# Kinetic Studies on Acid Hydrolysis of OPEFB in a Batch Reactor

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**Abstract.** Batch reactor was employed to investigate the hydrolysis of OPEFB fiber at 120$^{o}$C under low acid concentration conditions. Several concentrations of $H_2SO_4$ (2%, 4% and 6%) and reaction time (0-150 min) were evaluated. The OPEFB fiber was pretreated by mechanical reduction prior to the batch reaction. The maximum yield of xylose obtained from the batch reactor experiment was 80% for the pretreated OPEFB fiber. This occurred at 2% acid concentration and 120 minutes reaction time and 6% acid reaction. The maximum glucose yield from the OPEFB fiber was much lower at this temperature, about 10% of the calculated potential amount. The refined Saemen model was used to evaluate the kinetic of acid hydrolysis in the batch reactor at 120$^{o}$C for the three different acid concentrations.

 **Keywords:** OPEFB fiber, Dilute acid hydrolysis, Xylose

## 1.  Introduction

The first established dilute-acid hydrolysis process was the Scholler process, in which the wood material was kept in 0.5% sulphuric acid at 11-12 bar for approximately 45 minutes (Faith 1945). Temperature is an important parameter in the formation of sugar degradation products (Neureiter et al, 2002). A lower temperature (100oC-140oC) is normally applied in the hydrolysis of hemicellulose, meanwhile a higher temperature (180oC-250oC) always corresponds to the hydrolysis of cellulose. Another parameter affecting hydrolysis is the acidity of the system. The acidity is dependent on the type and concentration of acid used. The penetration of acid catalyst into the biomass, as well as dispersion in the reactor, can significantly affect the overall reaction, and consequently the reactor performance. Diffusivity of sulphuric acid is dependent on the nature of the lignocellulosic materials. It has been shown that the diffusivity of sulphuric acid is significantly higher in agricultural residues than in hardwood (Kim et al., 2001). The main objective of this work is to study the effect of sulphuric acid concentration on the hydrolysis of OPEFB fibre at 120oC as well as analysing the appropriate kinetic model. Oil Palm Empty Fruit Bunch has been chosen as raw material for production of bioethanol via acid hydrolysis due to its abundance in Malaysia. The OPEFB biomass contains cellulose, hemicellulose and lignin. Currently there are no reported investigations on acid hydrolysis of OPEFB fibre using a batch reactor at 120oC.

## 2.  Materials

The fibrous strands of OPEFB in shredded form were obtained from Hulu Seri Langat Palm Oil Mill. The fibre was washed thoroughly with tap water until the water was clean and colourless. The OPEFB fibre was then oven dried at 45°C until it reached a constant weight ±10% of original weight. The OPEFB fibre are dried and milled to 16 mesh or 1mm diameter particles.

### 2.1.  Material Characterisation

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Thermogravimetric Analysis (TGA) was used to determine the chemical composition (cellulose, hemicelluloses and lignin) of the OPEFB fiber used in this study. The TGA system consists of a Mettler Toledo model 851e with high temperature furnace controlled by an IBM compatible PC. The heating rate was set at 15oC/min in compressed air atmosphere and the maximum temperature ramp was set at 900oC.

## 2.2. Experimental Procedures

### 2.2.1. Acid Hydrolysis Using a Batch Reactor

Acid hydrolysis was carried out in a batch reactor with a working volume of 1 litre. 30g of OPEFB fiber is weighed and placed inside the stainless steel basket. The basket is then placed into the stainless steel reactor. 750ml of dilute sulphuric acid was pumped into the reactor. The time of the reaction starts when the reactor reaches its desired reaction temperature. Sampling was done at different reaction time. The sample was cooled in an icebath to stop the reaction. The solid material was separated and the filtrate (hemicellulosic fraction) was analysed for solubilised sugars (xylose and glucose).

### 2.2.2. Analysis Method

The concentrations of monomeric sugars in the soluble fraction were determined by a high-performance liquid chromatograph using a Bio-Rad HPX 87H column at 45°C, eluted at 0.6 mL/min with deionised water. Sugars were detected at 80°C temperature using a controlled Evaporative Light Scattering Detector (ELSD).

# 3. Results and Discussions

## 3.1. TGA Characterisation of OPEFB Fibre.

TGA was conducted in order to characterize their thermal behavior and to identify their constituents by the aid of their thermogravimetric curves. Thermal analytical methods have been widely used in the study of biomass thermochemical conversion processes (Marcia et al., 2009). Lignins, hemicelluloses and cellulose are the main components of the lignocelluloses cell walls, were therefore extensively analyzed, especially from the point of view of their thermochemical reactivity. The thermal degradation of OPEFB fibre presents four mass loss steps attributed to the release of humidity and to the decomposition of organic material (hemicellulose, cellulose and lignin). The composition of the main fraction of OPEFB fiber was (% dry weight basis): cellulose, 44.5%; hemicellulose 26.5%; lignin, 19.1%. This result was in agreement with previous studies of the principal components of empty fruit bunch using quantitative acid hydrolysis give the following composition of the main components (Rahman et al., 2006).

## 3.2. Effect of Acid Concentration

The main products from the sulphuric acid catalysed hemicellulose hydrolysis reaction were monomeric xylose and glucose. However, at the given temperature and acid concentrations, glucose were detected at a minimal level of 1.6g/l at 60 min data point and 6% acid concentration. Therefore, only xylose were plotted and analysed.

Figure 1 illustrates the overall effect of acid concentration at 120oC temperature on the xylose yields obtained. Two opposite trends were observed for two different regimes of reaction times. The first regime is from 0 to 75minutes reaction time where the xylose yield increase with increase of acid concentration. Conversely, the second regime from 75 – 150 minutes shows that increasing the acid concentration will have a negative effect on xylose yields. The highest amount of xylose 8.4g/l achieved at both 2% and 6% acid concentration, with 2% acid concentration has a longer reaction time at 120 minutes compare to 60 minutes reaction time at 6% acid concentration. It is noticeable that the decomposition rate is only excessive once the acid concentration is increased to 6% (w/w).

## 3.3. Determination of Reaction Rate Constants

Determination of rate constants, k1 and k2 depends on the order of reaction. With experimental data, the correct order would be determined by which function of rate equation best fit the linear requirement. Once the order is established, the rate constants are estimated from the slope of the linear plot (Table 1).

$$.Xylan \rightarrow Xylose \rightarrow Decomposed\ products \qquad (3.1)$$
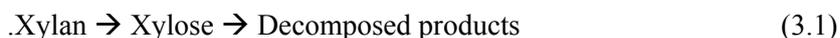
The hydrolysis reaction was modelled as a consecutive first order reaction.
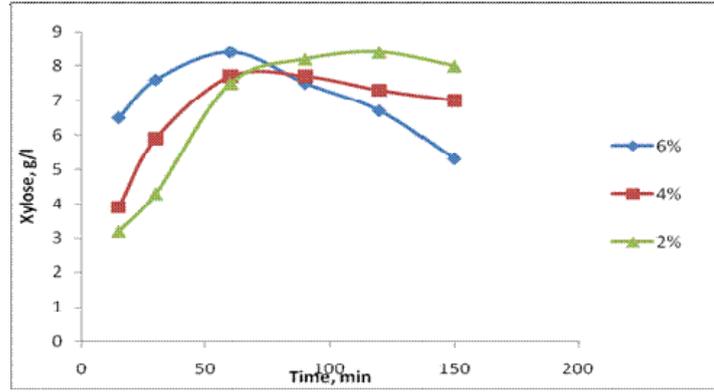
Fig. 1: Hemicellulose hydrolysis profile in OPEFB fiber by $H_2SO_4$ at $120^oC$.

$$k_1 \qquad k_2$$
$$A \rightarrow B \rightarrow C \qquad\qquad\qquad (3.2)$$
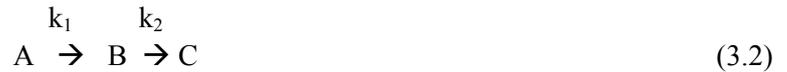
where

A= Xylan; B= Xylose; C= Decomposition products

$k_1$= sugar release rate; $k_2$= sugar decomposition rate

For a first order reaction, the rate can be calculated from the rate of formation of xylose can be described by equation 3.3.

$$\ln \frac{C_A}{C_{AO}} = -k_1 t \qquad\qquad\qquad (3.3)$$

Table 1: $k_1$ and $k_2$ values calculated at $120^oC$ and acid concentrations of 2%-6%.

|  | 2% $H_2SO_4$ | 4% $H_2SO_4$ | 6% $H_2SO_4$ |
|---|---|---|---|
| $k_1$ | 0.012 | 0.014 | 0.05 |
| $k_2$ | 0.001 | 0.001 | 0.05 |

## 3.4. Model Verification/Curve Fitting Using MATLAB

Since in this study our focus was to analyze the kinetics of the hemicelluloses hydrolysis reaction catalysed by sulphuric acid, the classic model Saeman were applied to our data to obtain insights on the reaction kinetics. The kinetics parameters were estimated based on minimization of errors between the experimental data and the kinetics model. The minimization of errors was initiated by providing initial guesses for each kinetics parameter.

$$\frac{dX_1}{dt} = -k_1 X_1 \qquad\qquad\qquad (3.4)$$

$$\frac{dX_2}{dt} = k_1 X_1 - k_2 X_2 \qquad\qquad\qquad (3.5)$$

$$[X] = \frac{k1[Xo]}{k1-k2}[\exp(-k_1 t) - \exp(-k_2 t)] \qquad\qquad\qquad (3.6)$$

Where Xo = potential xylan converted to xylose; $X_1$=Xylan; $X_2$=Xylose

In this study, MATLAB® was used to solve a set of weight fraction-based rate equations using the ODE solver function. The solution of the ODE equations were used to generate the simulated product distribution curves. The trial-and-error method was employed to determine the reaction rate constants that give the best fit to the experimental data, by considering the Sum Square Error and Regression Coefficient of the equation.
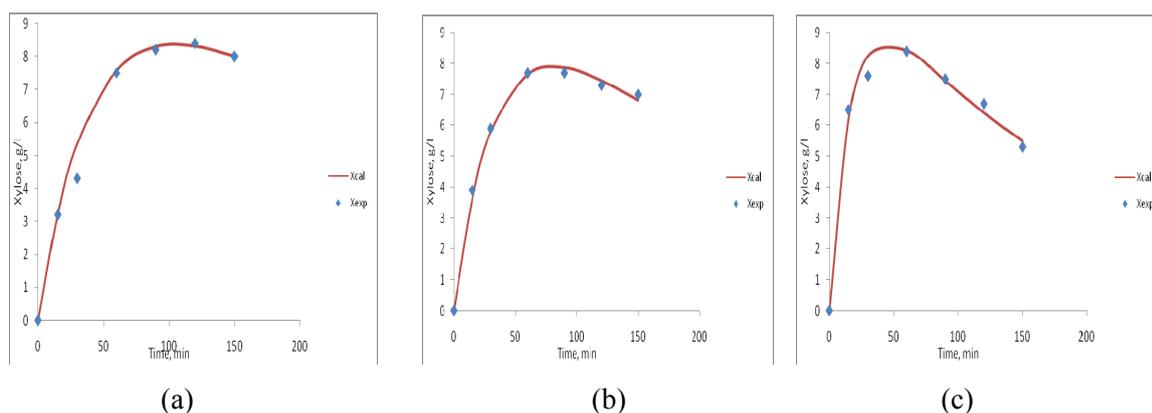
Fig. 2: Comparison between calculated and experimental value of xylose in hydrolysis of OPEFB at 120 oCwith (a) 2% $H_2SO_4$ (b) 4% $H_2SO_4$ and (c) 6% $H_2SO_4$.

## 3.5. Statistical Analysis

An analysis of variance (ANOVA) was performed for the statistical analysis of the experimental data by using PHStat add-in for Microsoft Excel. The fit quality of the model was evaluated using the statistical tests of coefficient of determination ($R^2$) and sum of squares error (SSE). The optimum criteria were determined by selecting the lowest values of SSE that is closer to zero, and the highest values of $R^2$ ($R^2 \approx 1$).

Table 2 shows the experimental and predicted data for acid hydrolysis at 120oC. The r2 shows a good agreement between experimental and predicted data for all regressions.

Table 2: $k_1$ and $k_2$ values from curve fitting estimation method at $120^oC$ and acid concentrations of 2%-6%.

|  | 2% H2SO4 | 4% H2SO4 | 6% H2SO4 |
|---|---|---|---|
| $k_1$ | 0.0240 | 0.028 | 0.060 |
| $k_2$ | 0.0025 | 0.004 | 0.005 |
| $r^2$ | 0.981 | 0.996 | 0.987 |
| SSE | 0.16 | 0.03 | 0.09 |

## 4. Conclusions

Dilute acids lead to a limited hydrolysis called prehydrolysis which affect the hemicellulosic fraction, leaving the cellulose and lignin fractions unaltered. Overall, the results for acid hydrolysis of OPEFB fiber indicate that the effect of acid concentration on the conversion of xylose is more critical at higher acid concentration for both rate of xylose formation and decomposition. A good fit between the experimental data and the kinetic model was obtained from curve fitting estimation via MATLAB application.

## 5. Acknowledgement

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