the reaction had been completed before proceeding to the equilibrium state. In Fig. 3(b) reaction has led to equilibrium state.
3.2. Effect of Steam/Char (S/C) Ratio on Gasification Phenomena

Fig. 3(a) shows that the equilibrium state is reached in t = 30 min. This phenomenon is faster than two other conditions in 750°C which reach its equilibrium state in t = 80 min (Fig. 3(b)) and t = 110 min (Fig. 3(c)). At 750°C, the addition of steam resulted in longer time of reaction to reach steady state which directs to equilibrium state. This is due to the higher ratio of steam/char resulted in increasing rate of nitrogen and steam flow into the bed according to the equation of continuity [15].

Figure 3 (d) - (f) shows effect of steam addition at temperature 825°C. At 825°C, it is predicted that gasification reaction has completed before reaching its equilibrium condition. Higher reaction rate will increase the bed reduction rate corresponding to bed volume. So that, when steady state is reached, bed volume reduction has exceeded minimum bed height required by the reaction to reach in equilibrium state.

To compare all conditions, highest H\textsubscript{2} concentration is considered as parameter for highest reaction kinetic which can be achieved by the reaction. After reaching highest H\textsubscript{2} concentration, it will decline which indicates the end of reaction. Reaction with steam/char ratio 2.2 in Fig.3 (d) reaches highest H\textsubscript{2} concentration at t = 40 min. Meanwhile, reaction with higher steam/char ratios (2.9 and 4.0) in Fig.3 (e) and (f) reaches its highest H\textsubscript{2} concentration at t = 50 min and t = 60 min.

For a given surface area, increasing steam flow rate to reactor will increase the steam and nitrogen flow rate also. Larger steam flow rate will cause higher accumulation rate resulted in higher steam partial pressure. This phenomenon is competing with the presence of friction which causes total pressure drop of gas in bed. Declining total pressure drop of gas requires longer time to reach steady state condition. By this reason, it needs longer time to reach equilibrium state at higher steam/char ratio.
3.3. Effect of Gasification Temperature on $H_2$/CO Ratio

![Graph showing the ratio of $H_2$/CO at different gasification temperatures with steam/char 2.9]

Fig. 4 shows that increasing temperature of reaction decreases $H_2$/CO ratio in syngas product. This may occur as a result of the effect of increasing temperature on dominant products of reactions. This assumption is explained by the effect of reaction temperature on free energy Gibbs. At 750°C, methane reforming and water gas reaction dominates the gasification process. Both reactions contribute to higher $H_2$ concentration in product [16]. Ratio of $H_2$/CO decreased by increasing temperature from 825°C to 900°C because there was a dominant shift to Boudouard reaction at this temperature range.

Methane Reforming : $CH_4 + H_2O \rightarrow CO + 3 H_2$  
Water Gas : $C + H_2O \rightarrow CO + H_2$  
Boudouard : $C + CO_2 \rightarrow 2 CO$

3.4. Effect of Gasification Temperature on Gas Yield

$H_2$ and CO production will increase in higher reaction temperature of solid waste gasification [17]. In contrast, based on work of Wu et al. (2010), at higher temperature $H_2$ production decreases while CO increases [18]. In this study, gas yield increases with increasing temperature at 900°C. Fig. 5 shows that at 900°C, both CO and $H_2$ yields increase which contribute to higher gas yield. Higher temperature will give effect to increase heat and mass transfer rate at catalytic reaction [17]. Besides, higher temperature is favored to decomposition and thermal cracking reaction [19].

![Graph showing gas yield at different gasification temperatures]

3.5. Effect of Steam/Char (S/C) Mole Ratio on $H_2$/CO Ratio
Table 1. Effect of Steam/Char Ratio on H2/CO Ratio at 750 and 825°C

| S/C Mole Ratio | H2/CO Mole Ratio |
|----------------|------------------|
|                | 750°C            | 825°C          |
| 2.2            | 1.68             | 1.25           |
| 2.9            | 1.14             | 1.01           |
| 4.0            | 1.11             | 1.55           |

Table 1 shows different effect in increasing steam/char ratio at 750°C and 825°C gasification temperatures. At 750°C, it shows that reaction starts to occur in steady state which led to equilibrium state, whereas at 825°C, it shows a phenomenon where the reactions have passed its equilibrium state. As a result at 750°C, H2/CO will decrease when S/C ratio is increased.

Considering to the transient state, H2/CO ratio reduced when this state was accounted for as an overall state. Previous study conducted by Lee showed that increasing steam/char in air-steam gasification will increase H2/CO ratio [20]. In contrast to Lee’s study, where steam was supplied continuously and at no transient condition, at present research, the addition of steam, which conducted naturally based on pressure difference between steam generator and the base of gasification reactor, was difficult to control its flow. Decreasing H2/CO ratio with increasing steam flow is predicted due to the effect of steam input excess to catalyst K2CO3 activation.

3.6. Effect of Steam/Char (S/C) Mole Ratio on Gas Yield

Fig. 6 (a) and (b) shows that there is no considerable effect of increasing steam/char ratio on the gas yield of gasification. It may be caused by different conditions to achieve their equilibrium state. At 750°C, the highest yield value is obtained in gasification reaction with S/C mole ratio 2.2. Total gas yield declines with increasing steam/char ratio 2.9 to 4.0. This phenomenon was observed for different span times for different mole ratios of steam to char to reach its equilibrium state.

However, at 825°C, different span times to reach their equilibrium do not clearly affect in total gas yield. It is predicted to relate with its catalyst reactivity. At higher temperature, the effect of high steam input in lowering K2CO3 catalyst reactivity was offset by the increase of gasification reaction temperature.

4. Conclusion

Highest H2/CO ratio 1.682 was obtained in gasification temperature condition 750°C and steam/char mole ratio 2.2. Highest gas yield 0.50 mole/g of char is obtained in gasification temperature condition 900°C and steam/char mole ratio 2.9. Optimum condition for syngas production was at 750°C and steam/char mole ratio 2.2 with gas yield 0.353 and H2/CO ratio 1.682. Transient state of reaction decreases H2/CO ratio and yield gas by increasing steam/char ratio.
Acknowledgements

This work was carried out under the frameworks of the projects of the development of steam catalytic gasification technology for Indonesian lignite coal to support production of synthetic fuel. The authors give their great thanks to the Directorate of Research and Public Services Universitas Indonesia for their financial support.

References

[1] Peningkatan Nilai Tambah Mineral Melalui Pengolahan dan Pemurnian Mineral. Peraturan Menteri Energi dan Sumber Daya Mineral Republik Indonesia Nomor 7 Tahun 2012 BAB VII Pasal 20: 14, ESDM RI, 2012.
[2] Ariyono, B.G, 2011. “Indonesian Coal Resource Development and Future Direction of Coal Export”, International Symposium on Clean Coal Day, Jakarta, Indonesia, pp. 6-14.
[3] Bell, D.A., 2011. “Coal Gasification and its Applications”, 1st ed. Elsevier, pp. 35-72.
[4] Tristantini, D., 2007. “The effect of synthesis gas composition on the Fischer-Tropsch synthesis over Co/Al2O3 and Co-Re/ γ-Al2O3 catalysts”, Fuel Processing Technology, vol. 88, pp. 643-649.
[5] Tristantini, D., 2009a, “Production of synthesis gas through oxidation of methane by Ca-oxide coal-char to achieve lower oxidation cost”, Proceedings of International Symposium on Sustainable Energy and Environmental Protection (ISSEEP) 2009, pp. 23-26.
[6] Tristantini, D., 2009b. “H2-poor bio-syngas in Fischer-Tropsch Synthesis over un-promoted and Rhenium promoted-alumina supported cobalt catalysts: effect of water addition”, Asean Journal of Chemical Engineering, vol. 9(1), pp. 1-10.
[7] Tristantini, D., Logdberg, S., Gevert, B., Borg, ø., and Anders, H., 2006, “Direct Use of H2-Poor Bio-Syngas Model In Fischer-Tropsch Synthesis over Un Promoted and Rhenium-Promoted Alumina-Supported Cobalt Analysis”, Symposia of American Chemical Society Division of Fuel Chemistry 2006, ISSN : 521-48-48.
[8] Tristantini, D., Logdberg, S., Gevert, B., Borg, ø., and Anders, H., 2006. “Hydrocarbon Production via Fischer-Tropsch Synthesis From CO-Rich Syngas Over Different Co-Fe/Al2O3 Bimetallic Catalysts: The Effect of Water”, Proceeding of 12th Nordic Symposium on Catalyst. Trondheim, Norway.
[9] Liu, K., Song, C., Subramani, V., 2010, “Hydrogen and Syngas Production and Purification Technologies”, Wiley, USA, p. 121.
[10] Li, C., Wu, H., and Qyun, D.M., 2002. “Volatilisation and Catalytic Effects of Alkali and Alkaline Earth Metallic Species during the Pyrolysis and Gasification of Victorian Brown Coal, Part I, Volatilisation of Na and Cl from a set of NaCl-loaded samples”, Fuel, vol. 81, pp. 143-149.
[11] Rolin, A.C., Richard, G., Martin, and Deglise, X., 1983. “Influence of Catalysts on Gasification of Biomass at Short Residence Time”, Energy from Biomass, p. 901.
[12] Artanto, A.K., 2013. “Produksi Coal Char dari Batubara Lignit melalui Pirolisa dengan Variasi Pemanasan”, Skripsi, Departemen Teknik Kimia Universitas Indonesia, Depok.
[13] Wang, J., Jiang, M., Yao, Y., Zhang, Y., and Cao, J., 2009, “Steam Gasification of Coal Char Catalyzed by K2CO3 for Enhanced Production of Hydrogen Without Formation of Methane”, Fuel, vol. 88, pp. 1572-1579.
[14] Hill, C.G.J., 1977. “An Introduction to Chemical Engineering Kinetics and Reactor Design”, John Wiley and Sons, USA, pp. 5-23.
[15] Nevers, N., 1983. “Fluid Mechanics For Chemical Engineers”, 2nd Ed. McGraw-Hill, USA, pp. 1-76.
[16] Hanna, M. A., Kumar, A., and Jones, D. D., 2009. “Thermochemical Biomass Gasification: A Review of the Current Status of Technology”, Energies, vol. 2, pp. 556-581.
[17] Liao, S., Zhou, Y., and Yi, C., 2012. “Syngas Production by Catalytic Steam Gasification of Municipal Solid Waste in Fixed-Bed Reactor”, Energy, vol. 44, pp. 391-395.
[18] Wu, Y., Wang, J., Wu, S., Huang, S., and Gao, J., 2010. “Potassium Catalyzed Steam Gasification of Petroleum Coke for H2 Production: Reactivity, Selectivity, and Gas Release”, Fuel Processing Technology, vol. 92, pp. 523-530.
[19] Xiao, B., Feng, Y., Cheng, G., Wang, J., and Goerner, K., 2011.” Influence of Particle Size and Temperature on Gasification Performance inExternally Heated Gasifier,”, Smart Grid and Renewable Energy, vol. 2, pp. 158-164.
[20] Lee, W. J., Kim, S. D., and Song, B. H., 2002. “Steam Gasification of an Australian Bituminous Coal in Fluidized Bed”, Korean Journal Chemical Engineering, vol. 19(6), pp. 1091-1096.