Kinetics of Oil Palm Empty Fruit Bunch Phenolysis in the Presence of Sulfuric Acid as a Catalyst

Ali Ahmadzadeh, Sarani Zakaria

School of Applied Physics, Faculty of Science and Technology, University Kebangsaan Malaysia, UKM Bangi 43600, Selangor, Malaysia

ABSTRACT: Oil palm empty fruit bunch (EFB) was successfully phenolyzed in the presence of sulfuric acid as a catalyst at different temperatures, reaction times, and percentage of catalyst used. Sulfuric acid was used as catalyst (5 and 8%) at the reacting temperature of 110–150°C with various reaction times. The kinetics parameters along with the weight of reacted EFB and phenol were calculated using the second- and third-order reaction kinetics models. The weight of the reacted EFB in phenol shows that about 97% of EFB was liquefied during the reaction. However, only 70% of phenol was reacted with EFB. The kinetic studies showed that the EFB phenolysis in the presence of sulfuric acid followed a bimolecular type of the second-order reaction. The activation energy calculated from the Arrhenius equation was 50.7 and 18.06 kJ/mol when the catalyst concentration was 5 and 8%, respectively. It can be depicted that the activation energy decreased as the catalyst increased. The reaction enthalpy showed that the liquefaction of EFB in phenol had dominantly followed the endothermic reaction. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3529–3533, 2007

Key words: kinetics; EFB liquefaction; activation energy; phenol; catalyst

INTRODUCTION

During the last six decades, many attempts and efforts have been made to utilize lignocellulosic and wood waste by using chemical or biochemical processing methods. Several techniques, such as olification,[1] biomass conversion,[2] liquefaction, and plasticization,[3] have been intensively studied and developed.

Lignocelluloses materials, depend on species, consists of approximately 40–50% cellulose, 20–30% hemicellulose, and 20–30% lignin. The structure of cellulose in most of the lignocellulosic material is similar, but the structure of lignin and hemicellulose is very different.[4] Cellulose is a thermoset, linear high-molecular weight polymer built up exclusively of β-D-glucose unit. The glucose molecule has three hydroxyl groups. Therefore, cellulose tends to form a significant number of hydrogen bonds. Lignin has major phenolic groups. Lignin and hemicellulose are thermoplastic.[4,5]

In Malaysia, the oil palm empty fruit bunches (EFB) is a major byproduct of the oil palm industry. After being milled at a palm oil mill, every ton of fresh fruit bunches produces ∼ 0.22 tons of EFB. Total amount of EFB are ∼ 2.96 × 10⁶ ton/year.[6] To date, these large amount of EFB have not been fully utilized commercially, despite many studies on the use of EFB for making tiles,[7] pulp and paper,[8] medium density fiber board,[9,10] particleboard,[11] cementboard,[12] solid carbon,[13,14] and polyurethane.[15,16]

Several studies have been carried out on wood waste liquefaction. The liquefaction of EFB has started recently.[17] However, there is no kinetic study of EFB liquefaction has been reported. Therefore, in this article, it was aim to study the bulk kinetics of EFB liquefaction carried out in the presence of sulfuric acid as a catalyst using the kinetics models.

EXPERIMENT

Materials

EFB was used as a raw material and was obtained from Sabutek Sdn. Bhd. The air-dry EFB was ground to 60–70 wire mesh by a ball mill. Then, it was dried at 105°C for 8 h in an air-circulated oven and kept inside of polyethylene bags. Sulfuric acid 97%, were used as a catalyst was obtained from Aldrich. Methanol, phenol, and other chemicals were supplied by Hamburg chemical, of extra pure grade, were used without further purification.

Liquefaction and sample preparation

EFB (30 g), phenol (90 g), and sulfuric acid as a catalyst (5%, 8% of initial input phenol weight) were charged into a four-neck glass reaction flask (500 mL) equipped with a reflux condenser, thermometer, and electrical stirrer.

The liquefaction reaction was carried out in as electrical heating mantle form 30 to 120 min at 110, 130, and 150°C. The preheating time was $\sim$ 10 min. The reaction mixture was diluted with methanol after cooling at room temperature. It was filtered using a glass-fiber filter no. 3 to separate the solid residue (methanol insoluble part) from the methanol soluble part. The residue was dried in an oven at (105 $\pm$ 2)°C to a constant weight. The amount of free phenol in soluble part (after removing methanol by distillation at 90°C), was measured using high performance liquid chromatography (HPLC) (Walter 1515 isocratic HPLC pump) equipped with a Walter 2487 Dual λ Absorbance detector and Walter C_{18} 5 μm symmetry column (4.6 mm i.d. $\times$ 150 mm length). The chromatographic zones were visualized under UV light (254 nm). Tests were performed at a flow rate of 1 mL/min using a methanol/water solution (1/2 v/v) as the mobile phase. In addition, the solution of pure phenol at different concentration of methanol was used as a standard solution for calibration purposes. Phenolated EFB samples were dissolved in methanol at a known concentration and were injected into the HPLC apparatus in the amount of 10 μL. Then, the amount of free phenol in the samples was calculated using the calibration curve.

RESULT AND DISCUSSION

The effect of reaction parameter on the liquefaction process

Table I lists the amount of free phenol remains after reacted at 110–150°C at different reaction times, with 5 and 8% of catalyst concentration. As presented in Table I, the amount of phenol decreases as the react-

TABLE I
The Value of Phenol (g) as a Function of the Reaction Time and Temperature

Reaction time (min)	Reaction temperature (°C)					
	The amount of phenol (g) at 5% catalyst			The amount of phenol (g) at 8% catalyst		
	110	130	150	110	130	150
0	90	90	90	90	90	90
30	55.29	41.94	40.5	43	39.6	31.5
60	52.39	39.56	37.96	37.8	34.2	29
90	50.4	39.83	35.1	34.2	32.4	25.36
120	48.7	37	31.98	32.4	29.4	26.25

TABLE II
**The Value of EFB (g) as a Function of the Reaction Time and Temperature**

Reaction time (min)	Reaction temperature (°C)					
	The amount of phenol (g) at 5% catalyst			The amount of phenol (g) at 8% catalyst		
	110	130	150	110	130	150
0	30	30	30	30	30	30
30	12.6	9.9	2.7	10	6.9	3
60	11.1	4.65	1.55	7.73	3.3	1.23
90	8.4	4	1.14	6.25	2.25	0.95
120	7.2	2.5	1	5.96	1.72	0.8

ing temperatures and reaction time increase. Under these experimental circumstances, the optimum reaction temperature and time are determined to be 150°C and 90 min, respectively, with 8% addition of sulfuric acid as catalyst. At these reacting conditions, the greatest of the reacted phenol is observed.

Table II shows the amount of EFB in the presence of sulfuric acid as catalyst reacted at various reacting temperatures, times, and catalyst concentration. The finding shows that the amount of EFB decreases exponentially with the increasing in the reaction temperature and time. The reaction time at 90 min and reacting temperature of 150°C are the optimum condition for the phenolysis of EFB. Note that $\sim$ 96% of EFB was liquefied in this condition.

Reaction kinetics

The kinetics of EFB liquefaction in phenol can be considered as an irreversible bimolecular reaction. It can be represented as the following equation:

$$A + B \rightarrow \text{condensed products} \qquad (1)$$
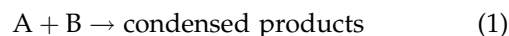
where A and B represent phenol reagent and EFB, respectively. The weight of residue (after drying) calls W_B and the amount of initial input EFB is W_{B0}. The amount of the unreacted phenol (free phenol as measured in Table I) was determined using HPLC known as W_A and the amount of initial input phenol called W_{A0}. While, W_A and W_B are the weights of the unreacted phenol and EFB respectively at time (t).

The rate constant of the reaction can be expressed in the following differential forms[18,19]:

$$-r_B = -r_A = -dW_B/dt = kW_A W_B \qquad (2)$$

By integration of the Eq. (2) the following equation is obtained:

$$\text{Ln}(W_A W_{B0}/W_B W_{A0}) = W_{B0}[(W_{A0}/W_{B0}) - 2]kt \qquad (3)$$
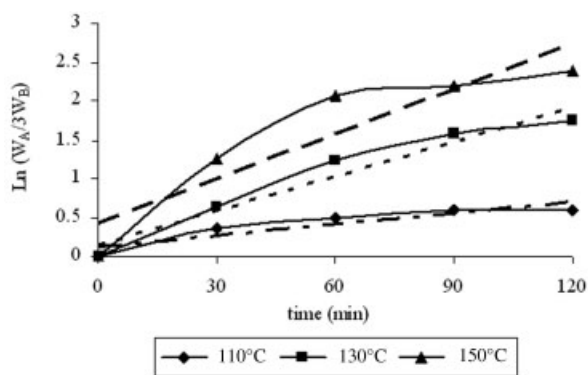
Figure 1 Second-order kinetics plot of EFB phenolysis at different temperature at 5% catalyst, (----) trend line of plots.

Considering $W_{A0}/W_{B0} = 90/30 = 3$, and if the equation is rearranged, the final form of equation will be as follow:

$$\text{Ln}(W_A/W_B) = \text{Ln } 3 + 30\, kt \quad (4)$$

From Tables I and II, it was found that 1 (g) of EFB reacted with 2 (g) of phenol. Therefore, it is wise to assume that the possible kinetics of the liquefaction of EFB in phenol can be considered as a third-order reactions. Hence, the rate constant of the reaction can be expressed in the following differential forms when the $W_{A0} \neq 2W_{B0}$[18,20]:
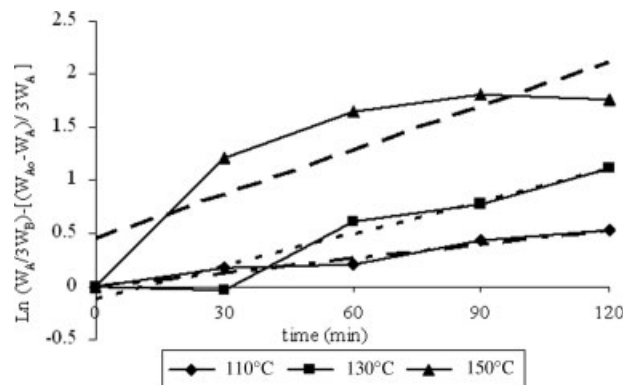
$$-r_A = -dW_A/dt = kW_A^2 W_B \quad (5)$$

After integrating Eq. (5) the following equation is obtained:

$$[(2W_{B0} - W_{A0})(W_{A0} - W_A)/(W_{A0}W_A)] + \ln(W_{B0}W_A/W_B W_{A0}) = (2W_{B0} - W_{A0})^2 kt \quad (6)$$
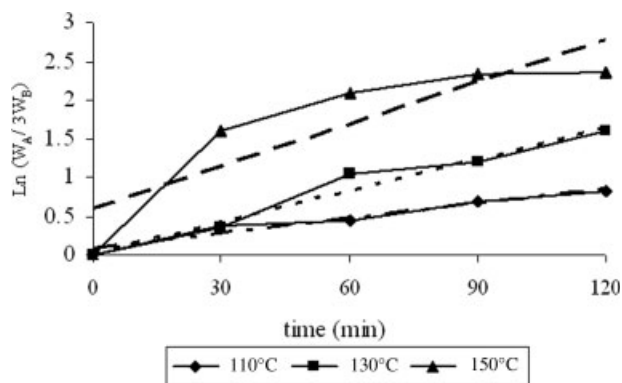
Figure 2 Second-order kinetics plot of EFB phenolysis at different temperature at 8% catalyst, (----) trend line of plots.
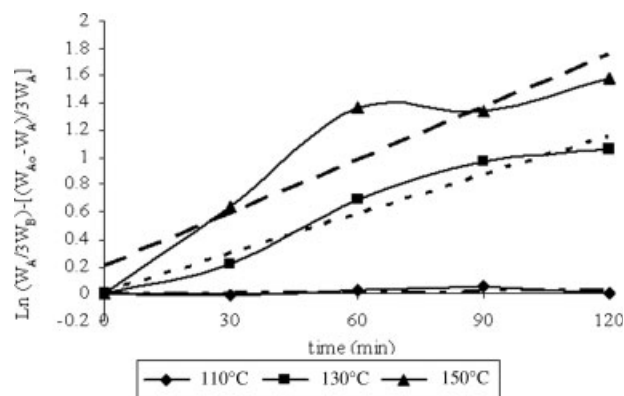

Figure 3 Third-order kinetic plot of EFB phenolysis at different temperature at 5% catalyst, (----) trend line of plots.

Considering $W_{A0}/W_{B0} = 90/30 = 3$, if the equation is rearranged, the final form will be as follows:

$$\text{Ln}(W_A/W_B) = \text{Ln } 3 + ((90 - W_A)/3W_A) + 900\, kt \quad (7)$$

The plots of eqs. (4) and (7) versus time (t), as shown in Figures 1–4 are linear. The rate constants of reaction are determined from the slope of the straight line plots of eqs. (4) and (7) against time at different temperatures as shown in Figures 1 and 2. The equations have given the data with regard to the characteristics of the correlation, such as, the slopes, intercepts, and correlation coefficient, are presented in Tables III and IV. From the calculations, the results for the reactions at 110°C with 8% catalyst do not follow the third-order kinetics reaction since the correlation coefficient is only 0.157 (Table IV). Therefore, it can be concluded that the reaction of phenolated EFB in sulfuric acid follows the second-order reaction.

From Table III, the reaction rate constant of EFB phenolysis increases with increasing reaction temperature and the amount of catalyst.

Figure 4 Third-order kinetic plot of EFB phenolysis at different temperature at 8% catalyst, (----) trend line of plots.

Temperature (°C)	Rate constant (k) $\times 10^3$ (min^{-1})	Equation	R^2	Catalyst (%)
110	0.217	$Y = 0.0065X + 0.0801$	0.9474	5
130	0.45	$Y = 0.0135X + 0.0273$	0.9676	5
150	0.607	$Y = 0.0182 X + 0.5904$	0.76315	5
110	0.16	$Y = 0.0048X + 0.1228$	0.8269	8
130	0.49	$Y = 0.0147 X + 0.1594$	0.9471	8
150	0.637	$Y = 0.0191 X + 0.435$	0.8464	8

This has indicated that the reaction occurs favorably at high temperature because of higher rate constants (0.637×10^{-3} min^{-1}). It is found that the effect of increasing temperature is sufficient compared to the amount of catalyst used.

The dependence of the rate constant of the phenolysis on temperature can be described using the Arrhenius equation:

$$k = k_o \exp(-E_a/RT) \tag{8}$$

The activation energy (E_a) of the reaction was determined using the rate constant (k) with the best correlation coefficient obtained from Table III. The E_a values calculated are 50.7 kJ mol^{-1} and 18.06 kJ mol^{-1} when the catalyst concentrations are 5 and 8%, respectively. This shows clearly that increasing of catalyst concentration has decreased the activation energy of reaction, and for this reason has increased the reaction rate.

One the other hand, detailed explanation for the transformation of reactants into products is given by the transition-state theory. According to the theory, reactants are first transformed into an unstable intermediate form call the activation complex (transition-state), and then they are decomposed spontaneously into products shows as the following reaction:

$$A + B \leftrightarrow AB^* \rightarrow \text{condensed products} \tag{9}$$

where AB* is the intermediate state at the top of the activation barrier. The probability of forming AB* can be determined by the equilibrium constant. The Gibbs free enthalpy (ΔG) of the reaction is calculated by using the Eyring equation, which gives the relationship between the reaction rate constant and Gibbs free enthalpy as follows[18,20]:

$$k = (k_B T/h) \exp(-\Delta G/RT) \tag{10}$$

where k is the rate constant (s^{-1}), k_B is the Boltzmann constant, and h is the Planck constant. Furthermore, the activation entropy and enthalpy were calculated from eqs. (11) and (12), respectively[19]:

$$\Delta H = \Delta G + T\Delta S \tag{11}$$

$$\Delta S = -d\Delta G + dT \tag{12}$$

The values of the Gibbs free enthalpy (ΔG) of EFB phenolysis shown in Table V is expressed as a function of reaction temperature and catalyst used. The Gibbs free enthalpy for the EFB phenolysis process increases with increasing reaction temperature at different amount of catalyst used. The increase of 20°C in reaction temperature has resulted in the increase of 5 kJ/mol in the Gibbs free enthalpy. The fact that ΔG has a high positive value (more than 135 kJ/mol) demonstrates that the activated complex is quite unstable. The reaction rate is governed by the rate of decomposition of the intermediate state, which reveals that the second step is the rate-controlling step.

The average amount of reaction enthalpy was (43.79 kJ/mol), and reaction entropy was (-0.238 kJ/mol K). The results were calculated using eqs. (11)

Temperature (°C)	Rate constant (k) $\times 10^3$ (min^{-1})	Equation	R^2	Catalyst (%)
110	4.86	$Y = 0.0044X + 0.0051$	0.9714	5
130	11.33	$Y = 0.0102X - 0.115$	0.9208	5
150	15.33	$Y = 0.0138 X + 0.457$	0.7454	5
110	0.22	$Y = 0.0002X + 0.0005$	0.1571	8
130	10.55	$Y = 0.0095 X + 0.0184$	0.9536	8
150	14.33	$Y = 0.0129 X + 0.2091$	0.8722	8

TABLE V
Values of Gibbs Free Enthalpy as a Function of the Reaction Temperature and the Percentage of Catalyst Used

Temperature (°C)	Catalyst amount (%)	(ΔG) kJ mol^{-1}
110	5	134.98
110	8	135.94
130	5	139.74
130	8	139.45

and (12). It can be understood from the positive value of the reaction enthalpy, that the EFB phenolysis reaction process has dominantly follows the endothermic nature. The negative value of the reaction entropy shows the polymerization process has proceeded.

CONCLUSIONS

EFB could successfully be phenolyzed in the presence of sulfuric acid as a catalyst at different temperatures, reaction times, and catalyst. The results showed that about 97% of EFB could be liquefied with phenol, whereas only 65% of phenol was found to react with EFB components at a temperature of 150°C. The kinetic studies demonstrated that the EFB phenolysis kinetics can be considered as a second-order reaction. The activation energy was found to be 50.7 kJ/mol and 18.06 kJ/mol when the catalyst was 5 and 8%, respectively. It is obviously showed by increasing the catalyst concentration, the activation energy will decreased. This has led to the increased in the reaction rate. Moreover, on the basis of the transition-state theory, it was found that the second step of EFB phenolysis reaction had a rate controlling-step via the activated complex at a first step because of its high positive Gibbs energy values. The reaction enthalpy also indicated that the EFB phenolysis was the endothermic reaction.

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