Kinetic Study of Steam Gasification of Palm Kernel Shell Char

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Abstract. In this work, we investigate the reaction mechanism of steam gasification reaction of palm kernel shell char. The experiment results which are used in this work are carried on at temperature of 1123, 1173, and 1223K. The isothermal steam gasification of palm kernel shell char is described by mathematic models including volumetric model (VM), grain model (GM), random pore model (RPM), and modified random pore model (mRPM). From results, we found that the RPM model can predict gasification of palm kernel shell char better than other models. The RPM model considers the overlapping of pore surfaces, which results in the reduction of surface area available for the reaction. The activation energy of gasification reactivity of palm kernel shell char is 152.63 kJ/mol for RPM model. The coefficient of determination of RPM model are 0.9920, 0.9995, and 0.9907 at 1123, 1173, and 1223 K respectively.

1. Introduction
Nowadays, palm oil production is a big industry in Thailand. The increasing of biodiesel demand in Thailand results in higher production of palm oil. Waste from palm oil production also increases as the industry grown. Palm kernel shell waste is also one of the wastes from palm oil production. When the waste from industry is left to environment it would affect to life and ecology. So, we have to search for alternative to solve or alleviate this problem. Activated carbon from palm kernel shell is considered as the alternative for this problem since it can be used in many ways. It consists of carbon that obtained from the activation of char, normally, activated carbon is used for adsorption process because of its high degree of microspore and high surface area.
Activated carbon can produce from two step reaction. Firstly, pyrolysis of biomass to obtained raw materials that carbon rich. Secondly, gasification reaction of char to eliminated contaminant in the pore. Generally, biomass gasification reaction is very complex involves a complex series of chemical reaction. So, it is difficult to find the mathematic model to describe the gasification reaction. The common mathematic model for describe the gasification reaction is gas-solid reactions model that involved four phenomena which are external mass transfer, pore diffusion, adsorption and desorption, and chemical reaction. The mathematics models for this work include volumetric model, grain model, random pore model, and modified random pore model. These models differ in term of primary assumption such as overlapping or non-overlapping of population of grain or pore on the solid. This research will report the suitable model and mechanism for steam gasification of palm kernel shell at different temperature.
2. Theory

2.1. Gasification reaction
Char gasification is two step including pyrolysis and gasification. The pyrolysis involved the evolution of compound of low molecular weight at temperatures between 300 – 500 \degree C. These compounds are mainly tarring and non-condensable gases. Normally, the pyrolysis residue remains about 70% of original mass. Usually, the gasification reaction is slower than pyrolysis reaction. So, only char gasification reaction is considered for this study. The main reaction for gasification reactions are shown following.

\[
\begin{align*}
\text{C} + \text{CO}_2 & \rightarrow 2\text{CO} \quad \Delta H = +172 \text{ kJ/mol} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \quad \Delta H = +131 \text{ kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{ kJ/mol} \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \quad \Delta H = -394 \text{ kJ/mol} \\
\text{C} + 2\text{H}_2 & \rightarrow \text{CH}_4 \quad \Delta H = -75 \text{ kJ/mol}
\end{align*}
\]

From the reaction, reaction (1) and (2) are endothermic reaction and they are considered as the important reaction for gasification reaction. The reaction (3) is exothermic reaction which provided energy for reaction (1) and (2). The shift reaction (4) occurs during high steam concentration and reaction (5) is more effective at high pressure. When gasification proceeds, the burn-out rate is used to determine the gasification rate.

\[
\begin{align*}
\frac{1}{W} \frac{dW}{dt} &= \frac{1}{1-X} \frac{dX}{dt} \\
X &= \frac{W_0 - W}{W_0}
\end{align*}
\]

Where \( r \) is normalized gasification rate
\( t \) is time
\( W \) is the char mass at time \( t \)
\( X \) is char conversion
\( W_0 \) is Initial mass of char

\[
\frac{-1}{W_0} \frac{dW}{dt} = \frac{dX}{dt}
\]

In this case, \( r' \) is consider as gasification rate

2.2. Volumetric model [1],[2]
Volumetric model considers a gas-solid reaction take place on a porous particle of general stoichiometry.

\[
A(gas) + bB(solid) \rightarrow product
\]

Accounting for the effect of solid lost on reaction rate, it may describe by using simple power law rate. For this reaction, the reaction rate is described in first order reaction:

\[
-r_A = kC_A C_B
\]

where \( k \) is rate constant base on unit volume of bulk solid.
Assumption in this mathematic model is consist of 1. The structure change of solid due to reaction is negligible.  
2. The system for this reaction is isothermal reaction.  
3. Pseudo-steady state approximation is valid.  
4. Gas film resistance is negligible.  
The conversion rate can be express as followed:

\[
\frac{dX_n}{dt} = bkC_A\eta(1-X_n)
\]  

(11)

2.3. Grain model[3],[2]
Grain model is involving heterogeneous gas-solid reaction with moving the boundary. For the grain model, the solid phases consist of unreacted core surrounded by the reacted shell. When the reactions are proceeding, the reacted zone will be expanded and the diffusion of reactant or product through this region may be one of rate limiting step. 
The non-react core model for this research is grain model. This model assumes that reacting char particles are considered as spherical grains whose radius decrease as the gasification reaction proceed. The reaction rate for this model expression are:

\[
X = 1 - \left(1 - \frac{kt}{3}\right)
\]  

(12)

\[
\frac{dX}{dt} = k\left(1 - X\right)^{2/3}
\]  

(13)

2.4. Random pore model [2],[4]
The random pore model is proposed by Bhatia and Perlmutter. The random pore model can be applied to gasification reaction. The random pore model assumes that there is random overlapping of pore surface which reduced the available for reaction. The equation for this model is:

\[
X = 1 - \exp\left[-\tau\left(1 + \frac{\psi}{4}\right)\right]
\]  

(14)

\[
\frac{dX}{dt} = k\left(1 - X\right)\left[1 - \psi\ln(1 - X)\right]
\]  

(15)

and

\[
\tau = \frac{K_0C^oS^o_t}{1 - \varepsilon^o_0}
\]  

(16)

where \(S_0^o\) is initial surface area at \(t = 0\)  
and \(S_0^o\) can find from pore volume distribution \((V_0^o)\) of char by equation below.

\[
S_0 = \int_0^{V_0^o(t)} \frac{V_0^o(t)}{r} dr
\]  

(17)

where \(V_0^o\) is pore volume distribution \((m^3/g)\) determine by CO2 at 273 K.  
\[
\psi = \frac{4\pi L_0(1 - \varepsilon^o_0)}{S_0^o}
\]  

(18)

where \(\psi\) is a structural parameter  
\(L_0\) is pore length at \(t = 0\)  
\(\varepsilon^o_0\) is char porosity at \(t = 0\)
2.5. Modified random pore model [2],[5]

The modified random pore model is developed from random pore model, it different from the random pore model by added the conversion term to random pore model. It can be written as:

\[
\frac{dX}{dt} = k(1-X)^n\sqrt{t - \psi \ln(1-X)}
\]  

(19)

where \(n\) is the dimension less power.

3. Result and Discussion

In this work, we employ the experimental result from Chang et al.[6] The reaction was done at three different temperature of 1123, 1173, and 1223 K. In their work, the material was heated from 298K to the designed temperature at a rate of 20°C/min. The steam of 5g/h was used as the gasifying agent. At first, we employ volumetric model (VM) to simulate gasification reaction of palm kernel shell char with steam. The result is shown below:

![Figure 1. Simulation of steam gasification of palm palm kernel shell char at temperature of 1123 K 1173 K and 1223 K using VM model vs experimental results.](image)

**Table 1. VM model parameter results**

| Parameter | Result          |
|-----------|-----------------|
|           | 1123 K | 1173 K | 1223 K |
| \(k\) (1/s) | 2.12 x 10^{-3} | 4.19 x 10^{-3} | 7.58 x 10^{-3} |
| \(R^2\)   | 0.9987 | 0.9961 | 0.9831 |
| Average \(R^2\) | 0.9926 |
| \(E_a\) (J/mol) | 145461.74 |
| \(A\) (1/s) | 12450.30 |

From Figure 1 and Table 1, the VM model seems to work at 1123 and 1173K better than 1223 K. However, the conversion of VM model is lower than experimental data. The results show that VM model is working well for reaction at temperature range of 1123 to 1223 K. The next model that we are using in this simulation is grain model (GM) model.

**Table 2. GM model parameter results**

| Parameter | Result          |
|-----------|-----------------|
|           | 1123 K | 1173 K | 1223 K |
| \(k\) (1/s) | 1.31 x 10^{-3} | 3.14 x 10^{-3} | 5.44 x 10^{-3} |
| \(R^2\)   | 0.9382 | 0.9953 | 0.9928 |
| Average \(R^2\) | 0.9754 |
| \(E_a\) (J/mol) | 162896.20 |
Figure 2. Simulation of steam gasification of palm kernel shell char at temperature of 1123 K, 1173 K, and 1223 K using GM model vs experimental results. From Figure 2 and Table 2, the conversion simulated from VM model is better than GM model. GM model can predict conversion at higher temperature (1173 and 1223 K) better than at lower temperature (1123 K).

Table 3. RPM model parameter results

| Parameter | Result |
|-----------|--------|
| k (1/s)   | 1.76 x 10^-3 | 3.40 x 10^-3 | 6.76 x 10^-3 |
| $\psi$    | 0.5025    | 0.5025    | 0.5025    |
| $R^2$     | 0.9920    | 0.9995    | 0.9907    |
| Average $R^2$ | 0.9941 |        |
| Ea (J/mol) | 153293.53 |
| A (1/s)   | 23482.25 |

From Figure 3 and Table 3, RPM model seems to work well at temperature range from 1123 to 1223 K. The coefficient of determination for RPM model is higher than 0.99 for those three temperatures.
From Figure 4 and Table 4, mRPM model work well at temperature of 1173 and 1223 K. However, the model is a little bit off at the temperature of 1123 K.

From the result of four models, the rpm model seems to work well for every temperature. Therefore, the mechanism of steam gasification should follow RPM mechanism model. During the reaction, there is random overlapping of pore surface which reduced available area for reaction.

4. Conclusion

In this research, we investigate the reaction mechanism of steam gasification reaction of palm kernel shell char. The experiment results which are used in this work are carried on at temperature of 1123, 1173, and 1223 K. There are four reaction models used in this work. Models are volumetric model, grain model, random pore model, and modified random pore model. From results, the random pore model gives better results at three temperatures than other three models. That means during the reaction, there is random overlapping of pore surface which reduced available area for reaction. The activation energy of gasification reactivity of palm kernel shell char is 152.63 kJ/mol for RPM model. The coefficient of determination of RPM model are 0.9920, 0.9995, and 0.9907 at 1123, 1173, and 1223 K respectively.
5. References

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