Thermochemical Equilibrium Modelling of Steam Gasification of Char From Pattukku Coal Using Cao as Co_2 Absorbent

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

[1]Chemical Engineering Study Program, Faculty of Industrial Technology, Universitas Muslim Indonesia Jl. Urip Sumoharjo KM. 05, Kampus II UMI, Makassar
[2]Chemical Engineering Department, Engineering Faculty, Universitas Gadjah Mada Jl. Grafika 2, Yogyakarta
Email: takdir_syarif@umi.ac.id

Abstract : Although it is not able to provide highly accurate results, mathematical models can provide guidance regarding the quantitative influence of design, raw material, and other operating parameters. In addition, the representation of gasification in the form of mathematical equations can help understand the importance of the influence of operating parameters on the performance of a gasifier and can give a good understanding of the mechanisms that occur. In this paper, the steam gasification of char from Pattukku coal using CaO as CO_2 absorbent in updraft gasifier was investigated. The aim is to determine the influence of temperature on syngas composition. A mathematical model based on the stoichiometric approach was developed in this study and the results were compared with experimental data. A mixture of coal and lime (CaO) with a ratio of 1:1.5 is fed into the reactor. The electric heater (furnice) is turned on to raise the temperature of the reactor until it reaches the desired reaction temperature (i.e. 600, 700, and 800 ^oC). When the reaction temperature is reached, steam was flowed from the bottom of the reactor to be reacted with the char present in the reactor. The steam gasification carried out at a fixed temperature for 60 minutes and every 15 minutes, samples were taken for analysis. Base on the result of the experimental and calculation showed if the temperature of gasifier increase by 100 ^oC, the volume of gas will increase by approximately 1.7 time. The calculation showed that the proposed model could quantitatively be applied to predict the gas composition of steam gasification of char.

Keywords: CO_2 absorbent, mathematical models, steam gasification, syngas composition, updraft gasifier.

1. Introduction

Combustion is one of the commonly used methods of coal utilization. Coal is usually burned in the form of powder or briquette. In the combustion process, coal is reacted with excess air to produce energy. The energy is then used for various purposes for example to produce steam in the boiler contained in the Steam Power Plant (PLTU). The coal combustion process not only produces energy but also produces polluting compounds such as NOx, SOx, and Volatile Organic Compounds (VOCs) that can pollute the environment.

Gasification is most efficiency compared than the other thermal process such as liquefaction, pyrolysis, and combustion. This process can convert solid fuels containing carbon into synthesis gas. The syngas is appropriate for use in transportation, manufacture of chemicals, electricity production. Gasification is a complex process, so in design and operation required an understanding of the influence of raw material and other operating parameters. For it takes a mathematical equations or modeling that can be used to perform the optimization process parameters Although it is not able to provide highly accurate results, mathematical models can provide guidance regarding the quantitative influence of design, raw material, and other operating parameters. In addition, gasification process representation in the form of mathematical equations can help understand the importance of the influence of operating parameters on the performance of a gasifier and can give you a good understanding of the mechanisms that occur.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

Until now, some researchers have published various theoretical and experimental works on the process of gasification. The main objective is to study the thermochemical process during the gasification and evaluate the effect of several variables such as the water content, raw material types and the operating conditions of the gasifier. Some researchers only focus at the final composition of gas. Gasification takes place at a high temperature so that the gas is considered to be at equilibrium. Therefore, the thermodynamic approach is considered the most appropriate. The thermodynamic equilibrium model can be developed with two approaches, stoichiometric and non stoichiometric models. The stoichiometric model is a model developed based on the chemical equilibrium constants approach. This method requires knowledge of the chemical reactions that occur as well as the flow of the reaction. This means that appropriate reaction and information about the value of equilibrium constants is needed. While the non stoichiometric model is a model that involves the minimization of Gibbs free energy. This model does not take into consideration the mechanism of the reaction to be an effective tool for calculating the gas composition when the direction of the reaction is unknown. Some researchers have used thermodynamic equilibrium models to predict the composition of gases. Using the thermodynamic model to predicted the syngas composition from biomass gasification in downdraft gasifier. Has developed the thermodynamic model for steam gasification of biomass in fluidized-bed gasifier.

In this paper, the steam gasification of char from Pattukku coal using CaO as CO_2 absorbent in updraft gasifier was investigated. The aim is to determine the influence of temperature on syngas composition. A mathematical model based on the stoichiometric approach was developed in this study and the results were compared with experimental data.

2. Themodynamic Equilibrium Model

The thermodynamic equilibrium model is developed based on the reaction that occurs during gasification. To use this model, knowledge of the reaction that occurs is needed. [1] reactions that may occurs in the process of gasification can be divided into four types i.e. water-gas reaction, boudouard reaction, shift conversion and methanation.

R1: Boudouard reaction: $C + CO_2 \Leftrightarrow 2CO$ $\Delta H^o_{rx,298K}$ = 172,58 kJ/gmol (1)
R2: Water gas reaction: $C + H_2O \Leftrightarrow CO + H_2$ $\Delta H^o_{rx,298K}$ = 131,38 kJ/gmol (2)
R3: Methanation reaction: $C + 2H_2 \Leftrightarrow CH_4$ $\Delta H^o_{rx,298\ K}$ = -74,90 kJ/gmol (3)
R4: Shift Conversion: $CO + H_2O \Leftrightarrow CO_2 + H_2$ $\Delta H^o_{rx,298\ K}$ = -41,98 kJ/gmol (4)

When in the gasification process added lime, CaO in lime will absorb the CO_2 present in the gas results. The equation of CO_2 absorption can be written as follows:

R5: CO_2 absoption: $CaO + CO_2 \Leftrightarrow CaCO_3$ (5)
From Eqs. (1-5), we can obtain the corresponding equilibrium constants to the mole fraction of each component as follows:

$$K_1 = \frac{y_{CO}^2}{y_{CO_2}} P \quad (6)$$

$$K_2 = \frac{y_{CO}\, y_{H_2}}{y_{H_2O}} P \quad (7)$$

$$K_3 = \frac{y_{CH_4}}{y_{H_2}^2} \frac{1}{P} \quad (8)$$

$$K_4 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{K_2}{K_1} \quad (9)$$

$$K_5 = \frac{1}{y_{CO_2}} \quad (10)$$

The Eq. (8) not use in the calculation because it can be calculated from Eqs. (5) and (6). Thus, the equilibrium constant of K_1 - K_3 and K_5 can be calculated using the equation as follows [17]

$$K_i = exp\left(K_{0i} + \frac{K_{1i}}{T}\right) \quad (11)$$

where A_i and B_i are parameters obtained from the simulation results. While the constraints used in this calculation is obtained from the mass balance of components as follows:

C: $N_C = n_{CO} + n_{CO_2} + n_{CH_4}$

$N_C = n_g(y_{CO} + y_{CO_2} + y_{CH_4})$ (12a)

H : $N_H = 2n_{H_2} + 4n_{CH_4} + 2n_{H_2O}$

$N_H = n_g(2y_{H_2} + 4y_{CH_4} + 2y_{H_2O})$ (12b)

O : $N_O = n_{CO} + 2n_{CO_2} + n_{H_2O}$

$N_O = n_g(y_{CO} + 2y_{CO_2} + y_{H_2O})$ (12c)

$\sum_{i=1}^{m} n_i = n_g = n_{H_2} + n_{CO} + n_{CO_2} + n_{CH_4} + n_{H_2O}$ (12d)

The equations used to predict the gas composition are obtained by rearranging Eqs. (6) - (8) and (10) as follows:

$f_1 = K_1\, y_{CO2} - P\, y_{CO}^2 = 0$ (13a)

$f_2 = K_2\, y_{H2O} - P\, y_{CO}\, y_{H2} = 0$ (13b)

$f_3 = K_3\, y_{H2}^2\, P - y_{CH4} = 0$ (13c)

$f_4 = K_4\, y_{CO2} - 1 = 0$ (13d)

The value of the equilibrium constant K_1 to K_4 is obtained from the calculation using Eq. (11). While the value of each parameters (K_{0i} and K_{1i}) on the Eq. (11) can be obtained by curve fitting in which the value of Sum of Square of Error (SSE) (Eq. 14) is to be minimized.

$$SSE = \sum_{i=1}^{k} \left(\frac{y_{data} - y_{cal}}{y_{data}}\right)^2 \quad (14)$$

Furthermore, Eqs. (13a) - (13d), (12a) - (12d), and (11) are solved by the Newton Raphson method combined with multi-variable optimization.

3. Experimental Setup

3.1. Preparation of Char

Two hundred grams of Pattukku coal is fed into a tubular reactor with a diameter of 3.5 cm and a height of 45. The pyrolysis was conducted at 450°C and 1 atm. To eliminate the existing air in the reactor, nitrogen gas was flowed from the bottom of the reactor before the process started. The experiment begin by turning on the electric furnace to heating the reactor. The process was carried out with a heating rate of 30 °C/minutes at fixed temperature (450°C). The temperature controller was turned on after the temperature reached 450 °C, and the isothermal process was held for 60 minutes. After that, the reactor was left until the temperature reached 30 °C. The elemental composition of ultimate analysis of the char and proximate analysis of the coal are presented in Table 1 and 2.

Table 1. Proximate analysis

Component	Composition (% wt/wt)
Volatile matter	38.28
Fixed carbon	47.92
Moisture	4.7
Ash	10.80

Table 2. Ultimate analysis

Component	Composition (% wt/wt)
C	68.93
H	2.99
O	24.39
N	1.81
S	1.88

3.2. Gasification Process

A mixture of coal and lime (CaO) with a ratio of 1:1.5 is fed into the reactor. Nitrogen was flowed from the bottom of the reactor for 15 minutes to remove air from the reactor before the process started. The electric heater (furnice) is turned on to raise the temperature of the reactor until it reaches the desired reaction temperature (i.e. 600, 700, and 800 °C). When the reaction temperature is reached, steam was flowed from the bottom of the reactor to be reacted with the char present in the reactor. The steam gasification carried out at a fixed temperature for 60 minutes and every 15 minutes, samples were taken for analysis. The gas compositions (H_2, CH_4, CO, and CO_2) were analyzed using Shimadzu GC-2010. The experiment was repeated with temperature variations of 600, 700, and 800 °C.

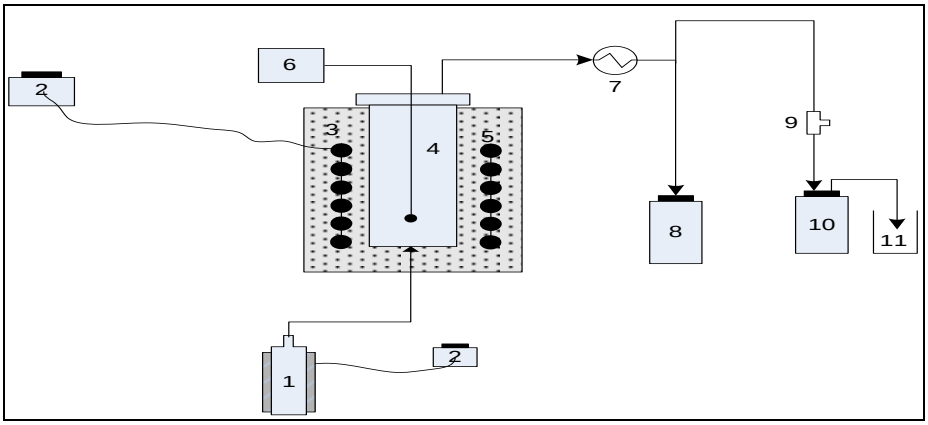


Figure 1. The schematic diagram of the experimental apparatus
(1) Steamer, (2) Regulator, (3) Isolator, (4) Reactor, (5) Coil heater, (6) Thermocouple, (7) Condenser, (8) Condensat tank, (9) Sampling gas, (10) Water tank, (11) Water reservoir

4. Result and Disscussion

4.1. Effect of temperature

In this study, the gasification process was run until 60 minutes in a three different temperatures, i.e. 600, 700, and 800 °C. Data obtained include the amount of gas produced and the composition of the four main gasses CH_4, CO, H_2, and CO_2. The volume of gas produced at any time was presented in Fig. 3.

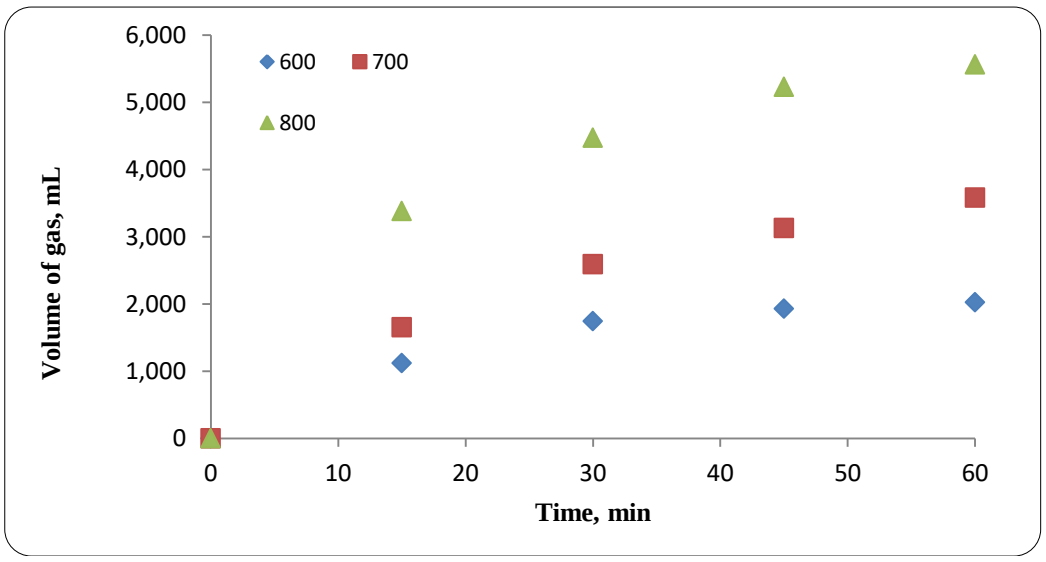


Figure 2. The relationship between the volume of gas and time at gasification temperature

Figure 2 shows the relationship between gas volume and time at various temperatures. From the figure it can be seen that the volume of gas produced will increase each time and a significant increase occurs until 45 minutes and after that is relatively slow. Furthermore, from Figure 3 it is also seen that with increasing temperature, the volume of gas produced also increases. This increase is due to the main reaction (Eq. (2)) is endothermic so that the temperature rise greatly influences the course of the process [18] [19]; In addition, at high reaction temperature and in the presence of steam will result in greater char reactivity so that the reaction between char and steam will be faster so that the resulting gas will be more and more [18] [9].

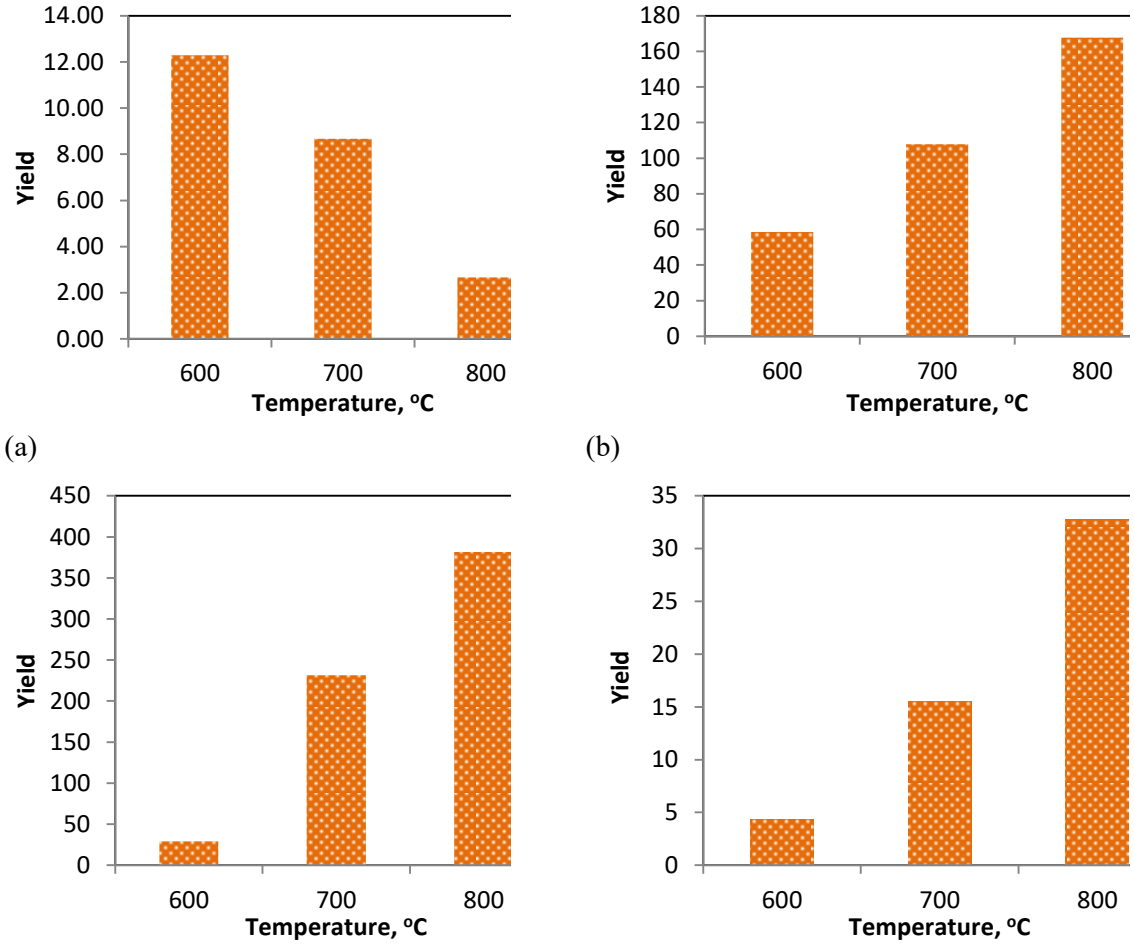


Figure 3. Effect of temperature on the gas composition at 600, 700, and 800 °C for 60 minutes (a. CH_4, b. CO, c. H_2, d. CO_2)

Figure 4 shows the effect of temperature on the yield of each gas. From Fig. 4, the yield of H_2 and CO gas increases with increasing temperature. At 600 °C, the yield of H_2 was 29 mL / g and then increased to 231 mL/g at 700 °C and 382 mL/g at 800 °C. While yield of CO at 600 °C was 59 mL/g and then increased to 108 mL/g at 700 °C and 168 mL/g at 800 °C. This increase is due to the reaction between char and steam (water gas reaction) is endothermic. So that with increasing temperature, the reaction will shift toward the formation of products (H_2 and CO).

The increasing of H_2 yield on gasification has also been reported [18]. In their study, gasified using pine bark with variations of temperature 500, 600, and 700 oC. From this study obtained that yield of H_2 rises with rising temperatures. Figure 4 also shows that CO yield rises, but the increase is not significant compared to CO_2 increase. This is because some CO reacts with H_2O to form CO_2 and H_2 in the gas phase (based on Eq. (4)) [20].

From Fig. 4 it appears that the yield of CH_4 is very small compared to the other gas. This is because the reaction between char and hydrogen (Eq. (3)) to form methane is very slow (Walker et al., 1959). Yield CH_4 decreases with increasing of reaction temperature. yield of CH_4 decreased to 5.7% when the temperature rose from 600 to 700 ^oC. While from 700 to 800 ^oC, yield of CH4 decreased to 26.3%. The effect of temperature on CH_4 yield has also been investigated [18] In their study it was found that by raising the temperature from 500 to 600 ^oC, yield of CH_4 decreased to 61.9%. Meanwhile, when the temperature is increased from 600 to 700 ^oC, CH_4 yield decreases to 53.13%. This decrease is due to the increasing temperature, the reaction of methane decomposition by steam (Eq. (15)) progresses faster (endothermic reaction). In addition, based on Eq. (3), with increasing temperature, the reaction will shift to the left.

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \qquad \Delta H^o_{rx,298\ K} = 206 kJ/gmol \qquad (15)$$

4.2. Validation Model

Experimental results are generalized using the thermodynamic equilibrium model. When the reaction temperature is relatively high, the reaction rate can be assumed to be faster so that equilibrium is achieved. The gas composition was approximated by stoichiometric approach as in Eqs. (11), (12a) - (12d), and (13a) - (13d).

The curve fitting method is used to obtain the value of each parameter present in equation (11). The gas composition from the laboratory experiment were compared to the gas compositions obtained from the calculation. The values of the parameters chosen were the ones that give the minimum value of the SSE (Eq. (14). The values of the parameters obtained are presented in Table 3. Meanwhile, the comparison of calculated results and the experimental data was presented in Figs. 5a-5c.

Table 3. The parameter values of model

Reaction No.	K_{0i}	K_{1i}
R1	-6.5693	7.5001×10^3
R2	11.309	-9.0457×10^3
R3	-23.734	2.0694×10^4
R5	1.6360	1.4197×10^3

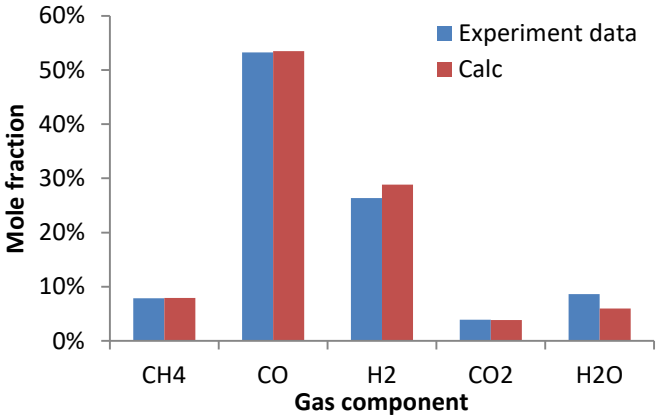


Figure 4. Comparison of mole fraction from thermodynamics model and experimental data at gasification temperature 600 °C.

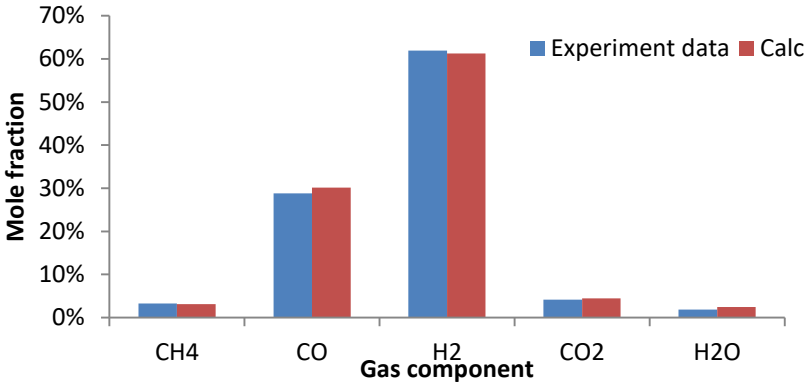


Figure 5.. Comparison of mole fraction from thermodynamics model and experimental data at gasification temperature 700 °C.

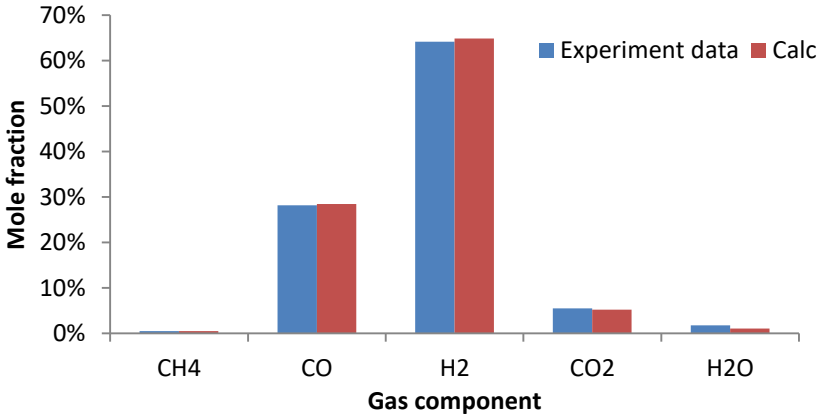


Figure 6. Comparison of mole fraction from thermodynamics model and experimental data

Figures 4-6 shows a comparison of mole fraction from the calculation result and the experimental data. From Figs. 5a-5c seems that the gas compositions from calculation results were matched with the experimental data. The smallest average of error obtained at a temperature of 600 was 8.6% while the largest average error was 10.8 % at the temperature of 800 °C. Sum of Squares of Errors obtained from the calculation at a temperature of 600, 700, and 800 °C were 1.12×10^{-09}, 1.25×10^{-11} and 5.43×10^{-08} respectively.

5. Conclusion

Based on the results of the experimental data and calculation, some conclusions could be obtained as follows: Rising temperatures will increase the volume of gas product. If the temperature of gasifier increases by 100 °C, the volume of gas will increase by approximately 1.7 times. Stochiometric approach could be used to predict the composition of gas produced from char gasification

6. References

[1] Acharya, B., Dutta, A., Basu, P., 2010. An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO. Int. J. Hydrogen Energy 35, 1582–1589.

[2] Basu, P., 2010, Biomass Gasification and Pyrolysis, US, Elsevier.

[3] Bell, D.A., Towler, B.F., Fan, M., 2011. Coal Gasification dan Its Applications, 1st ed. Elsevier.

[4] Bridgwater, A. V, 2003, Renewable fuels and chemicals by thermal processing of biomass. Chem. Eng. J. 91, 87–102.

[5] Demirbas, A., 2004, Combustion characteristics of different biomass fuels. Prog. Energy Combust. Sci. 30, 219–230

[6] Demirbas, A., 2016, Hazelnut Shell to Hydrogen-Rich Gaseous Products via Catalytic Gasification Process Hazelnut Shell to Hydrogen-Rich Gaseous Products via Catalytic Gasification Process, Energy Sources 8312, 25–33.

[7] Heidenreich, S., Ugo, P., 2015, New concepts in biomass gasification, Prog. Energy Combust. Sci. 46, 72–95.

[8] Jarungthammachote, S., Dutta, A., 2007, Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier. Energy 32, 1660–1669.

[9] Lim, Y., Lee, U., 2014. Quasi-equilibrium thermodynamic model with empirical equations for air – steam biomass gasi fi cation in fl uidized-beds 128, 199–210.

[10] Luo, S., Xiao, B., Hu, Z., Liu, S., Guo, X., He, M., 2009. Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: Influence of temperature and? steam on gasification performance. Int. J. Hydrogen Energy 34, 2191–2194.

[11] Mahishi, M.R., Goswami, D.Y., 2007. An Experimental Study of Hydrogen Production by Gasification of Biomass in The Presence of a CO2 Sorbent. Int. J. Hydrogen Energy 32, 2803–2808.

[12] Melgar, A., Perez, J.F., Laget, H., Horillo, A., 2007, Thermochemical equilibrium modelling of a gasifying process 48, 59–67.

[13] Meng, X., de Jong, W., Fu, N., Verkooijen, A.H.M., 2011, Biomass gasification in a 100 kWth steam-oxygen blown circulating fluidized bed gasifier: Effects of operational conditions on product gas distribution and tar formation. Biomass and Bioenergy 35, 2910–2924.

[14] Molina, A., Mondrago, F., 1998. Reactivity of coal gasification with steam and CO2. Fuel 77, 1831–1839.

[15] Pe, J.F., Laget, H., Horillo, A., 2007. Thermochemical equilibrium modelling of a gasifying process 48, 59–67.

[16] Smith, J.M., Van Ness, H.C., Abbott, M.M., 2005. Introduction to chemical engineering thermodynamics, 7th ed. McGraw-Hill.

[17] Stiegel, G.J., Maxwell, R.C., 2001, Gasification technologies : the path to clean , affordable energy in the 21st century. Fuel Process. Technol. 71, 79–97.

[18] Wang, X., Chen, F., Hong, B., Liu, H., Yu, G., Wang, F., 2013, The Steam Gasification of Coal Catalyzed by KOH for the Production of Hydrogen, Energy Sources, Part A Recover. Util. Environ. Eff. 35, 1583–1589.

[19] Yan, Q., Guo, L., Lu, Y., 2006. Thermodynamic analysis of hydrogen production from biomass gasification in supercritical water. Energy Convers. Manag. 47, 1515–1528. doi:10.1016/j.enconman.2005.08.004.