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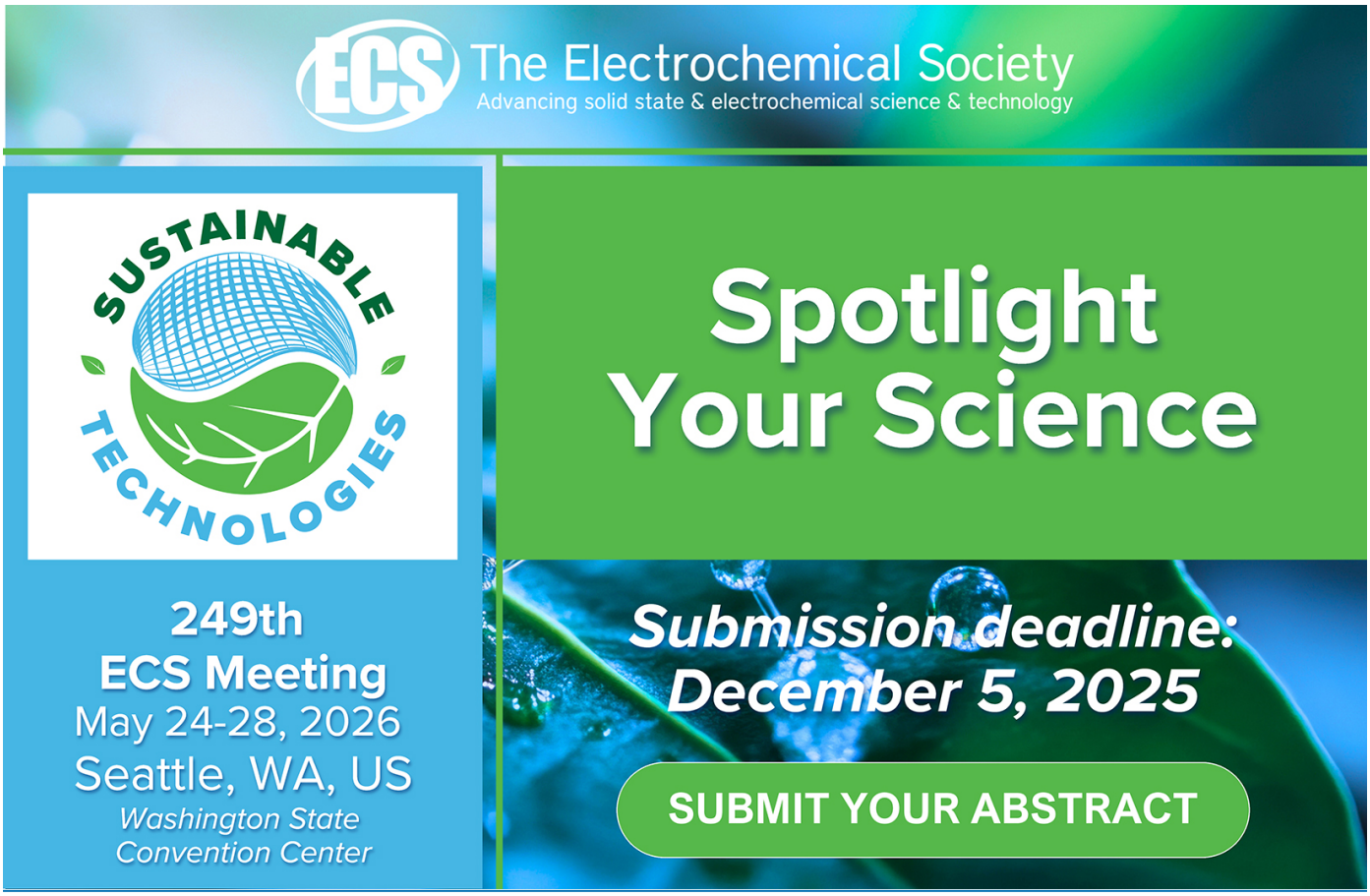

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Comparative Study of Various Pretreatment on Sugar Production from Mixed Rice Biomass

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Abstract. The aim of this work was to study the effectiveness of pretreatment methods by developing a comparative study of diluted acetic acid and hydrothermal pretreatment on reducing sugar production and inhibitors formation (Furfural) from the mixed rice biomass. Diluted acetic acid and hydrothermal pretreatment were carried out over a range of temperature (150 – 190 ºC) within 30 minutes to observe the reducing sugar production and inhibitor formation (Furfural). Seamen Model was used to obtain the rate of reaction in depolymerisation of lignocellulosic biomass. This experiment data were fitted the first-order kinetic model to obtain the reaction rate constant of production and degradation of sugar. In addition, Arrhenius equation was used to determine the activation energy of the reaction. From the result, it showed that the diluted acetic acid pretreatment had higher rate on reducing sugar production and inhibitor formation than the hydrothermal pretreatment. The activation energy for the formation sugar in hydrothermal pretreatment is found 29.1 kJ/mol which is higher than acetic acid pretreatment (23.9 kJ/mol).

1. Introduction

Total production of rice husks (0.48 Mtonnes) and rice straw (3.2 Mtonnes) in Malaysia were recorded [1]. These agricultural residues do not fully utilized in and plenty of them are disposed as waste. These biomass was resistance for digestion, difficult to decompose in the ground and low nutritional value for animals [2]. Rice husk and straw are lignocellulosic biomass consists of lignin, hemicellulose and cellulose. The utilization of raw or untreated biomass is usually resulted in low production due to its recalcitrant nature [3]. Therefore, pretreatment is essential process to open up the recalcitrant of lignocellulosic and to make the cellulose and hemicellulose easy to be accessed by enzyme hydrolysis or fermentation.

Pretreatment can be categorized into four main groups which are physical, chemical, physicochemical and biological pretreatment [4]. Chemical pretreatment is the most commonly widely used in industrial sector. High temperature in pretreatment process will lead to the degradation of the sugar [5] such as HMF, furfural and phenolic compounds. The production of furfural is based on the degradation of xylan into xylose in an acidic condition. Studying the performance of sugar production and degradation of biomass in acidic condition by kinetic modelling tells the interactions among biomass derived compound by the various reaction steps. In order to understand the kinetic mechanism of pretreatment, the mathematic interpretation is developed. The pseudo-first kinetic model is the simplest model to describe the kinetic mechanism of acid hydrolysis of biomass.

2. Methods

2.1. Biomass preparation Sample

Rice husks and straw were obtained from the local rice processing industry in Perlis. Rice husks and straw were washed and milled by grinder into small particles and sieved into 0.3 mm diameter. It was dried in oven (105^{o}C) and the mixed rice biomass were prepared by using 3:1 ratio (10g).

2.2. Pretreatment

Hydrothermal pretreatment was utilized the 10g of raw material in 100mL of distilled water inside the 500mL Stainless steel Batch Reactor (model: FB 70155/EUR) in School of Bioprocess Engineering. The ten gram of raw material sample in 100mL of 4% (v/w) acetic acid was used for diluted acid pretreatment. The mixed rice biomass was pretreated at temperatures 130^{o}C, 150^{o}C and 170^{o}C. The samples of pretreatments were taken out at 0, 5, 10, 15, 20, 25 and 30 minutes, respectively for different temperatures. Solids residues and hydrolysate after pretreatment were separated by vacuum filter and the solids residues were dried and weighted before and after drying. The hydrolysate was analyzed on sugars, degradation products formation and pH recorded.

2.3. Analysis

UV-Spectrophotometer (model 4001/4, made in USA, Genesys) was used to determine the concentration of reducing sugar [6] and furfural [7].

2.4. Yield calculation by kinetics of hydrolysis and estimation of activation energy

The first model to describe the hydrolysis of biomass was proposed by Seaman in 1945. This simple model explained that the decomposition of hemicellulose involved a series of pseudo-homogenous irreversible first-order reactions. The process depolymerisation of hemicellulose as shown in following reaction scheme:

$$\rightarrow \text{Hemicellulose} \rightarrow \text{Reducing sugar} \quad \text{Degradation product} \tag{1}$$

In this study, the total reducing sugar represented the combination of oligosaccharides and monosaccharides while the degradation product was referred to the furfural. In order to obtain the k1 and k2 value, the reaction above was separated as a single reaction as follow and use the experiment results to plot a first order reaction graph. The kinetic value was represented by the gradient value of the straight from the graph. Hence, the reducing sugar and furfural concentration as the function of time can be expressed as:

$$X = Xo \exp(kt) \tag{2}$$

$$F = Fo \exp(kt) \tag{3}$$

where X_o was the initial reducing sugar from hemicellulose (xylan), F_o was maximum theoretical concentration of furfural, k is the specific rate constant (min-1), X and F was the sugar concentration and furfural concentration at the time (g/L) and t was the time (min). On the basis of a first order reaction of the hydrolysis hemicellulose Equation (2) and (3) becomes:

$$\ln(X_o/X) = -kt \tag{4}$$

$$\ln(F_o/F) = -kt \tag{5}$$

The initial value for xylan in hemicellulose and furfural in sugar can be theoretically calculated by the Equation (4) and (5):

$$F_o = \frac{96\%\mathrm{P}}{132\ \mathrm{LSR}}\mathrm{X}_o = \frac{150\ \mathrm{C_{X_o}}}{132\ \mathrm{WSR}}\mathrm{x}\ 10 \quad (6)$$

$$\mathrm{x}\ 10 \quad (7)$$

Where CX_o was the initial concentration of xylan per 100g mixed rice biomass on dry basis; WSR is the water to solid ratio and 150/132 is the ratio of the stoichiometric factors, P was the xylose mass percent in raw material; 96/132 was the stoichiometry factor for furfural and LSR was the liquid to solid ratio [8]. The kinetic rate of reaction value from the Equation (4) and Equation (5) was used to fit the experimental data to the kinetic model. The activation energy in the hydrolysis reaction was estimated by the Arhenius equation as follow:

$$\mathrm{k} = \mathrm{k(T)} = \mathrm{Ae}^{-\mathrm{E}/\mathrm{RT}} \quad (8)$$

where A was the pre-exponential constant (min-1); E_a was the activation energy (kJ/mol); R was the ideal gas constant which was 8.314 J/mol.K and T was the actual temperature (K). The regression of the natural logarithm of the degradation rate constant (k) against (1/T) in which straight line curve was obtained indicated that the Arrhenius model was fulfilled and slope of this curve is equal to the Ea/R and allowed estimation of the activation energy [9].

3 Results and discussion

3.1 Total reducing sugar

Figure 1 shows the effect of total reducing sugar produced with different reaction times and temperatures. According to the figure 1 (a), sugar concentration at 150°C was gradually increased until it reached the maximum sugar production at 30 min (5.9 g/L). At 170°C, the graph showed that there was a step up increased about 88.1% throughout the reaction time and the highest production of sugar was occurred at 30 min (24.1 g/L). However, the behavior of hemicellulose hydrolysis at temperature 190°C was differed. The graph showed that sugar formation reached a peak after 20 min (29.1 g/L). After that, the graph showed a decline line as the sugar started to degrade. According to Vallejos et al., [10], xylose concentration increase with the temperature and begins to decompose after achieving maximum production. From the diluted acetic acid pretreatment, sugar generation showed a peak during 150°C and 170°C but was sustained in production for 30 minutes at 130°C. The yield of sugar in (130°C) increased 83.05% from 0.2 g/L to 1.3 g/L but still low compare to others temperature. When the biomass pretreated at 150°C, sugar production increased about 83.9% from 2.9 g/L to the maximum production (17.7 g/L) within 25 minutes. After that, the amount of reducing sugar started to decrease due to the degradation of sugar to form inhibitors. According to the Figure 1(b), the highest sugar production in acetic acid pretreatment happened at 170°C at 20 minutes. During this temperature, the amount of reducing sugar was increased about 81.9% from 5.4g/L to 29.7 g/L within 20 minutes and it showed that sugar degradation starts earlier than the temperature 150°C. This observation favoured the shorter time for sugar production when the temperature increases and earlier time for the sugar started to decompose after reaching to the maximum production. Lenihan et al. [11] found that the glucose reach its maximum production at 10 minutes in temperature 200°C while it need a longer time for 135°C which indicate the great amount of glucose was produced at 20 minutes. From the result, it also showed that more sugar was produced with the increasing of temperature. Same observation was found by Liu et al. [12] which highlighted that the highest xylose production happened at 150°C while for the lowest xylose production was at 110°C.

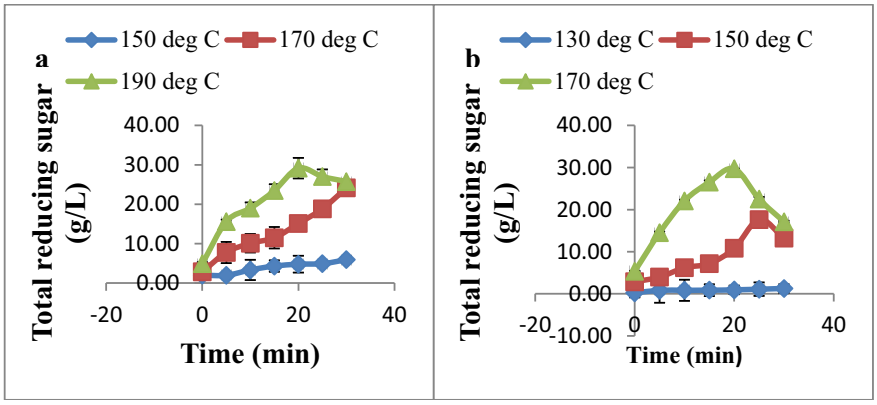

Figure 1. Effect of different temperatures and reaction times on sugar for (a) hydrothermal pretreatment (b) dilute acetic acid pretreatment

3.2 Furfural formation

Furfural was generated from the degradation of xylose under harsh condition. The formation of furfural in the diluted acetic acid and the hydrothermal pretreatment increased with the temperature and time. The furfural formation from xylose in both pretreatment methods was showed in Figure 2. This trend was similar as observed by Yadav et al., [8] on Pisumsativum waste (Pea pod) hydrolysis to furfural. Timung et al [13] also reported that the concentration of inhibitor formation was increased with the temperature and time. This research showed that the furfural concentration decreases when the reaction time is more than 60 minutes. The trends of furfural formation in both pretreatment methods showed sharp increase happened in high temperature (190 and 170ºC). Furfural formation (figure 2(a)) in hydrothermal pretreatment at 150ºC increased slightly about 53.1% from 0.4 g/L to 0.9 g/L. When the biomass treated at 170ºC, the releasing of furfural increased gradually from the initial time to 25 minutes and suddenly rising up to 3.9 g/L. The furfural was highest released at 190ºC after 30 minutes. The amount of furfural produced in hydrothermal pretreatment (85.32%) from 1.0 g/L to 6.9 g/L after 30 minutes. Figure 2(b) indicated the furfural production at 130ºC was slightly increased (58.8%) from 0.3 g/L to 0.7 g/L when the biomass is treated in diluted acetic acid. Higher amount of furfural released (150ºC) from the degradation of xylose compare to 130ºC. The maximum production at 150ºC was 3.0 g/L and increased steadily (87.7%). As for temperature 170ºC, the furfural concentration was rapidly increased about 86.6% from 0.8 g/L and made the highest furfural formation (6.0 g/L) after 30 minutes.

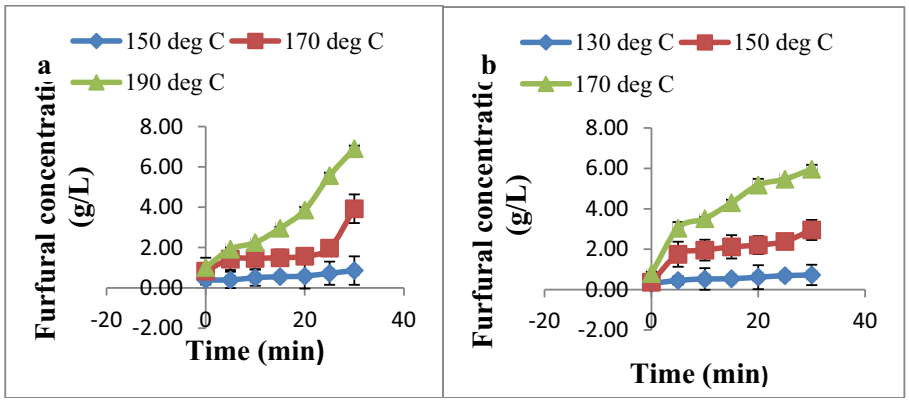

Figure 2. Effect of different temperatures and reaction times on furfural formation in (a) Hydrothermal pretreatment and (b) Diluted acetic acid pretreatment.

3.3 Comparison of hydrothermal and diluted acetic acid pretreatment

The dilute acid pretreatment and hydrothermal pretreatment have a significant effect on the solubilisation of hemicellulose; therefore the hypothesised is made to indicate that majority of sugar production is derived from conversion of xylan to xylose. Glucose is minority monomers in hemicellulose, hence it is negligible when make the calculation of xylan conversion. The completely conversion for xylan to xylose is theoretically calculated as 30.2 g/L. The percentage of xylan converted to xylose was presented in figure 3. It was found that there was loss of xylose happened in diluted acetic acid pretreatment. This phenomenon attributed the formation of furfural under harsh condition. The diluted acetic acid pretreatment at 150^{o}C showed that there was about 43.8% of xylan had successfully converted to xylose and sugar had started to decrease after 25 minutes. At 170^{o}C, xylose was degraded faster than 150^{o}C after achieving the maximum xylan conversion which was about 88.4% after 20 minutes. Under the same condition in hydrothermal pretreatment, it did not show any decreased in sugar level. It implies that sugar degradation did not occured and the xylose yield has a great potential to increase after 30 minutes. The pretreated liquor in hydrothermal pretreatment showed that there was 19.6% and 80.0% of xylan converted to xylose at 150^{o}C and 170^{o}C, respectively. This observation highlighted the higher conversion of xylan to xylose when mixed rice biomass was treated in the diluted acetic acid and xylose yield can be produced faster within a short period compared to the hydrothermal pretreatment. From the experiment, it also can be found that less severe condition is needed to release more sugar from hemicellulose due to its amorphous structure. Kootstra et al [14] obviously found that there was 59% (w/w) xylose yield in maleic acid hydrolysis while in hot water pretreatment only obtained 0.5% (w/w) xylose yield. This situation can be explained by the acidity of the medium that was used in pretreatment. Acid solution has a significant effect on hemicellulose hydrolysis due to its furanosidic structure [15]. The increasing temperature is able to lower the pH of the solution which enhances the activities of pretreament. Rosgaard [15] reported that the acidity of hot water is still lower than the diluted acetic acid solution although acetic acid is released in the hot water when temperature increases.

The maximum theoretical concentration of furfural is calculated as 19.3 g/L. This value is used to obtain the yield of furfural from xylose. Figure 3(a) showed the comparison yield of furfural from xylose in different pretreatment method. According to the Figure 3(b), the furfural generation increased with the time and temperature in both pretreatment methods due to the increasing of xylose production within 30 minutes. Under harsh condition, xylose converts to furfural making the high generation of furfural. By comparing of both pretreament methods, the highest xylose degradation occurred at 170^{o}C when biomass was pretreated in the diluted acetic acid. There was 30.9% furfural was released from xylose at 30 minutes. The lowest xylose degradation to furfural (4.4%) occurred at 150^{o}C in hydrothermal pretreatment. An expected finding was that the production of furfural in hydrothermal pretreatment was lower than the acetic acid pretreatment in the same temperature. This finding can be explained by the kinetic model of cellulose and hemicellulose hydrolysis which includes more than one formation of degradation products [16]. From the previous study, it explained that the formation of others degradation product is faster than the furfural formation. This make the furfural formation a lower kinetic rate and lead to the low production [17]. Zheng et al [18] reported that the hydrothermal pretreatmet has a great potential to enhance sugar production with the advantages of low generation of inhibitor. The result in this current study is fully agreed by this statement.

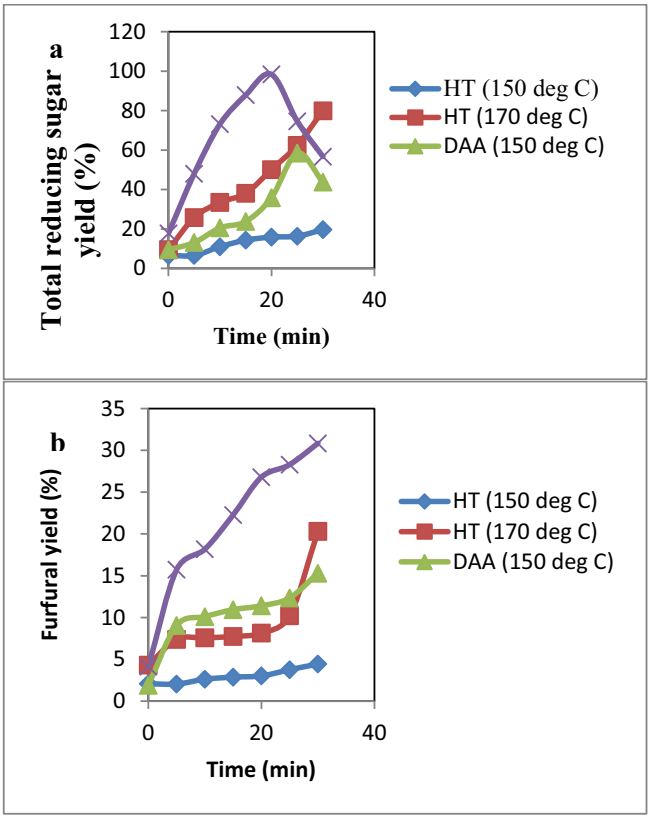

Figure 3. Comparison the percentage for (a) the conversion of xylan to xylose and (b) the conversion of xylose to furfural in hydrothermal (HT) and dilute acetic acid (DAA) pretreatment respectively.

3.4 Kinetic modelling for hemicellulose hydrolysis

The depolymerisation of hemicellulose leads to the formation of sugar monomers and the monomers will be further degraded to inhibitors with the increasing time and temperature. In this study, Seamen model had been described the hydrolysis of biomass lignocellulose. This model considers two-step reaction of formation and degradation of sugar respectively. The kinetic values for hydrolysis of hemicellulose are presented in Table 1 and 2. The results in both tables indicate the specific rate constant for the conversion of hemicellulose to xylose (k1) and the xylose decompose to furfural (k2).

Table 1. Value of k1 and k2 for mixed rice biomass at different temperatures for hydrothermal pretreatment

Temperature (°C)	Xylan to xylose (k_1)	Xylose to furfural (k_2)
150	0.0389	0.0260
170	0.0612	0.0384
190	0.0793	0.0603

Table 2. Value of k1 and k2 for mixed rice biomass at different temperature for diluted acetic acid pretreatment

Temperature (°C)	Xylan to xylose (k_1)	Xylose to furfural (k_2)
130	0.0430	0.0261
150	0.0702	0.0501
170	0.0805	0.0543

The value of k1 and k2 for both pretreatments increased with the temperature. From Table 1, the highest value of k1 and k2 are 0.0793 min-1 and 0.0603 min-1 for hydrothermal pretreatment, respectively. These values were differed when acetic acid is added in the pretreatment. As for the diluted acid pretreatment in table 2, the highest value for k1 and k2 were 0.0805 min-1 and 0.0543 min-1, respectively.

Curiously, there was a large portion of gap for specific rate constant value from low temperature to high temperature. This observation explains that the sugar production and sugar degradation at low temperature are much lower than the high temperature in both pretreatment methods. This analysis is consistent with the previous research of kinetic study of hemicellulose sugar production from hazelnut shells [19]. The hazelnut shells undergone the diluted acid hydrolysis pretreatment at 100oC, 110oC and 120oC temperature. It was found that the specific rate constant for the conversion of hemicellulose to xylose was significantly increased from 0.0051 min-1 to 0.0186 min-1 and the specific rate constant for sugar degradation also increased from 0.0038 min-1 to 0.0087 min-1. According to current study, all k1 values were higher than k2 for both pretreatments. It implies that the rate of formation of sugar is faster than the rate of degradation of sugar. Similar observation has been reported by the research of kinetic study of acid hydrolysis of rice straw which stated rice straw hydrolysis to sugar is faster than formation of inhibitors [20]. A comparison rate constant for both pretreatment results was illustrated in Figure 4. They obviously revealed that the rate of formation sugar and furfural were faster in the presence of acetic acid under the same temperature. It means that the diluted acetic acid pretreatment easier to generate inhibitors product. This observation was consistent with the previous result of the kinetic study of xylose yield in acid and hydrothermal ptretratment [21]. The researcher reported that the rate constant k1 is higher with the addition of diluted acid which result in faster process of hemicellulose depolymerisation to form sugars.

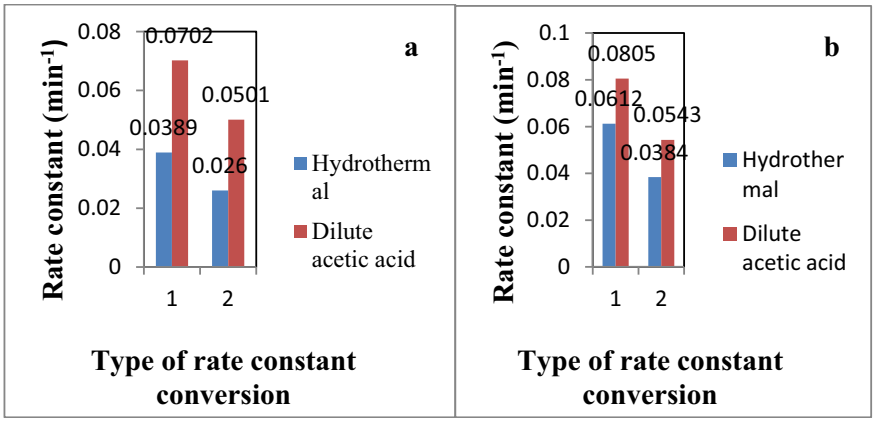

Figure 4. Comparison of the rate constant conversion in different pretreatment methods under (a) 150°C temperature and (b) 170°C temperature; 1: sugar production, 2: sugar degradation

3.5 Estimation of activation energy

Activation energy (Ea) is the minimum amount of energy that is needed in the chemical reaction to change a substance to another. Activation energy can be evaluated from various reaction rate constant as a function of temperature. Arrhenius equation provides the quantitative basis relationship between temperature and the rate of reaction proceeds. The specific rate constant value from Table 1 and Table 2 were used to fit the Arrhenius equation to develop the graphs. The activation energy can be estimated by the slope of the plot of In k versus 1/T (K). The higher the gradient value from the equation, the larger amount of activation energy is obtained during the pretreatment process. The calculated activation energy values are presented in Table 3. This result showed that the activation energy for the formation sugar in hydrothermal pretreatment is 29.1 kJ/mol which is higher than diluted acetic acid pretreatment

(23.9 kJ/mol). This finding indicates that the rate of reaction for the xylan conversion to xylose is faster in the presence of acid catalyst. In contrast, the hydrothermal pretreatment had higher activation energy of sugar degradation which was 34.2 kJ/mol while the activation energy of diluted acetic pretreatment was 30.2 kJ/mol. This value highlights that furfural is easier to be generated in the diluted acetic pretreatment.

Table 3. Activation energy for hydrothermal and dilute acetic acid pretreatments

Pretreatment method	Activation Energy (kJ/mol)	
	Hemicellulose to Sugar (Ea_1)	Sugar to Furfurral (Ea_2)
Hydrothermal	29.1	34.2
Diluted acetic acid	23.9	30.2

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