

Kinetic model for tar cracking in biomass steam gasification for hydrogen production

Muhammad Ammar ^{1,*}, M.I. Abdul Mutalib ¹, Suzana Yusup ¹, Abrar Inayat ², Basit Ali ¹, Kevin Kan ¹

¹Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia

²Department of Sustainable and Renewable Energy Engineering, University of Sharjah, 27272 Sharjah, United Arab Emirates

Abstract: The production of hydrogen from biomass gasification is a promising pathway for clean energy source to substitute fossil fuels. However, the production of tar in biomass gasification process is one of the major problems as it affects the utilization efficiency of biomass. Moreover, tar condenses at reduced temperatures causing process related problem like clogging or blockage in end use devices. It is necessary to reduce the tar contents in final product gas via cracking process before it can be utilized. The present work focuses on the development of kinetics model for reactions involved in tar cracking in biomass steam gasification for H₂ production. The developed model was simulated in MATLAB for determining numerical values of rate constants via optimization approach. Parametric study was performed with the effect of temperature, product yield and flammability factor. Model predicts that the production of hydrogen increase exponentially with the rise in temperature resulting in increase in flammability limit of the product gas. The model was then validated with literature and showed good agreement.

Key words: Hydrogen; Tar cracking; Biomass; Steam gasification; Kinetic modeling

1. Introduction

The major source of energy in the world is heavily dependent on finite fossil fuels that are depleting by day while the world energy demand is increasing continuously. According to World Development Indicators in the year of 2011, 81.5% of total energy utilization in the world is from fossil fuels, followed by 9.8% from combustible renewable and waste and 8.7% from other alternative such as nuclear energy. Hydrogen is one of the alternative source of energy that has potential to fulfil the energy demand because of its high energy contents. Hydrogen is mainly produced from combustion of fossil fuels such as natural gas steam reforming. Biomass is one of the potential source to generate renewable energy [Tanksale et al., 2010]. Gasification refers to a thermochemical process converting carbon sources mainly biomass, coal or natural gas into possibly hydrocarbon molecules as well as other side products such as carbon monoxide (CO), hydrogen (H₂) or carbon dioxide (CO₂).

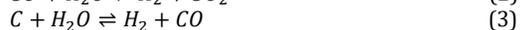
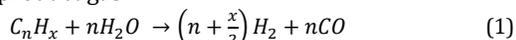
Biomass steam gasification not only produces useful products such as hydrogen (H₂) and carbon monoxide (CO), many by-products are also formed during the process including inorganic impurities like hydrogen sulfide (H₂S), fly ash, nitrogen oxides (NO_x), sulphur dioxide (SO₂) and organic impurities generally known as tars. The contents of tars may vary from lower hydrocarbons to long chain aromatic hydrocarbons. The production of tar is one of the main drawbacks in the produced gas from gasification of biomass for the utilization in power

generation or synthesis of further chemicals. The production of tar contents is much higher in steam gasification as compared to other gasification processes. However the production of hydrogen requires steam gasification in order to increase the hydrogen contents in product gas stream. It has advantage, the excess steam can be easily removed from the product gas and which enhances the energy contents of the product gas, so it is also preferred over the other gasification agents. Tar produced in biomass gasification is in vapor phase above 300 °C of temperature and is composed of condensable polynuclear aromatic hydrocarbons. Below 300 °C tar compounds condense and undergo polymerization reaction in which tar compounds react and fuse to form larger chain tar compounds. So these tar compounds cause operational problems to the equipment. The control and reduction of tar contents in biomass gasification is divided into two classes; primary and secondary tar removal methods. In primary method tar removal is done within the biomass gasifier while in secondary method tar removal is done in a separate setup downstream of the biomass gasifier [Devi et al., 2003]. Various research methods on tar cracking have been carried out by many researchers. Han & Kim [Han et al., 2008] has reviewed past literature on some of the possible methods on tar cracking.

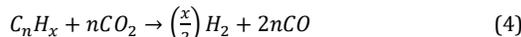
The removal of tar by thermal cracking and partial oxidation are highly dependent on the temperature and the residence time of the gases. According to Brandt & Henriksen [2000] to achieve a sufficiently high tar cracking efficiency from thermal cracking, the necessary temperature and residence time are 1250 °C and 0.5 seconds respectively.

* Corresponding Author.

Houben et al. [2004] has conducted another thermal cracking experiment with the temperature range of 900-1150°C and residence time ranging between 1 and 12 seconds. The results obtained by Houben [2004] shows that the concentration of tar decreases exponentially as the residence time increase and operating temperature exceed 900 °C. Morf [2002] has done experimental investigation for homogeneous tar conversion without the external supply of oxidants in a tubular flow reactor operated at temperature ranging from 500 to 1000 °C with residence time below 0.2 seconds. The highest conversion that Morf [2002] manage to obtain in the experiment is 88% at a reference reaction temperature of 990 °C and isothermal residence time of 0.12 seconds. According to Devi et al. [2003] the high hydrogen production during steam gasification can be attributed by the following chemical equations that represents tar reforming reaction which contributes to increase in H₂ and CO contents in product gas.



The presence of Carbon Dioxide in the atmosphere makes its use as gasifying medium to be promising. Tar reduction is also enhanced by dry reforming reactions of carbon dioxide. Minkova et al. [2000] stated that a mixture of steam-CO₂ gives the highest degree of carbonization in a rotating reactor for gasification of biomass. This mixture also produces large activity char, resulting to high ash content. CO₂ gasification in the presence of catalyst converts tars and decrease of the amount of Methane and C₂-fraction as well as increasing the Hydrogen and Carbon Monoxide yields. The significant decrease in Carbon Dioxide content was observed with CO₂/Biomass ratio of 1:16 indicating Carbon Dioxide converts into other products. The main chemical reaction equation with carbon dioxide as gasifying medium representing the reforming reaction of tar is:



The current research study focuses on the reaction kinetic modelling development of tar cracking for biomass steam gasification for Hydrogen (H₂) production in order to understand the kinetic reactions of tar cracking to prevent problems that occurred due to the presence of tar in the reactor and thus prolonging the operating time of the reactor for Hydrogen production. On the other hand, this research project also calculates the reaction constant of tar cracking by using optimization approach to optimize the utility system of tar cracking to enhance the production of Hydrogen most economically.

2. Methodology

Heavy hydrocarbons like toluene and hexane are the main components of tar produced during biomass steam gasification. The formation of tar during biomass gasification is the result of a series of complex chemical reactions. Tar decomposition mainly occurs as benzene and toluene undergoes steam reforming along with homogeneous water-gas shift reaction as shown in the reaction equation (7) to (11).

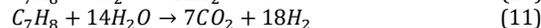
Benzene:



Water Gas shift (WGS):



Toluene:



Main reactions of tar cracking also has been reviewed in order to understand the fundamentals of tar cracking as mentioned by Li and Suzuki [Chunshan et al., 2009]. The kinetic behavior of reactions (7) - (11) listed can be represented through various alternatives. However, the reactions above are assumed to be first order reaction with respect to the concentration of the reactant using the rate expressions for subsequent rate equations [Inayat et al., 2012].

$$r_1 = k_1[C_6H_6][H_2O]$$

$$r_2 = k_2[C_6H_6][H_2O]$$

$$r_3 = k_3[CO][H_2O]$$

$$r_4 = k_4[C_7H_8][H_2O]$$

$$r_5 = k_5[C_7H_8][H_2O]$$

Here r is the rate of reaction and k is the reaction rate constant. The reaction rate constant with temperature dependency is defined by the Arrhenius equation:

$$k(T) = A_o \exp\left(\frac{-E}{RT}\right)$$

Where k is the reaction rate constant, A_o is pre-exponential factor or frequency factor, E is energy of activation, R is general gas constant and T is reaction temperature.

The overall volumetric rate of each component can be determined according to chemical reactions engineering rules using the equations (12)-(14):

$$R_{H_2} = 9r_1 + 15r_2 + r_3 + 15r_4 + 18r_5 \quad (12)$$

$$R_{CO} = 6r_1 - r_3 + 7r_4 \quad (13)$$

$$R_{CO_2} = 6r_2 + r_3 + 7r_5 \quad (14)$$

Lower and upper flammability limits can be calculated by using the formula:

a. Lower Flammability Limit (LFL)

$$LFL_{mixture} = \frac{1}{\sum \frac{x_i}{LFL_i}}$$

b. Upper Flammability Limit (UFL)

$$UFL_{mixture} = \frac{1}{\sum \frac{x_i}{UFL_i}}$$

The calculation of reaction kinetic parameters for the respective reactions was carried out by residuals between the model predictions and experimental results. The flow chart of residual minimization approach is shown in Fig. 1. The non-linear programming (NLP) constrained minimization is performed using MATLAB *fmincon* solver.

Experimental yields of carbon monoxide, carbon dioxide and hydrogen during homogeneous tar conversion obtained by Morf [2002] is used as equation constraints for optimization calculation. Three different temperatures of 600°C, 700°C and 800 °C are taken in to consideration for calculations.

After obtaining respective reaction rate constant from optimization approach, model is compared with experimental data to determine validity of model developed.

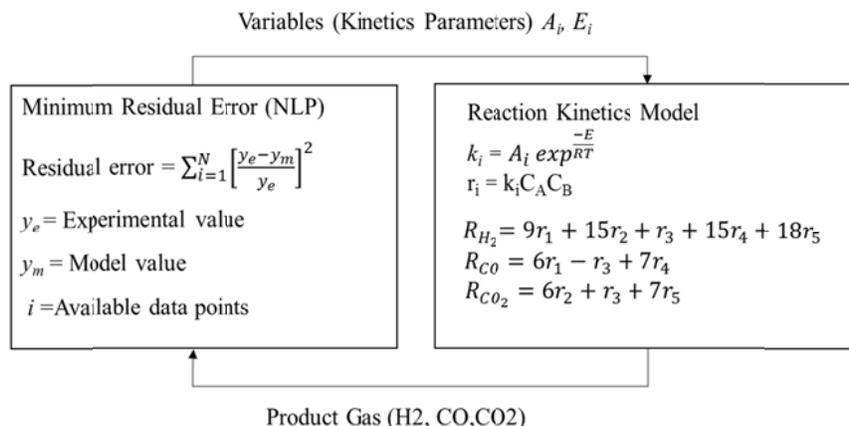


Fig. 1: Flow chart of residual minimization approach

3. Results and discussion

The kinetic parameters i.e. pre-exponential factor (A) and activation energies (E) calculated using the minimization of the residual approach are listed in Table 1. Using the optimized values of pre-exponential factor and activation energies in the kinetics model developed, the composition of the product gas from biomass steam gasification system was calculated.

Table 1: Kinetics parameters of the reactions

Reaction no.	Arrhenius Constant (A)	Activation Energy (Ea)
4	70.858	462.803
5	394.817	1048.977
6	703.498	-322.559
7	50.869	76.161
8	331.478	271.747

3.1. Effect of temperature on product gas composition

From reaction rate constant obtained, product gas composition can be calculated by using kinetic model developed as shown in the equations (9) to (11). The composition of combustible gases in product gas is very munching important since it specifies the product gas quality. Fig. 2 illustrates the effect of temperature on product gas composition in the range between 873 and 1123 K. The model results show that the product gas composition is remarkably affected by temperature change.

The increase in gasification temperature from 872K to 923K, decreased the production of hydrogen. With the further increase in gasification temperature from 923-1123 K, it was observed that there was an increase in hydrogen production and

reaches up to 44% by volume in product gas. On the other hand, the increase in gasification temperature from 872K to 923K, the production of carbon monoxide in final product gas increased but a decreasing trend was observed when the temperature was increased further. This can be associated with the occurrence of water gas shift reaction at higher temperature that causes the increase in hydrogen contents and decrease carbon monoxide in product gas.

The effect of temperature on the volumetric rate of product gas is investigated and shown in Fig. 2. It is observed that the production of hydrogen increases exponentially with the rise in temperature.

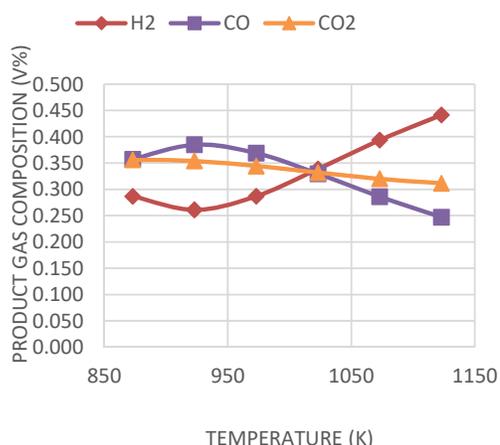


Fig. 2: Effect of temperature on product gas composition

This is due to the efficiency of thermal tar cracking where hydrogen production can be increased as temperature increases. Equations (7), (8), (10) and (11) are endothermic reaction whereas equation (9) is exothermic reaction resulting the

increase in production of hydrogen, carbon monoxide as well as carbon dioxide. The increase in gasification temperature initiates the tar cracking reactions along with the already undergoing biomass gasification reactions and eventually the volumetric rate of final gas production increases (Fig. 3).

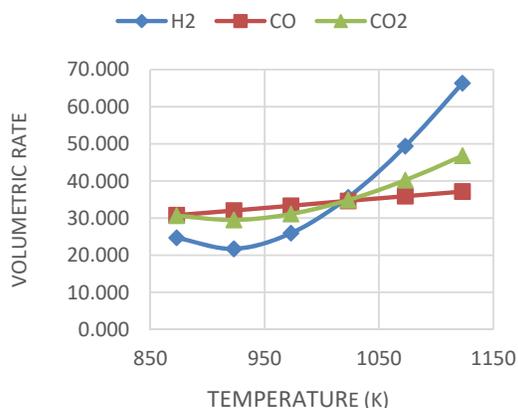


Fig. 3: Effect of temperature on volumetric rate

The H₂/CO and H₂/CO₂ ratios in product gas stream are also very important benchmark to describe the biomass gasification efficiency. Since product gas from gasifier is further utilized for the synthesis of chemicals or direct utilization of product gas as a fuel so these ratios are of very much importance. The Fig. 3 depicts the influence of temperature on H₂/CO and H₂/CO₂ ratios in the product gas from biomass steam gasification. The increase in temperature of biomass gasification increases these ratios exponentially. It is due to the fact that the cracking of tar components in biomass gasifier causes the increase in hydrogen production and the production of CO and CO₂ is relatively low compared to that of hydrogen at higher temperatures. So the H₂/CO and H₂/CO₂ ratios first decrease until 923K and increases at the temperature range of 923K to 1123 K. This exponential increase with the rise in temperature can be seen in Fig. 4.

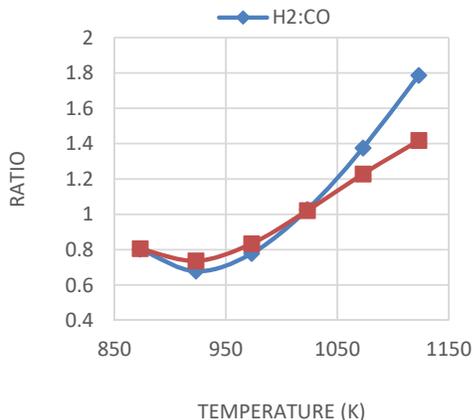


Fig. 4: Effect of temperature on ratio of products

3.2. Flammability limit

Flammability limit is defined as a concentration range in which fire or explosion may occur due to the presence of flammable substance when an ignition source is present. Since the flammability limit describes the concentration of the product gas at which it can be ignited at, so the flammability limit is an important benchmark to study the quality of the product gas. Flammability limit is constrained in to classes; first one being lower Flammability limit and second is upper flammability limit. Lower flammability limit is the minimum concentration of combustible gases in product and upper flammability limit is the maximum concentration at which gas will ignite [Ftwi, 2013]. Increase in hydrogen content as temperature increases may result in increasing in flammability limit range as shown in Fig. 5. Hydrogen gas is highly flammable and explosive may occur if there is any ignition source. Therefore the increase in temperature will increase the hydrogen content and subsequently it will result to a wider range of flammability Limit. But the lower flammability limit for the product gas remains the same with the rise in temperature. However, carbon dioxide gas is non-flammable gas and will not cause ignition. Thus presence of Carbon Dioxide will not affect the range of Flammability Limit.

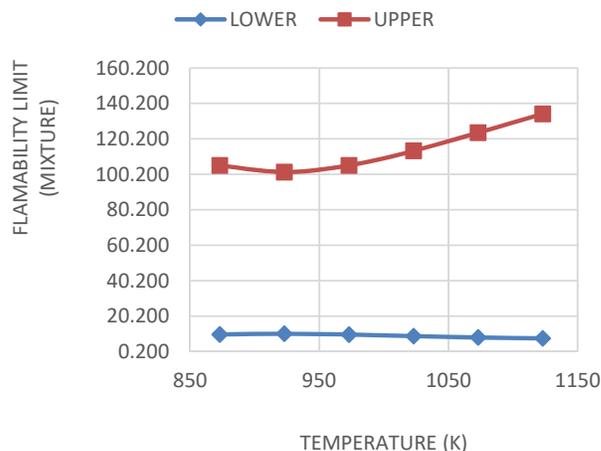


Fig. 5: Effect of temperature on flammability limit

3.3. Validation of model

The results obtained from the developed kinetic model are compared with the experimental results reported by Morf (2002) for validation of model. The validity of model is confirmed as the difference between the model and experimental value is very small and does not deviate much as shown in Fig. 6.

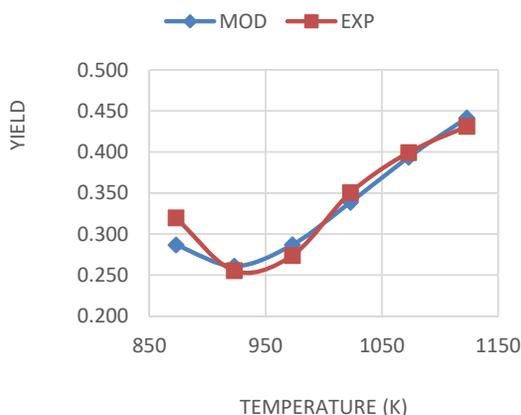


Fig. 6: Comparison of results of experimental and model developed

4. Conclusion and recommendation

Tar cracking in flue gas from biomass gasification is required for obtaining a feasible gasification process and more economical. The presence of tar in the gasifier will cause the decrease in efficiency of the biomass utility. It is necessary to eliminate tar contents in order to maintain the utility efficiency as well as to maximize the production of useful products from biomass and tar cracking.

This research project is expected to help in tar cracking by developing the kinetic modelling of the reaction in tar cracking as well as to obtain the reaction constant of tar cracking in order to enhance energy production from biomass. This research project is carried out by using simulation and optimization approach that can be justified theoretically. Tar produced during biomass gasification process can be cracked by increasing the gasification temperature from 923-1123K. Eventually increasing the hydrogen contents present in product gas resulting in tar free gas with higher energy contents. However this research project can be improvised by conducting laboratory experiment for tar cracking in biomass steam gasification at higher temperatures in order to justify the feasibility of this research project.

Acknowledgements

The authors gratefully acknowledge the financial support provided by the Ministry of Energy, Green Technology and Water (KeTTHA) and Universiti Teknologi PETRONAS, Malaysia to conduct the current research work.

References

- Chunshan Li, K.S., Tar property, analysis, reforming mechanism and model for biomass gasification—An overview. *Renewable and Sustainable Energy Reviews*, 2009. 13(3): p. 594-604.
- Devi, L., K.J. Ptasinski, and F.J.J.G. Janssen, A review of the primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy*, 2003. 24(2): p. 125-140.
- FTwi Yohannes Hagos, A.R.A. Aziz, and S.A. Sulaiman, Study of Syngas Combustion Parameters Effect on Internal Combustion Engine. *Asian Journal of Scientific Research*, 2013. 6: p. 187-196.
- Han, J. and H. Kim, The reduction and control technology of tar during biomass gasification/pyrolysis: An overview. *Renewable and Sustainable Energy Reviews*, 2008. 12(2): p. 397-416.
- Houben, M.P., Analysis of tar removal in a partial oxidation burner. 2004, Technische Universiteit Eindhoven.
- Inayat, A., et al., Process modeling for parametric study on oil palm empty fruit bunch steam gasification for hydrogen production. *Fuel Processing Technology*, 2012. 93(1): p. 26-34.
- Peder Brandt, U.B.H., Decomposition of tar in gas from updraft gasifier by thermal cracking, in *Proceedings of 1. World Conference and Exhibition on Biomass for Energy and Industry*. 2000: Seville, Spain.
- Philipp Morf, P.H., Thomas Nussbaumer, Mechanisms and kinetics of homogeneous secondary reactions of tar from continuous pyrolysis of wood chips. *Fuel*, 2002. 81(7): p. 843-853.
- Tanksale, A., J.N. Beltramini, and G.M. Lu, A review of catalytic hydrogen production processes from biomass. *Renewable and Sustainable Energy Reviews*, 2010. 14(1): p. 166-182.
- V. Minkova, S.P.M., R. Zanzi, E. Björnbohm, T. Budinova, M. Stefanova, L. Lakov, Thermochemical treatment of biomass in a flow of steam or in a mixture of steam and carbon dioxide. *Fuel Processing Technology*, 2000. 62(1): p. 45-52.