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The Effect of Temperature and Addition of CaO to Hydrogen Production from Pattukku Coal Char Gasification

Takdir Syarif[1,2,✉], Hary Sulistyo[2], Wahyudi Budi Sediawan[2], Budhijanto[2]

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[1]Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Muslim Indonesia
Jl. Urip Sumoharjo Km. 05 Makassar
[2]Department of Chemical Engineering, Faculty of Engineering, Universitas Gadjah Mada
Jl. Grafika 2 Yogyakarta 55281

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Abstract

Hydrogen is an environment-friendly fuel and has a high caloric value. Hydrogen as a molecule is not found in nature, but it is found in compounds with other elements. Besides catalytic steam reforming of natural gas, hydrogen can also be produced from thermochemical processes such as combustion, pyrolysis, and gasification. The process of gasification using steam as gasification agent can increase the yield of H_2 in the gas products. The objectives of this research are to study the influence of temperature and the addition of CaO on H_2 production. This research was conducted in an up-draft reactor for 60 minutes with three different temperatures; i.e. 600, 700, and 800 ºC and ratio of CaO:char of 0 and 0.5. Based on this study, the rise of temperature will improve the yield of H_2 and CO_2 in the gas products. At gasification temperature of 800 ºC, the yield of H_2 and CO_2 is maximum. Moreover, the addition of CaO can improve the char conversion and reduce the concentration of CO_2 in the gas products.

INTRODUCTION

As fossil fuel reserves depleted, the development of alternative energy becomes very important to prevent energy crises (Liu et al., 2010). Hydrogen is one of the most promising alternative energy sources. Hydrogen has a high heating value and is also called clean energy. Hydrogen does not exist freely in nature but is generally present in the form of compounds with other elements such as carbon in methane (CH_4), coal and petroleum (Moulijn et al., 2013; Florin & Harris, 2007).

Hydrogen can be made in several methods, including gasification. Gasification is a thermal process for converting solid materials containing carbon into fuel (Basu, 2010). Reactions in the gasification can be divided into five types: boudouard reaction, water-gas reaction, methanation reaction, shift conversion, and steam reforming. The equation of the reaction is as follows (Bell et al., 2011):

Boudouard reaction
$C+CO_2 \Leftrightarrow 2CO \quad \Delta H^o_{rx} = 172.58$ kJ/mol (1)
Water gas reaction
$C+H_2O \Leftrightarrow CO+H_2 \quad \Delta H^o_{rx} = 131.38$ kJ/mol (2)
Methanation reaction
$C + 2H_2 \Leftrightarrow CH_4 \quad \Delta H^o_{rx} = -74.90$ kJ/mol (3)
Shift Conversion
$CO+H_2O \Leftrightarrow CO_2+H_2 \quad \Delta H^o_{rx} = -41.98$ kJ/mol (4)
Steam reforming
$CH_4+H_2O \Leftrightarrow CO+3H_2 \quad \Delta H^o_{rx}=206$ kJ/gmol (5)

✉Corresponding author:
Department of Chemical Engineering, Faculty of Industrial Technology,
Universitas Muslim Indonesia, Jl. Urip Sumoharjo Km. 05 Makassar
E-mail: takdir_syarif@umi.ac.id

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In the process of gasification, coal or char is reacted with a gasification agent such as air, oxygen, steam, or CO_2. The composition of the gas formed depends on the operating conditions and the gasification agent. Air is a source of cheap raw materials. However, its use as a gasification agent will produce gas that has a low heating value of about 4-7 MJ/Nm^3. This is because N_2 from the air will reduce the concentration of the gas (Basu, 2010; Bell et al., 2011). Oxygen can be used as the gasification agent replaces the air to eliminate the influence of N_2 in the gas products. The gas produced will be dominated by the CO and CO_2 as well as have a high thermal value i.e. approx. 12-28 MJ/Nm^3 (Basu, 2010). The use of air or oxygen produces gas with low H_2 concentrations (Li et al., 2014).

The gasification process using steam will produce gas that has a high H_2 content and CO (Bell et al., 2011). The reaction between CO gas with H_2O (Eq. (4)) is exothermic so that it can become a provider of energy in the gasification process. The reaction between CO gas and H_2O also produces CO_2 gas that can reduce the concentration of H_2 in the product gas. To increase the concentration of hydrogen in the product gas, it is recommended the use of CO_2 adsorbent (Balasubramanian et al., 1999). The CO_2 adsorption reaction equation by CaO is as follows:

$$CaO+CO_2 \Leftrightarrow CaCO_3 \quad \Delta H^o_{rx} = -178.3 \text{ kJ/mol} \quad (6)$$

The use of a calcium-based adsorbent such as Ca $(OH)_2$ and $CaCO_3$ have been widely used in gasification processes (Madhukar & Goswami, 2007; Guoxin & Hao, 2009). Other than as an absorber, CaO can also significantly increase the reaction conversion (Sobah et al., 2013; Murakami et al., 2015) and alter the direction of equilibrium (Guoxin et al., 2008).

Limestone is a mineral rock that is widely available in Indonesia. The largest component found in limestone is calcium carbonate ($CaCO_3$) which is above 92%. The high content of calcium compounds and the relatively cheap causes these rocks have the potential to serve as the raw material for CO_2 absorbers in the gasification process. Before being used as a CO_2 absorbing agent, limestone is calcined first to convert $CaCO_3$ to CaO.

To study the potential utilization of limestone as the absorber material, conducted research that aims to find out the influence of the temperature and the addition of CaO against yield of hydrogen on gasification of Pattukku coal char.

RESEARCH METHODOLOGY

Raw Materials and Research Apparatus

The raw materials used are Pattukku coal obtained from the district of Bone South Sulawesi. This coal is low-rank coal with high sulfur content. The results of proximate analysis of raw materials can be seen in Table 1. Other raw materials used are N_2 gas (95%) obtained from U.P. Sumber Agung Sukses (SAS) Yogyakarta, steam, and CaO.

Table 1. Proximate analysis results of Pattukku coal

Volatile matter (% w)	Fixed Carbon (% w)	Moisture (% w)	Ash (% w)
38.28	47.92	4.70	10.80

Calcination Process

Two hundred of crushed limestone is placed on a ceramic plate then put into the furnace. The furnace is then turned on and the furnace temperature is set to 900 °C and the process was held for two hours. Calcined limestone is then analyzed its CaO concentration using EDX-8000 (Energy Dispersive X-ray Fluorescence Spectrometer). The results of the CaO content analysis are presented in Table 2.

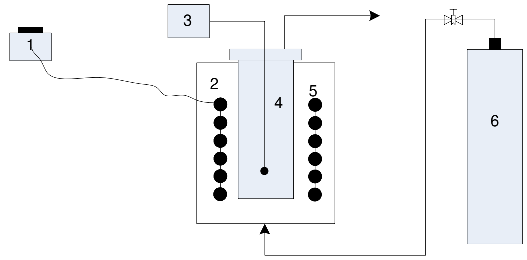
Table 2. Result of CaO analysis

CaO (%)	SiO_2 (%)	Al_2O_3 (%)	SO_3 (%)	Impurities (%)
94.012	2.814	1.59	1.013	0.571

Pyrolysis

The pyrolysis process is carried out in a tubular reactor (3.5 cm diameter and 55 cm high) at 450 °C and 1 atm pressure. A schematic diagram of the pyrolysis equipment is shown in Figure 1.

Fifty grams of Pattukku coal with a diameter of 3.35-4 mm are fed into the reactor. The air inside the reactor was removed by flowing the nitrogen from the bottom of the reactor for 15 minutes. The reactor is then heated using an electric heater (furnace) until it reaches a temperature of 450 °C. After the operating temperature is reached, the temperature controller is switched on and the isothermal process is run for 60 minutes. Char then analyzed using ultimate analysis. The results of the ultimate analysis are presented in Table 3.



1. Regulator
2. Isolator
3. Thermocoupel
4. Reactor
5. Heater
6. Nitrogen Tank

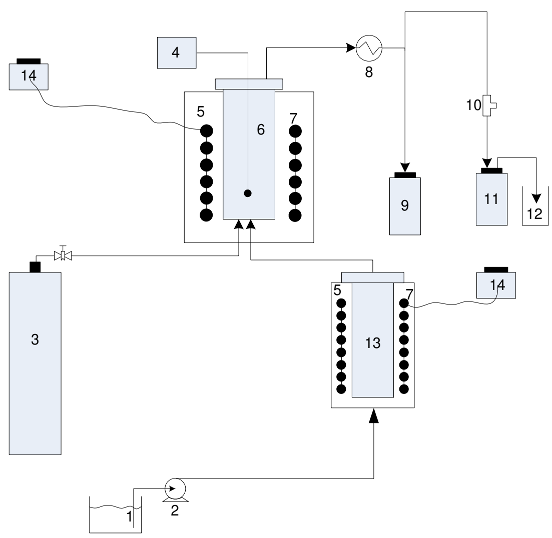
Figure 1. The schematic diagram of the pyrolysis apparatus.

Table 3. Ultimate analysis result

C (%)	H (%)	O (%)	N (%)	S (%)
68.93	2.99	24.39	1.81	1.88

Gasification

The reactor used in the gasification is an up-draft reactor with a height of 45 cm and a diameter of 3.5 cm. A schematic diagram of the pyrolysis equipment is shown in Figure 2.



1. Water Tank
2. Pump
3. Nitrogen Tank
4. Termocouple
5. Heater
6. Reactor
7. Isolator
8. Condensor
9. Condensate tank
10. Sampling gas
11. Water tank
12. Water rservoir
13. Boiler
14. Regulator

Figure 2. The schematic diagram of the gasification apparatus

One Hundred grams of char is fed into the reactor. The nitrogen was flowed from under the reactor to remove the air present in the reactor. The reactor was heated by using an electric heater to raise the temperature of the reactor. After the desired reaction temperature was reached, steam was passed from under the reactor to be reacted with the char present in the reactor. This process takes place at a constant temperature (isothermal) for 60 minutes. The non-condensed gas product was collected continuously in a tank containing water after it passed through the condenser. After the process is complete, samples were taken using syringe to analyze the gas composition using gas chromatography (GC) Shimadzu GC 2010 while the volume of gas produced was calculated based on the amount of water coming out from the gas reservoir.

To study the effect of temperature and CaO addition on hydrogen gas production, an experiment conducted with temperature variation i.e. 600, 700 and 800 °C) and ratio of CaO: char i.e. 0 and 0.5.

Method of Analysis

As much as 200 µL gas sample was injected into a port injector that has been preheated to a temperature of 40 ° C. The samples are then flowed to a packed column of 60 °C by the carrier gas. In the columns, the constituent components of the gas will be separated. One by one the gas component exits the column toward the thermal conductivity detector (TCD). The detection result is then recorded by the recorder (chromatogram). The number of peaks present in the chromatogram shows the amount of gas components present in the sample while each of the peak area represents the composition or quantity of the gas component. The value of each gas composition is obtained by comparing the peak area of the sample gas component with the standard peak gas area. The gas components analyzed include CH_4, CO, H_2, and CO_2.

Calculation of Yield Gas and Carbon Conversion

Yield gas for each gram of char is obtained by dividing the total gas volume (mL) produced after the gasification process with the initial mass of sample (g).

$$Yield\left(\frac{mL}{g}\right) = \frac{Vgas}{mc} \qquad (7)$$

The carbon conversion is calculated by the equation:

$$\eta_C = \frac{nCH_4 + nCO + nCO_2}{n_C} x100\% \quad (8)$$

where n_{CH4}, n_{CO}, n_{CO2} are the mol of each gas component, whereas n_C is mol C in the initial sample.

RESULT AND DISCUSSIONS

Effect of Temperature

The composition of each component present in the gas product and the yiels of gas at various temperatures is presented in Table 4. While for the compositions of each component is the gas product as shown in Figure 3.

Table 4 shows that the gas yield increases with increasing temperature. The gas yield at 600 °C was 29.3 mL/g and rising to double that at a temperature of 700 °C, (33.6 mL/g). Significant increase occurred at temperatures of 800 °C i.e. 137.1 mL/g or about six times compared to the yield of gas obtained at a temperature of 600 °C. Conversion of carbon also increased. The carbon conversion rises by 1.5 times when the temperature is raised from 600 to 700 °C and becomes doubled when the temperature rises from 600 to 800 °C. The same trend is also shown from the results of research conducted by Madhukar and Goswami et al (2007). The results of both researchers showed that the conversion has increased by 1,3 times when the reaction temperature is increased from 500 to 600 °C.

Table 4. Gas compositions, Yield of gas, and carbon conversion without CaO

Temp. (°C)	Gas Composition (%)				Yield (mL/g)	η_C (%)
	CH_4	CO	H_2	CO_2		
600	1.3	71.4	3.1	24.2	29.3	2,02
700	0.6	31.6	34.2	33.6	62.9	2,95
800	0.3	14.2	62.6	22.9	166.4	4,43

The increase in gas yield and carbon conversion are caused at high temperatures, the kinetic energy of the particles will increase and the collision energy between the particles will be greater so that the reaction will take place more quickly. Increased carbon conversion is also caused by the reaction between carbon (C) and steam (H_2O) is an endothermic reaction. Under the Le Chatelier principle, when the temperature system is raised, the response of the system will lower the temperature. As a result, the reaction will shift toward a reaction that absorbs heat (endotherms). Thus, when the temperature is increased, the reaction conversion will increase so that the gas yield will increase. At high reaction temperatures and in the presence of steam will lead to greater reactivity of the char so that the gas that will form more and more (Madhukar & Goswami, 2007).

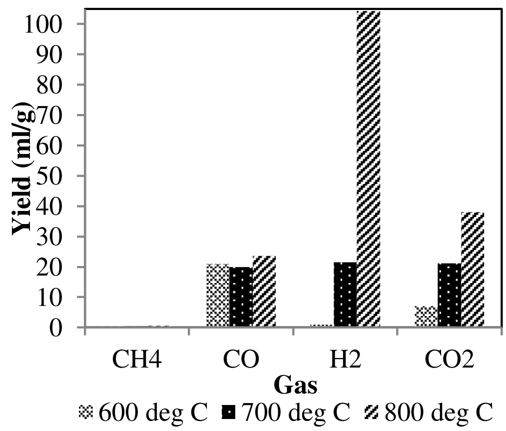


Figure 3. The effect of temperature on the yield of each gas component (without the addition of CaO)

Figure 3 shows the effect of temperature on the gas yield of each component for treatment without the addition of CaO. From Figure 3 it shows that the higher the temperature, the higher the yield of H_2 and CO. The rise in temperature from 600 to 800 °C resulted in the yield of CO gas rising from 21 mL/g to 24 mL/g, while the yield of H_2 increased from 1 mL/g to 104 mL/g. This is because the reaction of H_2 and CO formation is an endothermic reaction so that with higher temperature, the reaction will lead to the formation of the product (Luo et al., 2009; Wei et al., 2007; Madhukar & Goswami, 2007).

The increasing trend of composition and the yield of H_2 in the gasification process has also been reported by Madhukar & Goswami (2007). In their study, pine bark gasification is carried out with temperature variations of 500, 600, and 700 °C. From the results of this study obtained that the composition and the yield of H_2 rise along with rising temperatures.

Figure 3 also shows an increase in CO yield, but the increase is not significant compared to an increase of CO_2. This is because some CO reacts with H_2O to form CO_2 and H_2 in the gas phase based on Equation (1) (Luo et al., 2009).

Figure 4 shows the effect of temperature on the yield of CH_4. Figure 4 shows the yield of CH_4 is very small compared to the other gas components. This is because the reaction between char and hydrogen to form methane is very slow (Walker et al., 1959). The yield of CH_4 is also seen to decrease. This decrease is due to the reaction of methane decomposition by steam (equation 5) is an endothermic reaction, where if the temperature of the system is raised, the reaction will shift toward the formation of the product.

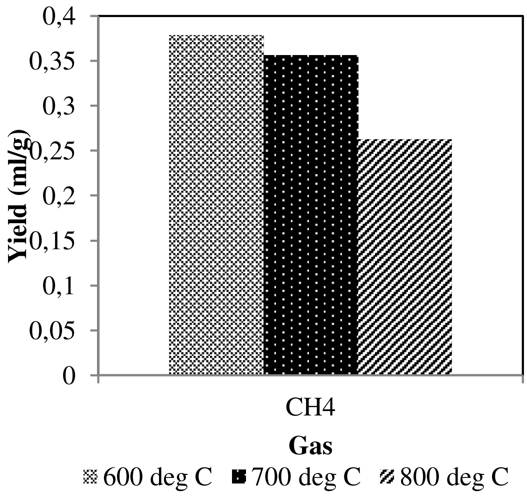


Figure 4. The effect of temperature on the yiel of CH_4 (without the addition of CaO)

Effect of CaO Addition

Table 5 shows that the yield of gas increased significantly. Comparing the yield in tables 4 and 5 shows that at a temperature of 600 °C the yield increased about 38.6% (from 29.3 to 47.7 mL/g). At a temperature of 700 °C, the yield increased about 52.6% (from 62.9 to 96.0 mL/g), whereas at 800 °C the yield increased significantly by approximately 146.2% (from 166.4 to 409.6 mL/g). Table 5 also shows an increase in char conversion. Conversion of char increased about 1.5 times at 600 °C (from 2.02 to 3.1%), 1.7 times at 700 °C (from 2.95 to 5.2%) and 1.9 times at temperature 800 °C (from 4.43 to 8.2%).

Table 5. Gas compositions, Yield of gas, and carbon conversion with the addition of CaO

Temp. (°C)	Gas composition (%) CH_4	CO	H_2	CO_2	Yield (mL/g)	η_C (%)
600	7.3	68.8	9.9	14.0	47.7	3.1
700	4.5	48.3	24.6	22.6	96.0	5.2
800	0.7	19.6	72.0	7.7	409.6	8.2

Figure 5 shows the effect of temperature on the yield of each component at various temperatures with the addition of CaO. Comparing the results in Figure 3 and Figure 5 shows that each gas (other than CO_2) increases with the addition of CaO. At temperatures of 800 °C, CH_4, CO, and H_2 increased about 441.8%, 239.8% and 183.2% respectively while CO_2 decreased about 7.4%.

The increase in reaction conversion due to CaO addition can be explained by the following water-gas reaction mechanisms as follows:

$$C+2H_2O \Leftrightarrow CO_2+2H_2 \quad \Delta H^o_{rx} = 100 \text{ kJ/mol} \qquad (9)$$

The addition of CaO in the gasification process will absorb the CO_2 formed so that the partial pressure of the product will drop and the system will shift the direction of the reaction to the formation of the product. The carbonation reaction (equation 6) is an exothermic reaction which will cause an increase in temperature inside the reactor. Rising temperatures will cause the endothermic reactions to take place more rapidly and encourage reactions toward the formation of the product so that the conversion of the reaction will increase and also will increase the yield of H_2. The addition of CaO will increase the reaction rate and absorb CO_2 so that the yield of each gas increases (Sobah et al., 2013; Murakami et al., 2015). The same results were also shown by some previous researchers (Madhukar and Goswami, 2007; Guan et al., 2007; Wei, 2008; Wang et al., 2006).

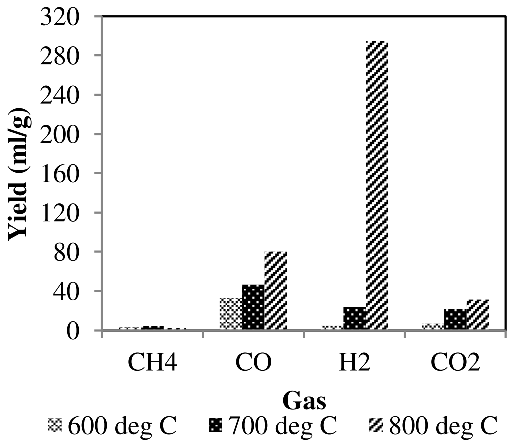


Figure 5. The effect of temperature on the yield of each gas component (withthe addition of CaO)

In the $C/H_2O/CaO$ gasification system, the carbonation reaction is a key step, not only for CO_2 adsorption but also for the enthalphy balance in the gasifier (Wang et al., 2006). The relationship between the pressure equilibrium of CO_2 (P_{eq, CO_2})

and the temperature in the carbonation process can be expressed in terms of the following empirical equations (Abanades et al., 2003):

$$\log_{10} P_{eq}(atm) = 7{,}079 - 8308/T(K) \qquad (10)$$

where Peq is the pressure equilibrium of CO_2 (atm) and T is temperature (K). From Equation (9) we can graph the relationship of Peq versus T as follows (Madhukar & Goswami, 2007).

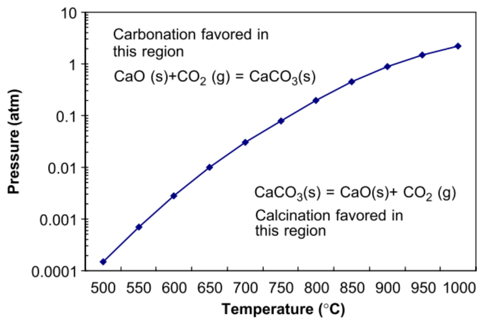


Figure 6. Partial pressure of CO_2 as a function of temperature

Table 4 shows that at 600 °C, the concentration of CO_2 is 24.2%. When the gasifier operating pressure is 1 atm, the partial pressure of CO_2 at that temperature is 0.24 atm. Based on these results, the CO_2 partial pressure exceeds the CO_2 equilibrium pressure at 600 °C so that when gasification with CaO addition is carried out at this temperature there will be CO_2 adsorption.

CONCLUSION

Hydrogen is one of the alternative sources of energy that are environmentally friendly. The production of hydrogen through the gasification process can be increased by absorbing CO_2 present in the product gas. From the results of this study can be concluded that:

1. Rising reaction temperature will increase reaction conversion and the yield of H_2. A significant yield of H_2 occurs at a temperature of 800 °C.
2. The use of CaO can increase the conversion of the reaction and decrease the concentration of CO_2 thus increasing the concentration of H_2 in the gas product.

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