Syngas Compositions And Kinetics Of South Kalimantan Lignite Coal Char Gasification With Steam

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Abstract. The aim of this research was to investigate the gasification of a South Kalimantan lignite coal char in the temperature range of 873-1073 ^{o}K and steam condition to evaluate the reactions rates and the product gas compositions. Prior to the gasification experiments the raw char was pyrolysed under nitrogen atmosphere and at a temperature of 673 ^{o}K. The gasification experiments were conducted in a fixed bed reactor, at atmospheric pressure, isothermal conditions, equipped with cooling system, gas reservoir, and temperature control. Char from coal pyrolysis weighed then gasified at variations of temperature. Gas sampling is done every 15 minutes intervals for 90 minutes. The reactivity study was conducted in the kinetically controlled by the heterogeneous reaction between solid carbon from the char and a gas phase reagent. Two theoretical models were tested to fit the experimental data and the kinetic parameters were determined. It was found that an increase in temperature enhances the reaction rate and also the formation of H_2, CO, CH_4, and CO_2. The results show that higher temperature contributes to more hydrogen production The gasification kinetics was suitably described by the Random Pore Model. Activation energy determination of char gasification reactions by using Arrhenius graph.

1 Introduction

1.1 Indonesian Coal

Coal is considered the cheapest and most widely abundant fossil fuel in the world (Kurt, 2008).Indonesia has the potential coal that potential enough.Total coal from Indonesia reserves is ± 28 Billion tons consisting of probable reserves ± 17 billion and proven reserves ±10 billion tons. In reserves, Indonesia has 3% of world reserves at 28 Billion of 948 Billion tons (Sihite, 2012). The world existing reserves are about 50% is low rank coal (LRC). In terms of world reserves, Indonesia has a 5% low rank coal reserves. For more practical and commercial means, LRC in this paper refers to Indonesia Government version Keppres No.13/2000:

- coal with high moisture content (>35%), and low calorific value (<5100 kcal/kg adb)
- coal rank lignit to sub bituminous C included

Total Indonesian LRCis 49.44% that spread in South Sumatera 38.01%, South Kalimantan 7.68%, East Kalimantan 3.75%. Coal gasifiction in Indonesia stipulated by Keppres No.5/2006. The inititative is to replace the use of natural gas by LRC. (Tirtosoekotjo,2006). Hydrogen is considered as the major energy carrier of the future, so an increase in the demand for hydrogen can be expected. Nowadays, there is increasing interest in lower cost fuels that can be used to produce mixtures of hydrogen and carbon monoxide by means of gasification.

1.2 Gasification Reaction

The most practical technologies for coal conversions and utilizations are carbonization, gasification and combustion (Speight, 2012). Coal gasification is process for converting carbon in coal by using a gasifying agent under restricted amount oxygen into fuel gas which consists hydrogen, carbon monoxide, carbon dioxide and methane. The coal gasification process is divided into two main steps ; pyrolysis and char gasification. Char gasification step is a controlling step for overall conversion process because its reaction rate is much slower than the pyrolysis step. As a result, kinetics of the char gasification step can provide a basic knowledge and crucial for a better understanding and a proper reactor design for the coal gasification proces (Molina, 1998, Bayarsaikhan, 2005).

Usually the following reactions are used in gasification (Highman, 2008) :

a. Boudard reaction :

$$C + CO_2 \leftrightarrow 2CO \quad + 172\ MJ/kmol \qquad (1)$$

b. Water gas reaction

$$C + H_2O \leftrightarrow CO + H_2 \quad + 131\ MJ/kmol \qquad (2)$$

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c. Methanation reaction

$$C + 2H_2 \leftrightarrow CH_4 \quad -75\ MJ/kmol \tag{3}$$

d. Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad -41\ MJ/kmol \tag{4}$$

1.3 Chemical reaction kinetic models

Since coal properties differ widely, kinetic data of coal gasification shoud be specific. The design optimization and operation require characterizing the reactivity and kinetics of char gasification. Char-steam kinetics have been widely investigated . Koba (1980) found that rates of steam gasification with lignite and bituminous coal were almost 2-5 times higher than gasification use CO_2.

Considering that the gasification is a single step reaction , the H_2O partial pressure is constant and the reaction rate (*dX/dt*) are expressed by Equation 5 (Jüntgen, 1983; Fermoso *et al*., 2009):

$$dX/dt = k(T)\,f(X) \tag{5}$$

where the temperature dependent term is the gasification rate coefficient, (*k*, 1/min), and *f(X)* is a structural term, related to the changes of coal char properties during the reaction. *k(T)* is expressed by means of the Arrhenius relation given by Equation 6,

$$k = A exp(-E_a/RT) \tag{6}$$

where *A* (1/min) is the frequency factor, *Ea* (kJ/mol) is the activation energy, *R* is the constant of gases (8.314 J/mol/K) and *T* (K) is the gasification temperature.

f(X) is provided by the *n*th-order model and in this work, two representative gas-solid models were applied in order to calculate the kinetic parameters.. These are known as single-step gas–solid kinetic models, which have received more attention in recent years.

The first model is the volumetric model (VM) or first order reactionThe Volumetric Model (V) is a simplified gas-char heterogeneous model, since it considers that the reaction is similar to a homogeneous reaction and that the surface area decreases with conversion (Wen, 1968; Ishida and Wen, 1971):

$$\frac{dX}{dt} = k_v(1 - X) \tag{7}$$

The second model is the random pore model (RPM), which was presented for the first time by Bhatia and Perlmutter (1980):

$$\frac{dX}{dt} = (1 - X)\sqrt{1 - \psi\, ln(1 - X)} \tag{8}$$

The Random Pore Model (RP) is the only one that contemplates structural changes in the coal char in the gasification process, by using the parameter Ψ (pore structure parameter) , it is expressed by:

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \tag{9}$$

Where S_o, L_o, ε_0 represent the initial pore surface area, pore length, and porosity

2 Methodology

2.1 Proximate and Ultimate Analysis

Coals samples from South Kalimantan were used in this study. Proximate analysis (ash, volatile matter and fixed carbon) was determined according to the standard ASTM E-1131. It is the simplest means of characterization of coal leading to its evaluation in respect of its quality, rank and type, and in turn broadly indicating its suitability for a particular mode of use. The analysis is done on air dried sample of coal. Ultimate analysis is expressed in terms of percentages of C, H, N, S and O. The elements C, H, N and S are being determined while O is obtained by difference. Ultimate analysis (C, H, N, S and O) and calorific values were determined according to the standards ASTM D-5373 and ASTM D-2015,

Table 1. Proximate analysis of lignite coal

Analytical parameter	Result (%) dry base
moisture (%)	37,743
ash (%)	2,071
volatile matter (%)	24, 656
fixed Carbon	35,530
calori (kal/g)	4303,203

Table 2. Ultimate analysis of char from lignite coal

Analytical parameter	Result (%) dry base
carbon (% adb)	65,70
hidrogen total (% adb)	4.12
nitrogen (%adb)	1,06
sulphur total (%adb)	0.27

2.2 Pyrolisis

The coal sample was grounded, sieved and devolatilised in a fixed bed reactor heated by an electric furnace . Conditions applied during pyrolysis heating rate of 20 ^oC/min up to the final temperature of 450 ^oC and residence time of 90 minutes. The resulted chars were cooled down under a flow of nitrogen to room temperature. Chars from low-temperature pyrolysis of lignite coal below 450 °C were more reactive than higher temperature chars (Meng, 2014).

2.3 Surface area measurement and SEM

Porous structure analysis was carried out in liquid N_2 and at 78 K, and surface areas were calculated using the BET method. BET theory introduces the concept of multimolecular layer adsorption of adsorbate on adsorbent. The fundamental assumption of this theory is that the forces active in the condensation of gases also are responsible for the binding energy in multimolecular adsorption. Convention has established that the quantity of gas adsorbed is expressed at S.T.P and the pressure is expressed as a relative pressure (P/P0) which is the actual gas pressure P (mmHg) divided by the saturation

pressure P0 (mmHg) of the adsorbing gas at the analysis temperature.

Table 3. BET analysis of char from lignite coal

Parameter	Result		Methode
Surface area	5,610	m^2/g	SAA
Pore volume	$19,175x10^{-3}$	Cc/g	SAA
Pore radius	68,358	Angstrom	SAA

The changes in char morphology was investigated using scanning electron microscopy (SEM). the image shows lignite char coal pyrolysis results at a heating rate of 20 ^oC / min until it reaches temperature of 450^oC and held for 90 minutes. The pore holes appear on the char

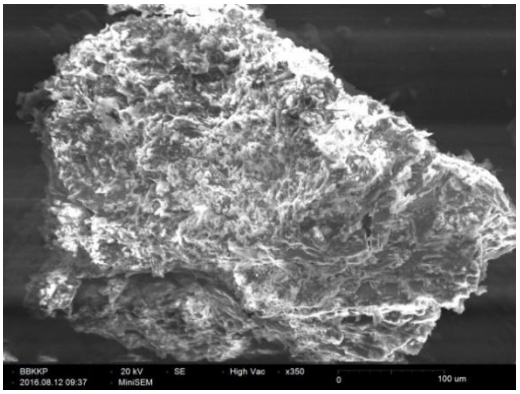
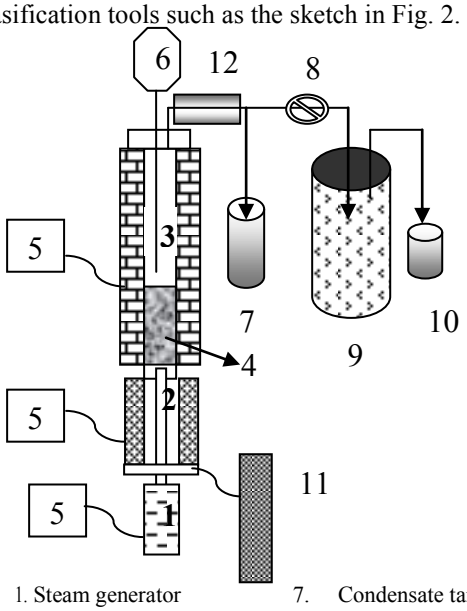


Fig.1. Micro photograph with 350 magnification showing the pores on the char

2.4 Gasification

The charcoal to be gasified is weighed as much as 10 grams each time the gasification is carried out using steam carried out on the fixed bed reactor. a series of gasification tools such as the sketch in Fig. 2.



1. Steam generator
2. Super heated steamer
3. Gasification reactor
4. Char coal
5. Power Reguletor
6. Thermocoupel
7. Condensate tank
8. Sampling gas
9. Gas reservoir +water
10. Water reservoir
11. Nitrogen
12. Conndenser

Fig, 2. The schematic of the experimental apparatus

Before gasification begins, it is done flushing using a nitrogen stream. The pressure used in gasification is 1 atmosphere. The steam was discharged in the reactor after the gasification temperature was reached and the gas loading resulting from the reactor was carried out after 15 minutes of 5 ml and fed into the tube which then analyzed the gas composition offline using gas chromatography equipment (Figure 3).

The data generated during the gasification takes place is the amount of gas volume that is collected from the gasification result measured by the addition every 15 minutesA gas analyzer, which can determine the instantaneous contents of CO, CO_2, CH_4, and H_2.

Fig. 3. Gas Chromatography

The result data from the GC tool is the calculation of peak area which is then converted to concentration. The concentration is then used to calculate the number of moles of each gas in each gas volume

3 Result and discussion

3.1. Volume and composition syngas

The gasification reaction is an endothermic reaction, so an increase in temperature will be accompanied by gas formation, it is apparent in an increase in the amount of gas formed each time shown in Figure 4. The resulting gas volume is strongly influenced by the operating temperature of the gasification, which at a temperature of 800 ^oC produces volume more gas at the same time. At a 90 minute observation resulted in a volume of 15,900 ml of gas at a temperature of 800 °C, 12,150 ml at a temperature of 700 °C and 9,150 ml at a temperature of 600 °C

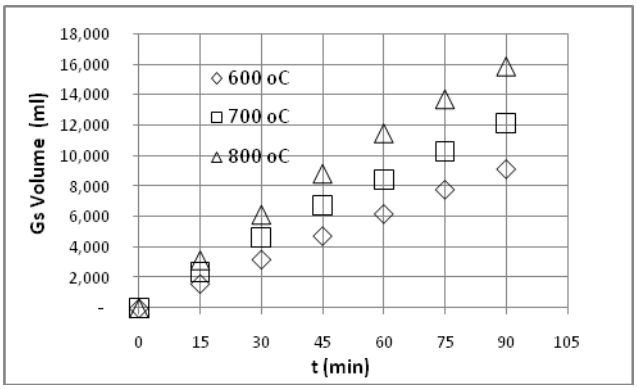


Fig. 4. Gas release rates during the steam gasification of char under 600 ºC,700 ºC,800 ºC,1 atm pressure.

The gas formation is due to the reaction between steam and charcoal, it appears in the reduction of the amount of charcoal weighed at each end of the gasification. The charcoal used in gasification is shown in Table 4.

Table 4. The amount of char used in the gasification

Temperature(°C)	Char (gram)		
	Before	after	used
600	10	7.2936	2.7064
700	10	6.3592	3.6408
800	10	5.3452	4.6548

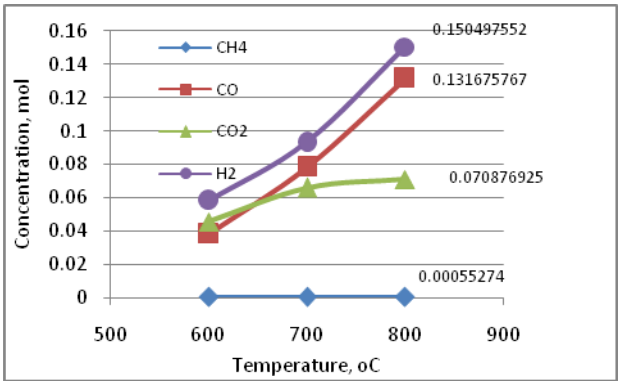


Fig. 5. Gas concentration under different temperature

The Fig. 5 show the tendency of increasing gasification temperature will result in higher H_2 gas that is at temperature of 800°C with concentration reach 15,0497%. At a temperature of 600 °C indicates the amount of CO_2 gas is higher than CO gas but at a temperature of 700 °C and 800 °C CO_2 concentration begins to decrease. The amount of mole concentration of methane gas formed in very small amounts under all conditions of temperature.

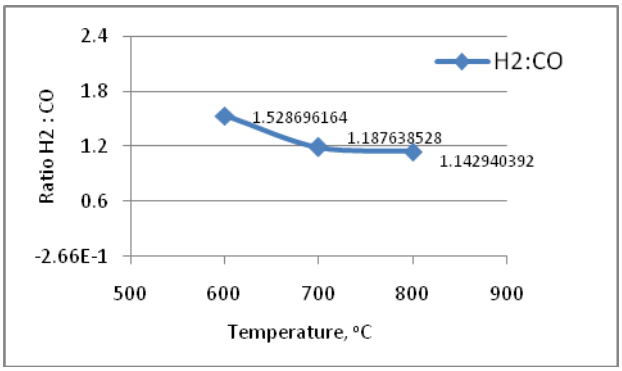


Fig. 6. Ratio H_2/CO under different temperature

At temperature of 600°C producing a ratio of H_2/CO greater than the temperature of 800°C, but the volume of gas produced is lower. Synthesis gas with a stoichiometric ratio (H_2/CO) at 2 or ranging from 1 to 2 is generally used in major synthesis-gas-based chemicals production.

3.2 Char conversion

Carbon conversion was calculated based on moles of CO, CO_2, and CH_4 by using Eq. (10) as follows:

$$X_{char} = \frac{n_{CO}+n_{CO_2}+n_{CH_4}}{n_{C_{char}}} \; x\,100\% \qquad (10)$$

The carbon conversion profiles for the gasification experiments of the coal char are shown in Figure 4. From Fig.7it can be seen that the carbon conversion will increase by time significantly. The final carbon conversion at gasification temperature of 600 ºC, 700 ºC, and 800°C are 15.42%, 26.47%, and 37.10% respectively. This indicates that temperature is the factors that can increase conversion reaction. In higher temperature, the kinetic energy of molecules will also be greater so that collisions among molecules become more frequent and this causes the reaction occurs faster.

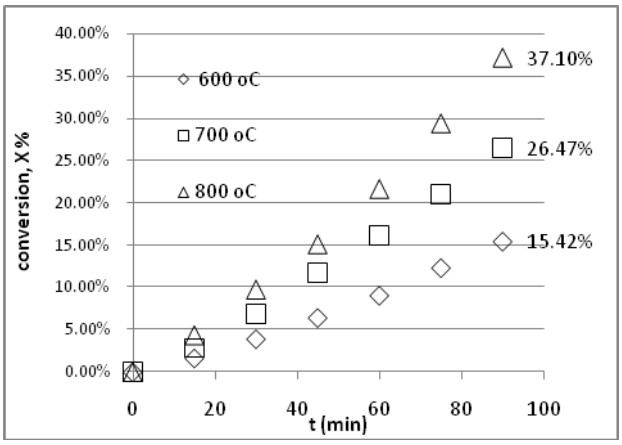


Fig. 7. Carbon conversion for 90 minutes

3.3 Validation of the RPM and Volumetric

The kinetic measurements from this research were tested. The conversion time data for each run were fitted

against the Random Pore Model (RPM) and Volumetric Model. The curve fitting method is used in which the value of Sum of Square of Error (SSE) is minimized.

$$SSE = \sum_{i=1}^{m} \left(\frac{X_{data} - X_{calculate}}{X_{data}} \right)^2 \quad (11)$$

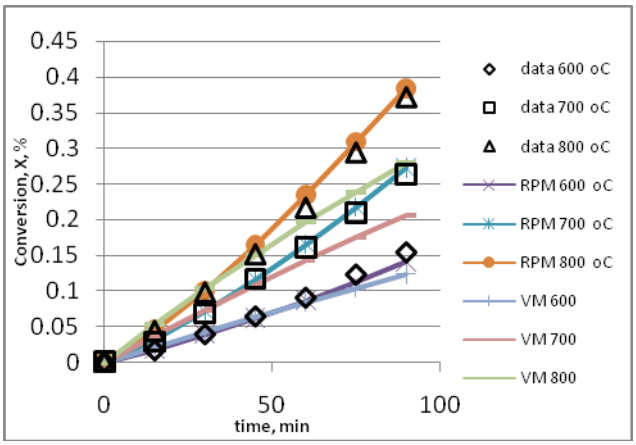


Fig. 8. Comparison betwen measured conversion carbon data with RPM and VM

On the graph shows the value of the data more appropriately approximated by RPM.Calculations using RPM have smaller SSE than using VM. Therefore, the next kinetic parameter calculation uses the RPM approach.

3.4 Calculation of the Kinetic Parameters by Random Pore Model

The Arrhenius plot is a relationship between the apparent rate and its reaction temperature (1/T), and therefore , it can be used to calculate the apparent activation energy (E) as illustrated in Figure 9. From this Arrhenius's plot, the activation energies is observed (Table 5),

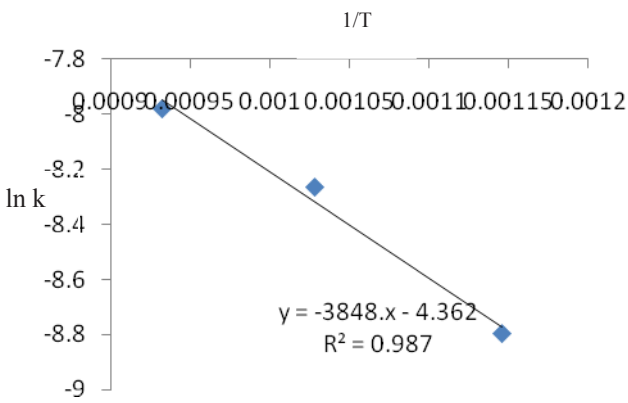


Fig.9. Arrhenius Graph Constant Model RPM

Table 5. Arrhenius constant and parameters on the RPM approach

T	k_{RPM}	SSE	A	E/R	E, kJ/mol
600	0.0151	3.249942%	0.01275	3848	31.9923
700	0.02576	2.77679%			
800	0.03424	2.17269%			

The activation energies is similar with Turkish coal (30,8 kJ/mol) and Indian coal (32 kJ/mol) that calculated by Jayaraman (2013) . Coals from India and Turk have been investigated in the TGA apparatus at a temperature range of 25-1250°C with heating rates of 35 and 45 K/min.

4 Conclusion

The properties of lignite from South Borneo are suitable for applications such as for gasification utility. The char was gasified under steam temperature 600°C , 700°C and 800°C show that the temperature dependence of the reaction .

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