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Formic Acid Production from Palm Oil Empty Fruit Bunches

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Abstract

Formic acid (FA) is a weak acid that has potential as hydrogen storage, so it can be used directly as fuel for fuel cells technology. FA can be generated as a byproduct from hydrolysis process of lignocellulose biomass. Palm oil empty fruit bunches (POEFB) is one of palm oil industry waste in Indonesia and could be used to produce chemicals such as FA. In this study, we investigated the production of FA from POEFB hydrolysis process using sulfuric acid catalyst, and we determined kinetic model of FA production from POEFB hydrolysis process. FA production was done in a pressurized reactor with temperature around 150 - 170ºC using 1M sulfuric acid catalyst. The highest FA was formed at reaction temperature of 170ºC after20 minutes reaction that produced 0.031 mol/L and 46.6 %molFA yield. FA production kinetics were also investigated by compared two kinetic models. The first model (model 1) predicted FA production from C5 (pentose sugars) and C6 (hexose sugars). On the other side, the second model(model 2) predicted FA production only from C6 sugars. Model 2 was a kinetic model that can describe FA production from POEFB hydrolysis process. Based on these kinetic model, activation energy of cellulose hydrolysis, HMF formation, humins formation and FA formation were 86.739 kJ/mol, 104.157 kJ/mol, 74.397 kJ/mol and 86.706 kJ/mol, respectively.

Keywords: palm oil empty fruit bunches; acid hydrolysis reaction; formic acid; kinetic reaction.

INTRODUCTION

Biomass is organic material that derived from living organisms [1]. Waste biomasses such as agricultural residue, agro-industrial waste and liquid waste are the raw material that has potential to be used as source of biohidrogen, biomethane and other biochemical [2]. Lignocellulose biomasses which was widely available in nature are candidates that can be used as raw material for biofuel and biochemical production with low production cost [3].

Indonesia has great opportunity to utilize many biomasses as alternative fuel. One of Indonesia biomasses that can be used as alternative fuel is palm oil. Indonesia palm oil is the largest palm oil producer in the world. Indonesia palm oil reaches 27 million tonnes production capacity in 2012 [4]. One of the wastes from oil palm plantation is palm oil empty fruit bunches (POEFB).

POEFB as biomass can be converted into fuel like hydrogen fuel. Hydrogen energy is one alternative energy that use fuel cells technology to convert chemical energy into electrical energy [5]. Biomasses as a raw material for hydrogen energy production are very attractive because it comes from a renewable material [6]. The conversion process of biomass into hydrogen can be produced from gasification or reforming process using supercritical water which both of these processes are very expensive to be applied [7,8]. One alternative method for producing hydrogen is to produce formic acid from biomass hydrolysis process as fuel for the fuel cell technology.

Formic acid (FA) as a weak acid that used as energy storage and chemical synthesis has unique properties such as non-toxicity, favorable energy density, and biodegradability [9]. In general, many industries utilize FA such as textiles, pharmaceuticals and food chemicals [10]. Besides that, FA application as fuel is also very large. FA canis decomposes at high temperatures, and FA can produce hydrogen gas which acts as hydrogen donor in water or other solvent [11]. Because of its unique properties, FA has potential as hydrogen storage that can be used as fuel for fuel cells technology[5,10,12-14].

FA production can be formed with hydrogenation process of CO_2 using hydrogen gas [15,16]. However, this process has problems from many aspects such as large scale production, hydrogen gas storage and hydrogen gas transportation [17]. On the other side, FA can be produced using more simple technology from biomass or sugars with varieties of production methods [6,17,18-20].

FA can be generated as a byproduct in many biorefinery plants[9]. Lignocellulose biomass such as POEFB can be converted into FA through hydrolysis process using acid catalyst. Lignocellulose biomass consists of cellulose, hemicellulose, lignin and ash [21]. Cellulose which is consists of C6 (hexosesugars) can be hydrolyzed to 5 - hydroxymethylfurfural (HMF) and dehydrated to levulinic acid and FA [22]. On the other side, C5 (pentose sugars) from hemicellulose can be decomposed into xylose which can be dehydrated into furfural [23]. After that, FA can produce from formyl group cleavage or aldehyde group hydrolytic fission of furfural [24].

FA that can be produced from final decomposition products of HMF and furfural at high temperatures in biomass hydrolysis process make research about formic acid is very interesting topic. Nowadays, there are not many researches that focus in FA as the main product from biomass hydrolysis. Therefore, the purpose of this study was to produce and investigate FA kinetic production from POEFB hydrolysis process using sulfuric acid catalyst.

MATERIALS AND METHODS

Materials: POEFB fiber came from palm oil industry named PTPN 5 Kertajaya, Banten, Indonesia. POEFB fiber was reduced to 20 mesh, washed, dried, pretreated by soaked aqueous ammonia solution 13.13% for 14 hours [25], washed with water to neutral the pH from ammonia, dried until moisture content reach 1 – 5% and keep in plastic bag until further uses. Ammonia solution (25%) which was supplied by Merck, Germany used as the pre-treatment chemical. Sulfuric acid (96.1%) from Mallinckrodt, England was used as the acid catalyst. Standards analytical grade of formic acid were purchased from Sigma Aldrich, United States.

Kinetic experiments

Kinetic experiments were done by pressurized stirred reactor. POEFB and water was added to reactor with ratio 1:25. Then reactor tightly sealed and heated. When the desire temperature reached, sulfuric acid catalyzed (1M) was injected into reactants. The reaction times started when sulfuric acid catalyst was released into reactor. The samples were taken in 10, 20, 30, 45, 90, and 120minutes reaction at 150, 160 and 170°C for 120 minutes reaction.

FA Analysis

FA concentration analysis was performed using high performance liquid chromatography (HPLC) with Aminex HPX - 87H Ion Exclusion Column. The eluent was sulfuric acid 0.006 N with flow rate 0.6 ml/min. HPLC detector was Refractive Index Detector with the temperature of detector and column were 60°C.

FA kinetics model calculation

In this study, determination of FA kinetic model from POEFB hydrolysis process divided into two models. The first model (model 1) predicted FA formation from hexose sugars (C6 sugars) and pentose sugars (C5 sugars) as shown in Figure 1. On the other hand, the second model (model 2) predicted FA production only from hexose sugars (C6 sugars) as shown in Figure 2. Model 2 was modified from levulinicacid production model based on Girisuta *et al.* (2013) [26].

From Figure 1, we can make kinetic equations:

$$\frac{dC_{glucan}}{dt} = -k_1 \,.\, C_{glucan} \tag{1}$$

$$\frac{dC_{glucose}}{dt} = k_1 \,.\, C_{glucan} - k_2 . C_{glucose} - k_3 . C_{glucose} \tag{2}$$

$$\frac{dC_{HMF}}{dt} = k_2 . C_{glucose} - k_4 . C_{HMF} \tag{3}$$

$$\frac{dC_{FA}}{dt} = k_4 . C_{HMF} + k_8 . C_{furfural} \tag{4}$$

$$\frac{dC_{DP}}{dt} = k_3 . C_{glucose} + k_7 . C_{xylose} + k_9 . C_{furfural} \tag{5}$$

$$\frac{dC_{xylan}}{dt} = -k_5 . C_{xylan} \tag{6}$$

$$\frac{dC_{xylose}}{dt} = k_5 . C_{xylan} - k_7 . C_{xylose} - k_6 . C_{xylose} \tag{7}$$

$$\frac{dC_{furfural}}{dt} = k_6 . C_{xylose} - k_8 . C_{furfural} - k_9 . C_{furfural} \tag{8}$$

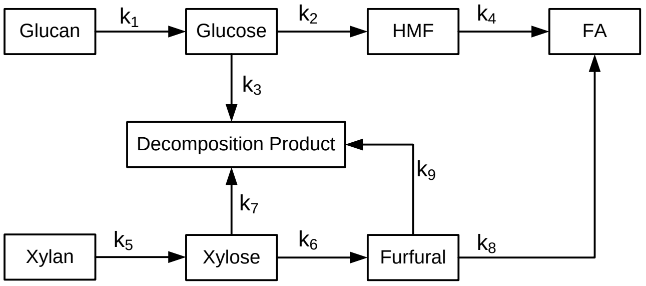


Figure 1: Reaction scheme of FA production from C5 and C6 sugars (Model 1).

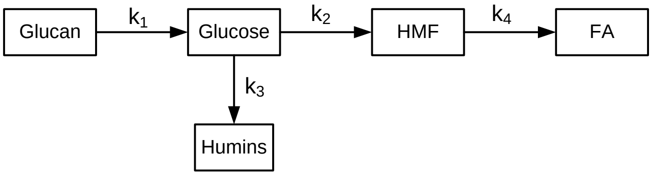


Figure 2: Reaction scheme of FA production from C6 sugars (Model 2).

From Figure 2, we can make kinetic equations:

$$\frac{dC_{glucan}}{dt} = -k_1 . C_{glucan} \tag{9}$$

$$\frac{dC_{glucose}}{dt} = k_1 . C_{glucan} - k_2 . C_{glucose} - k_3 . C_{glucose} \tag{10}$$

$$\frac{dC_{HMF}}{dt} = k_2 . C_{glucose} - k_4 . C_{HMF} \tag{11}$$

$$\frac{dC_{FA}}{dt} = k_4 . C_{HMF} \tag{12}$$

$$\frac{dC_{HUM}}{dt} = k_3 . C_{glucose} \tag{13}$$

From the kinetic equations above, we need to determine 9 reaction rate constants for model 1and 4 reaction rate constants for model 2. Reaction rate constants can be solved using minimization of the sum of square error between the experimental data and the model. Minimization error of experimental data at various temperatures in 1M acid catalyst concentration were formulated:

$$SS = \sum_i \sum_j ([j]_{i\,exp} - [j]_{i\,model})^2 \tag{6}$$

Minimization of sum of square error can be determined by fminsearch optimization (Nedler - Mead Method) using MATLAB. The value of pre-exponential factor and activation energy were determined using Arrhenius equation. Systematically, the relationship between reaction rate constant (k) and temperature (T) was expressed by the Arrhenius equation [27]:

$$\mathrm{k} = \mathrm{A} \exp\left(-\frac{\mathrm{Ea}}{\mathrm{RT}}\right) \tag{7}$$

Where k was reaction rate constant, A was pre – exponential factor, Ea was activation energy (kJ/mol), R was gas constant (kJ/mol.K) and T was temperatur (ºK).

RESULTS AND DISCUSSION

Temperature and Reaction Time Effect in FA production

Based on Figure 3, the highest FA can be produced at reaction temperature of 170ºC after 20 minutes reaction time that produced 0.031 mol/L and 46.6% molFA yield. This means that FA favorably formed at higher reaction temperature which was 170ºC.Danon*et al.* (2013) also found that FA and tar were formed from furfural degradation process at temperature around 160 - 200ºC [28]. On the other side, from the hexose sugars pathway, according to Girisuta *et al.* (2013), who studied the kinetic of levulinicacid production from sugarcane bagasse had produced levulinic acid and FA in temperature around 150 - 200ºC [26].

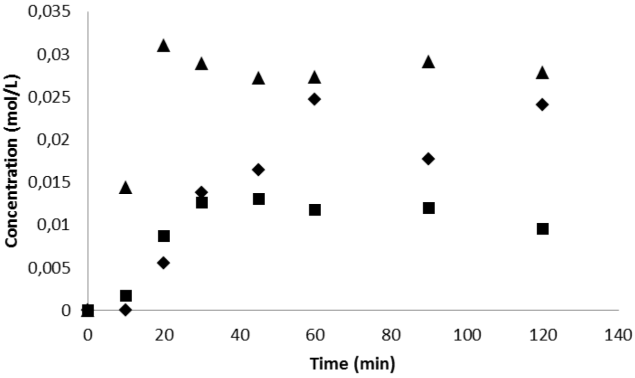


Figure 3: Comparation of FA production in different temperature and reaction time

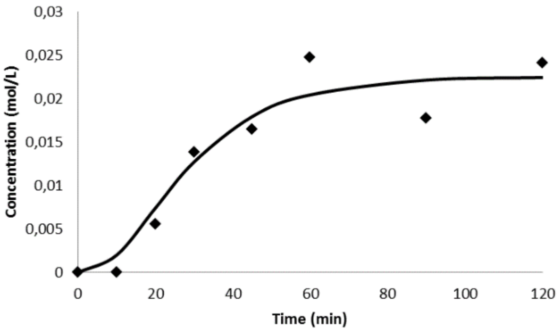
(♦; 150ºC, ■; 160ºC,▲; 170ºC).

It can be seen from Figure 3 that the highest FA tend to form in reaction time around 20-30 minutes at reaction temperature of 160 and 170°C and relatively constant during subsequent reaction time. Another phenomena can be seen at reaction temperature of 150ºC which the highest FA form after60 minutes reaction and remained constant during subsequent reaction time. This can be happened because of the lower reaction temperature, so FA production required longer reaction time to form.

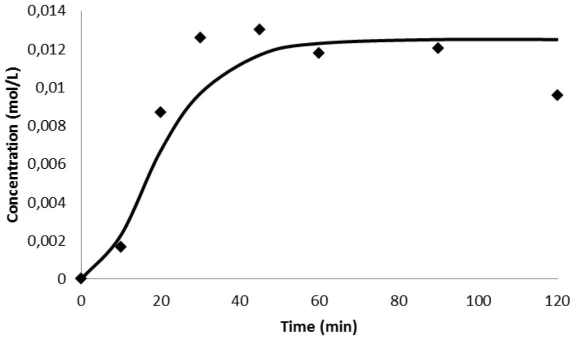
From this research, FA yield was 46.6% mol which was lower than other studies. Albert *et al.* (2012) had produced 53% FA yield fromxylan for 24 hours process reaction with catalytic oxidation process of Keggin-type polyoxometalate (H5PV2Mo10O40) and p-toluenesulfonic acid as additive [6]. On the other side, Gromov*et al.* (2016) had produced FA yield around 65-66% mole from hydrolytic oxidation cellulose with homogeneous Mo-V-P heteropolybifunctional acid catalyst [19]. Based on process complexity from Albert *et al.* (2012) [6] and Gromov*et al.* (2016) [19], we can say that the low yield of FA in this study was still better in terms of economy and simplicity because FA from this research can be produced from hydrolysis reaction of lignocellulosic biomass feedstock with low sulfuric acid catalyst concentration.

Kinetic Study of FA production from C5 and C6 Sugars (Model 1)

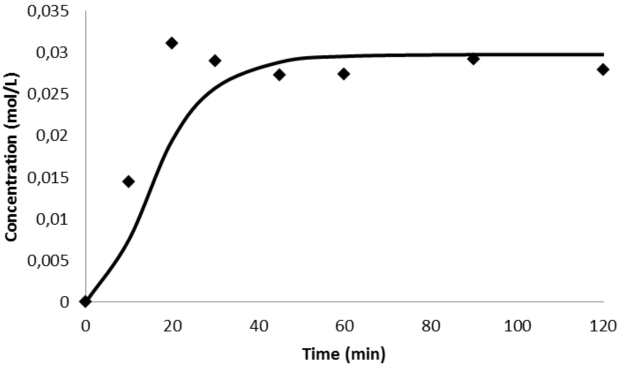
In model 1, FA formation can be predicted from hexose sugars (C6 sugars) and pentose sugars (C5 sugars). According to Figure 4, the optimization results from experimental data and model 1 produce sum of square error value at reaction temperature of 150, 160, and 170°C were 5.1, 2.3, and 2.0, respectively. From this value, it can be seen that the optimization process already maximum because of the low sum of square error value. Activation energy and pre - exponential factor calculation of model 1 was done by Arrhenius equation, so the activation energy and pre - exponential factor can be seen in Table 1.



(a) 150 °C



(b) 160 °C



(c) 170°C

Figure 4: Model 1 optimization results between experimental data (♦; FA) and model (dashed lines).

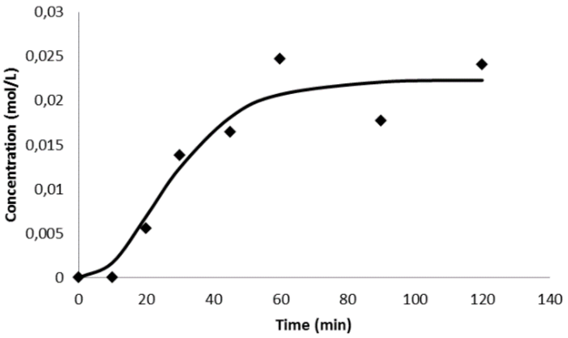
Table 1: .Kinetic parameters of model 1 for FA production.

Reaction Rate Constants	Temperature (°C)			Pre–exponential factor A (s^{-1})	Activation energy Ea (kJ/mol)	R^2
	150	160	170			
k_1	0.092	0.122	0.155	9.68×10^{3}	40.7	0.998
k_2	0.077	0.003	0.006	5.96×10^{-27}	-201.1	0.570
k_3	0.155	0.142	0.078	4.58×10^{-8}	-53.2	0.834
k_4	0.063	0.102	0.146	7.92×10^{6}	65.5	0.995
k_5	0.017	0.083	0.193	5.02×10^{21}	189.7	0.974
k_6	0.001	0.087	0.082	1.07×10^{40}	345.9	0.751
k_7	0.076	0.138	0.047	3.17×10^{6}	-36.4	0.187
k_8	0.120	0.108	0.185	1.40×10^{3}	33.3	0.562
k_9	0.258	0.095	0.067	2.25×10^{-14}	-105.4	0.934

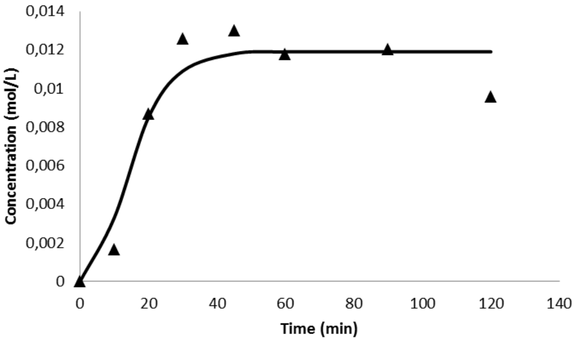
Based on Table 1, the results of kinetic parameters calculation from model 1 produced some negative value on activation energy. This proved that the more complex kinetic model would give more complex optimization calculations. In addition, negative value on activation energy described the mismatch between model 1 and FA production experimental data. Therefore, there should be review about another kinetic model.

Kinetic Study of FA production from C6 Sugars (Model 2)

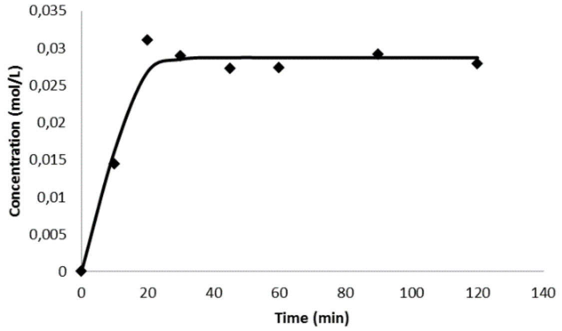
According to model 2, FA formation was predictedonly from C6 sugars. Kinetic model was based on Girisuta *et al.,* (2013) which described FA as a byproduct from levulinic acid production from sugarcane bagasse [26].



(a) 150 ºC



(b) 160 ºC



(c) 170 ºC

Figure 5: Model 2 optimization results between experimental data (♦; FA) and model (dashed lines).

From Figure 5, the results of optimization between experimental data and model 2 was resulted in the value of the sum of square error at reaction temperature of 150, 160 and 170°C were 4.7, 1.2, and 2.6, respectively. The optimization results from model 2 was better than model 1 because of the smaller error values. Activation energy and pre - exponential factor calculation of model 2 was done by Arrhenius equation, so the activation energy and pre - exponential factor can be seen in Table 2.

Table 2: Kinetic parameters of model 2 for FA production.

Reaction Rate Constants	Temperature (ºC)			Pre– exponential factor A (s^{-1})	Activation energy Ea (kJ/mol)	R^2
	150	160	170			
k_1	0.097	0.186	0.295	5.13×10^9	86.7	0.992
k_2	0.033	0.033	0.127	1.92×10^{11}	104.2	0.738
k_3	0.065	0.151	0.168	1.12×10^8	74.4	0.842
k_4	0.097	0.181	0.295	5.04×10^9	86.7	0.996

From Table 2, the results of kinetic parameters calculation from model 2 was better than model 1. It was known from the simplicity of the model and the positive value in all activation energy. Therefore, based on the sum of square error and activation energy calculations, model 2 was chosen as a model that can predict FA production from POEFB hydrolysis process.

Model 2 that predicted FA production from C6 sugars was more suitable than model 1. This happened because model 1 theory about FA formation from C5 sugars can be ignored. FA production from C5 sugars was very small. Danon *et al.* (2013) and Williams and Dunlop (1948) which demonstrated furfural degradation products got small concentration of FA as one of furfural degradation products [28,29]. Moreover, FA production mostly derived from C6 sugar had been widely studied as a byproduct from levulinic acid production [22,23,26,30-46].

According to Table 2, the highest and the lowest activation energy for FA production came from glucose hydrolysis reaction. This proved that temperature had big effect in glucose hydrolysis process. The higher the temperature would make glucose tend to form HMF than humins. On the other side, if the reaction temperature was low, the glucose would tend to form humins.

Based on Table 3, comparing the same kinetic model from Girisuta *et al.* (2013) [26] and Dussan *et al.* (2013) [47], the activation energy of cellulose hydrolysis, HMF formation, and humins formation in this study were quite low which were 86.7 kJ/mol, 104.2 kJ/mol and 74.4 kJ/mol. Beside that, Shuai and Pan (2012) stated that general activation energy of cellulose hydrolysis at various temperatures and acid concentrations was 170-180 kJ/mol [48]. The low activation energy of cellulose hydrolysis, HMF formation, and humins formation in this study can be caused by POEFB particle size reduction and ammonia pretreatment before POEFB hydrolysis process. Smaller particle size and ammonia pretreatment can make accessibility of POEFB more effective to produce FA which resulted the low activation energy in FA production.

Table 3. Kinetic parameters comparation for FA production.

	Reaction rate constants	[26]	[47]	This study
Pre-exponential factor A (s^{-1})	k_1	1.59×10^{18}	2.69×10^{21}	5.13×10^{9}
	k_2	6.56×10^{18}	2.36×10^{17}	1.92×10^{11}
	k_3	6.94×10^{19}	2.38×10^{20}	1.12×10^{8}
	k_4	$2.71 \times 10^{14*}$	$6.58 \times 10^{14*}$	5.04×10^{9}
Activation energy Ea (kJ/mol)	k_1	144.85	188.9	86.7
	k_2	152.14	155.5	104.2
	k_3	161.41	186.2	74.4
	k_4	101.63*	121.3*	86.7

*Pre-exponential factor and activation energy of levulinic acid production

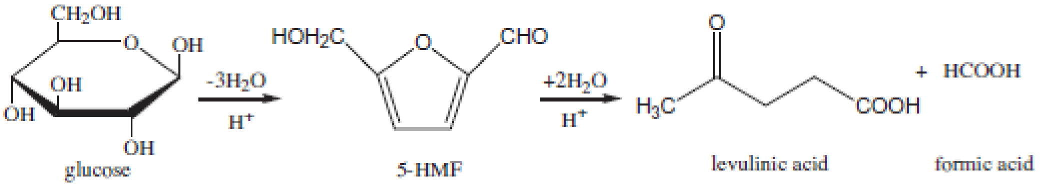


Figure 6: Scheme of glucose decomposition to levulinic acid and formic acid [31].

CONCLUSION

In this study, we investigated FA production from POEFB hydrolysis reaction. FA production was done in pressurized reactor at reaction temperature of 150 - 170ºC with 1M sulfuric acid catalyst. The highest FA was formed at reaction temperature of 170ºC after 20 minutes reaction that produced 0.031 mol/L and 46.6% molFA yield. Model 2 that predicted FA only from C6 sugars can describe FA production from POEFB hydroysis reaction. Based on kinetic model calculations, the activation energy of cellulose hydrolysis reaction, HMF formation, humins formation and FA formation were86.739 kJ/mol, 104.157 kJ/mol, 74.397 kJ/mol and 86.706 kJ/mol, respectively.

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