Kinetics study on non-isothermal thermochemical liquefaction of corncobs in ethanol-water solution: Effect of ethanol concentration

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Abstract. Corncobs are potentially processed into bio-oil through thermochemical liquefaction processes. It is difficult to construct kinetics models based on the compounds involved in the reaction. It would be made four kinetic models based on four reaction products, i.e., solids, bio-oil, gas and volatile products. The purposes of the study were to seek kinetics model of thermochemical liquefaction of corncobs in ethanol-water solution and to study the effect of ethanol concentration. The experiment of liquefaction processes of corncobs in ethanol-water solution using sodium carbonate catalyst was performed in the 150 ml autoclave equipped with a magnetic stirrer in the temperature up to 280°C. Four kinetic models were applied to predict the yield of four reaction product lumps. The calculation results were compared to the experimental data. Compared to the others, model 4 was the most realistic and closely matching to the experimental data. In model 4 the reaction mechanism was assumed that biomass (corncobs) first decomposed into bio-oil, followed by decomposition of bio-oil into volatile products reversibly and, finally, volatile products decomposed into gaseous products. The yield of bio-oil increased from 42.05% to 54.93% by increasing to ethanol concentration of 0% to 40%.

1 Introduction

As economic and human population growth, the world's energy needs are also increasing. Unfortunately, most of the world's energy needs now are still met from fossil fuels, which are limited, non-renewable and environmentally unfriendly. Since long time ago many scientists have searched for alternative energy sources that have positive properties and contrary to the nature of fossil fuels, as well as finding a process technology to convert them into applicable fuels. One of the alternative energy sources that possesses these characters is biomass. Meanwhile, thermochemical technology have been developed to convert biomass into energy besides biochemical technology [1].

The main biomass thermochemical conversion technologies are gasification, hydrothermal liquefaction (thermochemical liquefaction), pyrolysis, direct combustion, and supercritical fluid extraction. The advantages of thermochemical liquefaction process over other thermochemical processes are that is able to process wet biomass and require relatively lower operating temperatures [2].

The use of methanol and ethanol solvent in the liquefaction of *Ulva fasciata* algae could produce bio-oil with yield of 44% and 40%, instead of using water solvent reaching only 11%. Alcohol compounds were also useful in converting organic acid compounds in bio-oil to esters. Alcohol compounds were also capable of

lowering oxygen content in bio-oil and producing more valuable hydrocarbon compounds with hydrogen and carbon elements from biomass [3].

Liu and Zhang [4] and Wang et al. [5] examined the effect of solvent types on thermochemical liquefaction of pine wood. Their results showed that the yield of bio-oil is higher with solvents of ethanol than with water solvents or acetone.

Biomass decomposition by thermochemical liquefaction processes involves many complex compounds and reactions [6, 7]. Therefore, the reaction rate equations are not arranged according to the compounds involved, but are arranged according to the pseudo-component or group of compounds separated by phase difference in the room temperature.

Some researchers conducted kinetics studies of thermochemical liquefaction against biomass or cellulose. Zhang et al. [8] developed seven models of thermochemical liquefaction kinetics of grassland perennials based on groups of compounds according to their phases, namely solid (biomass), liquids, gases and char. All models are still based on isothermal reactions. The reaction mechanism model closest to the experimental data was that biomass was decomposed as a parallel reaction to liquid, gas and char.

Shi et al. [7], Zhang et al. [9], and Zhang et al. [10] formulated the effect of temperature on the rate of solid decomposition of cellulose or biomass regardless of the

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mechanism of the reaction. The rate of solid decomposition was measured with thermo gravimetric analysis. The developed model was able to calculate the decomposition rate, but this model had not yet taken into account the rate of liquefaction products formation.

The study of thermochemical liquefaction processes on corncobs in water medium was done by Gan and Yuan [11]. In the study, it was studied about the quantity and quality of liquefaction products, instead of studying the kinetics.

Valdez and Savage [12] studied the mechanism and kinetics of thermochemical liquefaction reactions of *Nannochloropsis sp.* isothermally. There are five lumps involved in the reaction, i.e., solids, heavy biocrude, light biocrude, aqueous phase products, and gas.

So far, no researcher studied the mechanism and kinetics of thermochemical liquefaction reaction non-isothermally on biomass, especially corncobs.

The objectives of the research were to study on the mechanism and kinetics of thermochemical liquefaction of corncobs in the ethanol-water solution non-isothermally and the effect of ethanol concentration towards the rate of bio-oil production.

2 Methods

The corncobs, as the main raw material in the research, were obtained from Wonogiri, Central Java. The corncobs were dried under sunshine for about 6 hours. The dried corncobs were grinded and sieved to particle size of 40 mesh to obtain corncobs powder. The powder was further dried in the oven at 100°C for 24 hours and stored in the sealed plastic bag. The corncobs powder was characterized for chemical composition analysis. The result was that corncob was mainly composed of 34.21% hemicellulose, 40.46% cellulose, and 11.36% lignin.

Fig. 1. The sketch of autoclave reactor.

The liquefaction process of corncobs in the ethanol-water solution experimentally carried out in the 150 mL autoclave reactor equipped with magnetic stirrer (Fig. 1). Four grams of corncob powder was put in the reactor, followed by the addition of 0.2 grams of Na_2CO_3 catalyst and 100 mL of ethanol-water solution. The ethanol-water solution was varied at 0%, 20% and 40% (v/v). Nitrogen was blown into the autoclave for 4 minutes to dissipate air inside. The heating process was started at room temperature up to 280°C. The liquefaction process was

finished at a certain time for sampling, by stopping the heating process and being followed by cooling with air fan.

The products were taken after the reactor was cooled and reached the room temperature. The gas product was collected in a gas bag. The remaining product of the reaction was filtered through filter paper to obtain the solid product. The filtrate was evaporated by a rotary vacuum evaporator to obtain the bio-oil. The volatile product was calculated from the difference between the weight of the starting biomass and the weight of the final product.

The yield of products of liquefaction were defined as follows.

$$\text{bio-oil yield} = \frac{\text{weight of bio-oil}}{\text{initial weight of biomass}} \quad (1)$$

$$\text{gas yield} = \frac{\text{weight of gas}}{\text{initial weight of biomass}} \quad (2)$$

$$\text{solid yield} = \frac{\text{weight of solid residue}}{\text{initial weight of biomass}} \quad (3)$$

$$\text{volatile yield} = 1 - (\text{bio-oil yield} + \text{gas yield} + \text{solid yield}) \quad (4)$$

There were four product lumps, i.e. solid (S), bio-oil (B), volatile (V), and gas (G). It was developed four kinetic models for predicting the yield of four product lumps.

The actual reactions were quite complex. Therefore, the simplification of the reaction mechanism must be considered. All the reactions were assumed homogeneous and pseudo first order. The solid product were the biomass that has not been decomposed. It was assumed that there was no solid from reaction products. The ethanol-water solution was quite a lot in the system, so the solvent was not involved in the kinetic equations of the models. For all the kinetic equations, x_B , x_G , x_S , and x_V are yield of bio-oil, gas, solid, and volatile, respectively.

2.1 Model 1

In this model, the reaction mechanism was assumed as depicted in Fig. 2.

Fig. 2. Reaction scheme of model 1.

The kinetic equations of model 1 were as follows.

$$\frac{dx_B}{dt} = k_1 x_S \quad (5)$$

$$\frac{dx_G}{dt} = k_3 x_S \quad (6)$$

$$\frac{dx_S}{dt} = -(k_1 + k_2 + k_3) x_S \quad (7)$$

$$\frac{dx_V}{dt} = k_2 x_S \quad (8)$$

2.2 Model 2

In model 2, the reaction mechanism was assumed as shown in Fig. 3.

Fig. 3. Reaction scheme of model 2.

The kinetic equations of this model were as follows.

$$\frac{dx_B}{dt} = k_1 x_S - k_2 x_B \quad (9)$$

$$\frac{dx_G}{dt} = k_3 x_V \quad (10)$$

$$\frac{dx_S}{dt} = -k_1 x_S \quad (11)$$

$$\frac{dx_V}{dt} = k_2 x_B - k_3 x_V \quad (12)$$

2.3 Model 3

The reaction mechanism of model 3 was assumed as shown in fig. 4.

Fig. 4. Reaction scheme of model 3.

The kinetic equations of the model were as follows.

$$\frac{dx_B}{dt} = k_1 x_S - k_2 x_B - k_3 x_B \quad (13)$$

$$\frac{dx_G}{dt} = k_3 x_B \quad (14)$$

$$\frac{dx_S}{dt} = -k_1 x_S \quad (15)$$

$$\frac{dx_V}{dt} = k_2 x_B \quad (16)$$

2.4 Model 4

The reaction mechanism of model 4 was assumed as shown in fig. 5.

Fig. 5. Reaction scheme of model 4.

The kinetic equations of the model were as follows.

$$\frac{dx_B}{dt} = k_1 x_S + k_3 x_V - k_4 x_B \quad (17)$$

$$\frac{dx_G}{dt} = k_5 x_V \quad (18)$$

$$\frac{dx_S}{dt} = -k_1 x_S \quad (19)$$

$$\frac{dx_V}{dt} = -k_3 x_V + k_4 x_B - k_5 x_V \quad (20)$$

k_j is the reaction rate constant, where j is the reaction number. k_j is depend on the temperature (T) of the reaction system, and it is described by Arrhenius equation:

$$k_j = A_j \exp\left(-\frac{E_j}{RT}\right) \quad (21)$$

where A_j is the pre-exponential factor, E_j is the activation energy, R is the gas constant.

The sistem temperature was not constant or time dependent as the process was non-isothermal. The correlation of temperature (T) and time (t) was discribed by equation (22).

$$T(t) = \begin{cases} a + bt, & t \leq t_1 \\ T_0 + ct^d, & t_1 < t \leq t_2 \\ T_1, & t > t_2 \end{cases} \quad (22)$$

where a , b , c , d , T_0 , T_1 , t_1 , and t_2 was determined by the experimental data.

The unknown kinetic parameters (A_j , E_j) were estimated by the nonlinear least square method, with the following objective function (i.e., the sum of the squares of the differences between the calculation results and the experimental data):

$$SSE = \sum_{i=1}^N \left((x_{B,cal,i} - x_{B,dat,i})^2 + (x_{G,cal,i} - x_{G,dat,i})^2 + (x_{S,cal,i} - x_{S,dat,i})^2 + (x_{V,cal,i} - x_{V,dat,i})^2 \right) \quad (23)$$

SSE is sum of squared errors. In equation (23), the subscripts “cal” and “dat” represent the calculation and the experimental results, respectively. N is the total number of experimental data.

The kinetic parameters (A_j , E_j) were obtained by minimizing of equation (23). The kinetic equations were simultaneous first order differential equation, which were solved by Runge-Kutta method with initial condition $x_S = 1$ and $x_B = x_G = x_V = 0$ to estimate the yield of the products (x_B , x_G , x_S , x_V) each time interval.

3 Results and discussion

This section reports the evaluation of the kinetic models and the effects of ethanol concentration, based on the actual products yield from experimental data with variations in ethanol concentrations.

3.1 Evaluation of kinetic models

The four kinetic models were applied to the three experimental data with variation in ethanol concentration. The best model was determined based on the smallest sum of squared errors (SSE) and mean absolute errors (MAE). The SSE and the MAE values of each model are shown in table 1. Table 1 shows that model 4 has the smallest SSE and MAE values, so model 4 is considered the best model that can approach experimental data.

Table 1. The sum of squared errors (SSE) and the mean of absolute errors (MAE) of the models.

Model	SSE	MAE
1	0.0093	1.4886
2	0.0045	0.8819
3	0.0049	0.9140
4	0.0043	0.8803

Model 4 was tried to be applied to the experimental data. One of the experimental data, the products yield with ethanol concentration of 20% and the calculation results with model 4, is shown in fig. 6. It is seen that the experimental data was approached quite well by model 4.

Fig. 6. Experimental data (discrete point) and calculated (continuous curves) product yields with model 4 using ethanol concentration of 20%.

3.2 Effect of ethanol concentration

The effect of ethanol concentration was studied with model 4 approach, which was selected as the most appropriate model. Fig. 7 and 8 shows the difference in the yield of bio-oil products due to different ethanol concentrations. The three curves show that when the reaction time reached 100 minutes the bio-oil yield reached the maximum value. In that case, the production of bio-oil reached equilibrium. Using ethanol solution from 0% to 40% was able to increase the maximum bio-oil yield from 42.05% to 54.93%.

Fig. 7. Yield of the products at the end of liquefaction process with different concentration of water-ethanol solution.

The biomass conversion can be calculated by subtracting 100% with the percent yield of solid product. In fig. 7 and 9, we can see that the increase in ethanol concentrations had no significant effect on the increase in biomass conversion, which only increased from 76.57% to 78.3%. The increase in bio-oil yield was not obtained from the increase in biomass decomposition rate, but it was obtained from the decrease in volatile production from 28.95% to 21.7% (fig. 7 and 10). Thus, the increase in ethanol concentration could decrease the rate of volatile formation as well as encouraging the rate of bio-oil formation.

Fig. 8. Profile of bio-oil yield against time with variation of ethanol concentration.

The research results of Zhang and Zhang [13], Chen et al. [14], Yuan et al. [15], and Cheng, et al. [16] also showed the synergistic effect of co-solvent ethanol on the increase in bio-oil production of thermochemical liquefaction processes, although each used different biomass feedstocks.

Fig. 9. Profile of solid yield against time with variation of ethanol concentration.

Chen et al. [14] stated that the conversion and yield bio-oil of *Dunaliella tertiolecta* reached a maximum by using 40% ethanol solution at 320°C, but decreased if the concentration of ethanol was more than 40%. Biomass conversion reached 98.24% and maximum bio-oil yield reached 64.68%.

The results of Yuan et al. [15], which examined the effect of ethanol concentration on rice stalk liquefaction, showed that the bio-oil yield reached the maximum value with 50% ethanol solution at 300°C. The result was similar to the research of Cheng et al. [16] on the liquefaction of pine wood in ethanol solution, which had result that the maximum bio-oil yield (65%) could be achieved with 50% ethanol solution at 300°C.

Fig. 10. Profile of volatile yield against time with variation of ethanol concentration.

According to Chen et al. [14], the presence of ethanol caused the reaction of ethanol with amides and carboxylic acids to form ethyl ester, which was quite abundant in bio-oil. In addition, ethanol also becomes a hydrogen donor in liquefaction process.

The gas yield increased from 5.58% to 11.77% with the addition of ethanol concentration up to 40% (fig. 7 and 11). This result differed from that of Cheng et al. [16], which had result that the yield of gas did not changed much with the addition of ethanol concentration, except at the concentration of ethanol close to 100%, where gas yield decreased slightly.

Fig. 11. Profile of gas yield against time with variation of ethanol concentration.

Although the addition of ethanol concentration up to 40% could increase the bio-oil yield up to 54.93%, it is recommended that the ethanol concentration applied is 20% for economic reasons. The increase in bio-oil yield with the addition of ethanol concentration from 20% to 40% was not significant, compared to the increase in price of ethanol.

The effect of addition of ethanol concentration was also seen in the activation energy value of biomass decomposition reaction (E_1) to bio-oil which decreased from 19,927.2 J/mol to 16,158.1 J/mol (table 2). The decrease in the activation energy resulted in the increase in the rate of bio-oil formation.

Table 2. The energy activations, E (J/mol), from calculation with model 4.

Ethanol Concentration	E ₁	E ₃	E ₄	E ₅
0%	19927.2	27459.8	26641.5	34205.7
20%	17591.8	34704.4	24385.4	25692.5
40%	16158.1	28473.9	24380.7	23931.5

4 Conclusions

The kinetics study on non-isothermal thermochemical liquefaction of corncobs in ethanol-water solution had been performed for the effect of ethanol concentration. From the reaction without ethanol (or only water) to the reaction with ethanol concentration up to 40%, the activation energy decreased from 19,927.2 J/mol to 16,158.1 J/mol, so the reaction rate constant increased as well as the reaction rate to form bio-oil. Though, it was the highest yield of bio-oil achieved, but it was suggested to use ethanol concentration up to 20% for the economic reasons. Model 4 was found to be the best one for approaching the experimental data of thermochemical liquefaction of corncobs in the ethanol-water solution. In model 4 the reaction mechanism was assumed that biomass (corncobs) first decomposes into bio-oil, followed by decomposition of bio-oil into volatile products reversibly and finally volatile products decompose into gaseous products.

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