Production of furfural from palm oil empty fruit bunches: kinetic model comparation

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Abstract. Furfural is a chemical compound that can be applied to pharmaceuticals, cosmetics, resins and cleaning compound which can be produced by acid hydrolysis of biomass. Indonesia's demand for furfural in 2010 reached 790 tons that still imported mostly 72% from China. In this study, reaction kinetic models of furfural production from oil palm empty fruit bunches with submitting acid catalyst at the beginning of the experiment will be determine. Kinetic data will be obtained from hydrolysis of empty oil palm bunches using sulfuric acid catalyst 3% at temperature 170^{o}C, 180^{o}C and 190^{o}C for 20 minutes. From this study, the kinetic model to describe the production of furfural is the kinetic model where generally hydrolysis reaction with an acid catalyst in hemicellulose and furfural will produce the same decomposition product which is formic acid with different reaction pathways. The activation energy obtained for the formation of furfural, the formation of decomposition products from furfural and the formation of decomposition products from hemicellulose is 8.240 kJ/mol, 19.912 kJ/mol and -39.267 kJ / mol.

1. Introduction

Furfural is a chemical compound that is applied to pharmaceuticals, cosmetics, resins, and cleaning compound. In addition, furfural is widely used as an extracting agent, solvent, vulcanizing agents, flavoring agents, commercial components of pesticides, antiseptics, disinfectants, and so on. Furfuryl alcohol compound is a chemical produced from hydrogenation process of furfural and consuming 62% furfural world market [1].

Industries that produce furfural in Indonesia are still few in number. The consumption of furfural in Indonesia is steadily increasing. In 2010, the needs of furfural in Indonesia reached 790 tons. During this time, the needs of furfural in Indonesia met through import, especially from China, which is the largest furfural manufacturer in the world [2].

Furfural can be produced from biomass through hydrolysis. Palm oil as one of the largest agricultural commodities in Indonesia can be used in furfural production. Around 22-23% of the total fresh fruit bunches become solid waste in the form of Palm oil empty fruit bunches (POEFB) . POEFB is a lignocellulose biomass (cellulose, hemicellulose, and lignin) that can be hydrolyze into a variety of chemical compounds.

Furfural is generally produced with hydrolysis of hemicellulose into pentose which is then dehydrated into furfural. Acids, such as H_2SO_4 and HCl, can catalyze hydrolysis reaction of hemicellulose. Studies

have been conducted on sulfuric, hydrochloric, phosphoric, and nitric acids that may improve hydrolysis of hemicellulose and cellulose [3]. However, sulfuric acid is commonly used to hydrolyze polysaccharides into monosaccharaides [4].

Researches on kinetic reactions of furfural production have been done by Dussan et al., Hua et al., and Liu et al. [5,6,7] at different lignocellulosic materials, but there is no research that focus on kinetic model comparation of furfural production. This research studies furfural kinetic models based on POEFB with submitting sulfuric acid catalyst at the beginning of the experiments.

2. Method

2.1. Experiment

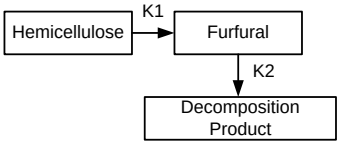
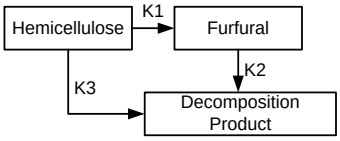
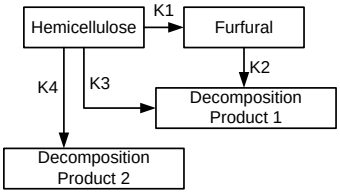
The raw material used was POEFB with the composition of the cellulose - alpha, hemicellulose, and lignin 40.3%, 31.2% and 23.2%, respectively. POEFB particle size was reduced to 30 mesh, washed with water, dried, soaked with aqueous ammonia solution 5% for 24 hours, washed with water until neutral, dried and then hydrolyzed to produce furfural. Hydrolysis process for the formation of furfural was done by pressurized reactor with 1 liter volume. Mass ratio of POEFB and 3% sulfuric acid solution was 1:20. The time to reach the desired temperature was about ± 30 minutes. The reaction times start when the desired reaction temperature was reached. The experimental data were taken every 5 minutes at 170°C, 180°C and 190 °C for 20 minutes with 3% sulfuric acid catalyst was add at 30^{o}C. Furfural concentration analysis was performed using HPLC with Aminex HPX - 87H Ion Exclusion Column. The eluent was H_2SO_4 0.008 N with flow rate 1 ml/min. The detector was Refractive Index Detector with the temperature of detector and column were 35^{o}C.

2.2. Kinetics Model

Reaction kinetic models to be tested in this study consist of three models. In the first model hemicellulose is converted into furfural and then furfural is converted into decomposition products. The second model is modification of the first model in which hemicellulose is also produced decomposition products. While the third model assumes the hemicellulose decomposition products are divided into two products.

Xylose which is a degradation compound from hemicellulose before furfural is not included in this reaction models. This is due to research methods that add acid catalyst in the beginning of the experiment. With this method, there isn't xylose concentration detected at the desire reaction temperatures. Furfural kinetic models are shown in table 1. C_{HC}, C_F, and C_{DP} are hemicellulose concentration, furfural concentration, and decomposition products concentration.

Tabel 1. Furfural Kinetic Reaction Models

	Furfural Kinetic Reaction Models	Kinetic Reaction Equations
First Model		$\frac{dC_{HC}}{dt} = -K_1 C_{HC}$ (1) $\frac{dC_F}{dt} = K_1 C_{HC} - K_2 C_F$ (2) $\frac{dC_{DP}}{dt} = K_2 C_F$ (3)
Second Model		$\frac{dC_{HC}}{dt} = -K_1 C_{HC} - K_3 C_{HC}$ (4) $\frac{dC_F}{dt} = K_1 C_{HC} - K_2 C_F$ (5) $\frac{dC_{DP}}{dt} = K_2 C_F + K_3 C_{HC}$ (6)
Third Model		$\frac{dC_{HC}}{dt} = -K_1 C_{HC} - K_3 C_{HC} - K_4 C_{HC}$ (7) $\frac{dC_F}{dt} = K_1 C_{HC} - K_2 C_F$ (8) $\frac{dC_{DP1}}{dt} = K_2 C_F + K_3 C_{HC}$ (9) $\frac{dC_{DP2}}{dt} = K_4 C_{HC}$ (10)

2.3 Calculation of Kinetic Data

Reaction rate constants (k_1, k_2, k_3, and k_4) obtained by optimized experimental data with kinetic models using optimization toolbox fminsearch on MATLAB software. In the calculation process, the concentration of hemicellulose in POEFB was assumed 0.0354 mol/L at the desired reaction temperature. Reaction rate constants at temperature of 170°C, 180°C and 190°C will be plotted with the Arrhenius equation to get the activation energy.

3. Results and Discussion

3.1. Determination of Kinetic Model

Data was taken every 5 minutes for 20 minutes at 170^{o}C, 180^{o}C and 190^{o}C. Reaction kinetic models selected by optimization value sum of square error of experimental data on kinetic models using MATLAB software with optimization toolbox fminsearch. Error occured in the first and third model simulation. First model isn't optimum because this model doesn't consider the hemicellulose degradation reactions that can produce variety of products beside furfural. The third model predicted that will be other kinds of decomposition products from hemicellulose. However, this model is not very significant to determine kinetic model because basically hemicellulose consists of pentose and hexose sugars [8]. Generally, pentose and hexose sugars in acid hydrolysis process will produce the same decomposition products.

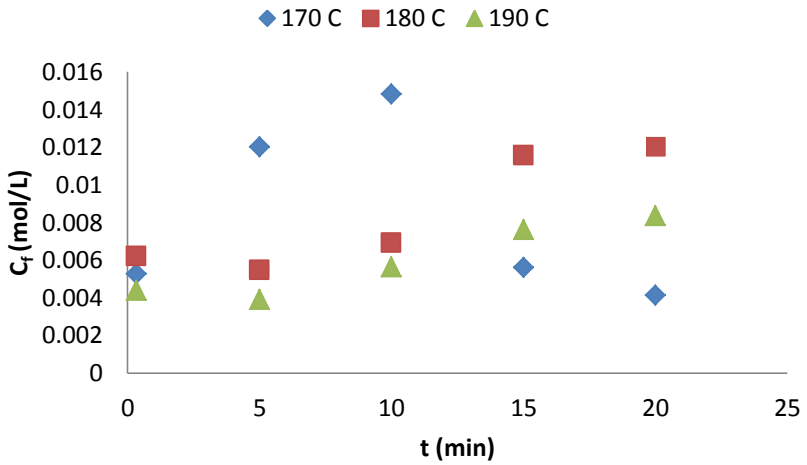


Figure 1. Furfural Concentration Data

Based on the optimization results, second model more suitable to describe the kinetic of furfural production. Second models can describe the general prediction that occur in the conversion process of hemicellulose into furfural, furfural into decomposition products and hemicellulose into decomposition products. Hemicellulose consist of pentose sugars and hexose sugar that can produce a variety of decomposition products from hydrolysis reaction with acid catalyst. Hydrolysis process with acid catalyst will convert pentose sugars in hemicellulose into furfural compound [8]. Danon et al. [9] showed that furfural will be decomposed into two major products which is formic acid and resinous tars. On the other side, hexose sugars will be converted to HMF (5-hydroxymethylfurfural) which then will be converted into levulinic acid and formic acid [10,11]. From the various studies mentioned above, it shows that hemicellulose can be converted to formic acid from different pathways. The detail description on second kinetic model can be seen in figure 2.

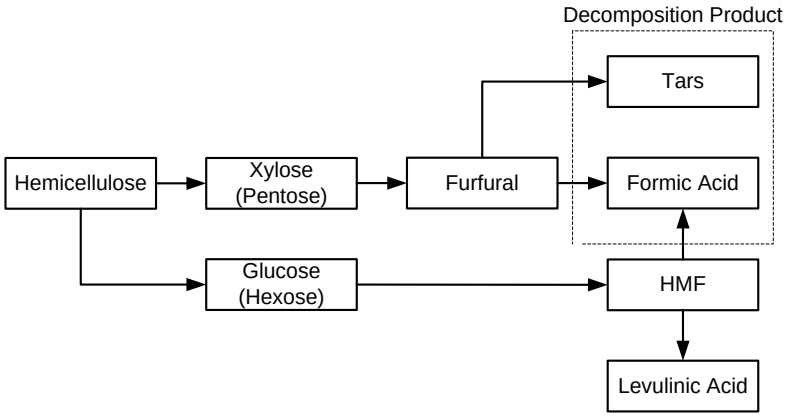


Figure 2. Second Model Detail Scheme

3.2. Energy Activation Calculation

Second model reaction rate constants was calculated from optimization furfural data with the model in each temperature using fminsearch MATLAB optimization toolbox. Activation energy (E) was calculated using Arrhenius equation with plot In K versus 1/T [12].

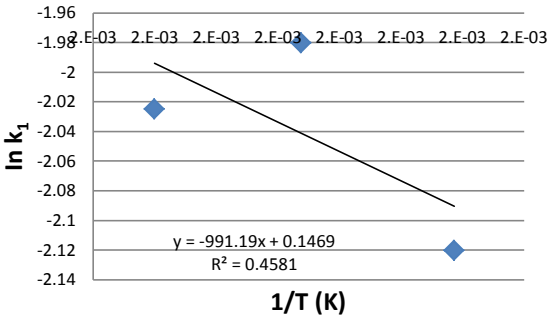
$$Ink_A = In\ A - \frac{E}{R}\left(\frac{1}{T}\right) \quad (11)$$

Tabel 2. Second Model Reaction Constants

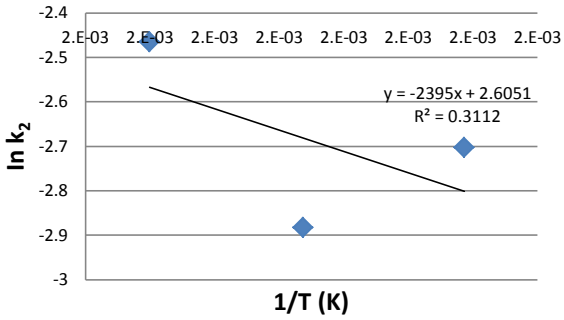
Temperature (^oK)	1/T	k_1	In k_1	k_2	In k_2	k_3	In k_3
443	0.002257	0.12	-2.12026	0.067	-2.70306	0.1	-2.30259
453	0.002208	0.138	-1.9805	0.056	-2.8824	0.087	-2.44185
463	0.00216	0.132	-2.02495	0.085	-2.4651	0.063	-2.76462

Tabel 3. Second Model Activation Energy

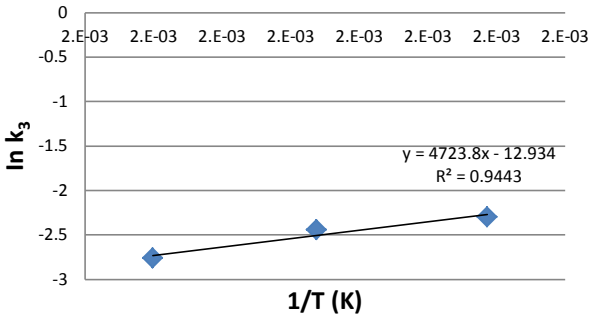
Reaction Rate Constants	Activation Energy (kj/mol)
k_1	8.240
k_2	19.912
k_3	-39.267



(a)



(b)



(c)

Figure 3. Arrhenius Plot In k versus 1/T (a) k_1 (b) k_2 (c) k_3

Based on table 3, the activation energy of k_2 (furfural into decomposition products activation energy) was 19.912 kJ/mol which was less than the value of activation energy from previous studies such as 60.3 kJ/mol [13], 132 kJ/ mol [14] and 106 kJ/mol [15]. The low activation energy happened because the effect of submitting sulfuric acid catalyst in the beginning of the experiments. Acid catalyst made the formation of furfural and decomposition products started early which was resulted in low furfural concentration at the desired temperature. The low furfural concentration effects smaller activation

energy value to convert furfural become decomposition products. The same phenomenon also applied to the activation energy of k_1 (hemicellulose into furfural activation energy) which was 8.240 kJ / mol. The activation energy of k_3 (hemicellulose into decomposition products activation energy) is in negative value. This indicates that the reaction rate decreases with increase the temperature. Therefore, further researches need to investigate chemical reactions of hemicellulose especially hexose sugars into decomposition products.

4. Conclusion

Kinetic model that describes the production of furfural with submitting sulfuric acid catalyst in the beginning of the experiments was the kinetic model where in this model hemicellulose and furfural will tend to produce the same decomposition products namely formic acid. Hexose sugars in hemicellulose were converted into formic acid at the end of the reaction pathway. The activation energy obtained by this study for the formation of furfural from the hemicellulose, the formation of decomposition products from furfural and the formation of decomposition products from hemicellulose are 8.240 kJ/mol, 19.912 kJ/mol and -39.267 kJ/mol. Formic acid as final decomposition product of hexose and pentose sugars must have detail examination in future.

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