ACID HYDROLYSIS OF PRETREATED PALM OIL LIGNOCELLULOSIC WASTES

Ghasem Najafpour*

Department of Chemical Engineering, Noshirvani Institute of Technology
University of Mazandaran, Babol, Iran
najafpour@nit.ac.ir - najafpour8@yahoo.com

Asmida Ideris

School of Chemical Engineering, Kolej Universiti Kejuruteraan and Teknologi Malaysia
Kuantan, Pahang 25000, Malaysia
asmida@ump.edu.my

Sadegh Salmanpour

Department of Chemical Engineering, Islamic Azad University
Sari Branch, Sari, Iran
Salmanpour@gmail.com

Mohammad Norouzi

Department of Chemical Engineering, University of Peyame-Nour
Sari, Iran
mnorouzi346@yahoo.com

*Corresponding Author

Abstract   Palm oil solid wastes consist of cellulose, hemicellulose and lignin. In this study, a single stage of acid hydrolysis process of palm oil empty fruit bunch (EFB) for production of fermentable sugar was carried out under moderate temperature (45°C) and ambient pressure. The effect of four different process variables such as solid size, HCl concentration, solid percentage and temperature were investigated. In addition, the effect of pretreatment with 0.5-1M NaOH solution in acid hydrolysis was also investigated. Smaller particles provided more surfaces for acid-solid contact and longer reaction time was necessary if the large solid particles were used. High acid concentration improved the reaction rate and sugar yield. Therefore, the sugar yield was found to be dependent on acid concentration and the employed temperature as well. For a reaction time of 40 minutes, 5 % EFB solid with 15, 20, 25 and 30 percent of HCl, EFB lignocellulose fibers conversion of 36, 60, 65 and 80 % were achieved, respectively. The sugar concentration in acid hydrolysis of the pretreated fibers with 0.5 M sodium hydroxide solution resulted in 35 % more sugar.

Keywords   Acid Hydrolysis, Pretreated Fibers, Agro-Wastes, Fermentable Sugars

چکیده   ضایعات پس مانده نخل شامل سلولز، همی سلولز و لیگنین است. در این تحقیق از خوشه های الیاف نخل فاقد میوه در عملیات هیدرولیز تک مرحله‌ای برای تبدیل به قند قابل تخمیر در دمای ۴۵ درجه ســانتیگراد استفاده شد. چهار پارامتر مؤثر اعم از اندازه ذرات، غلظت اسید، در صد مواد جامد و دمای واکنش بررسی شــد. درمان الیاف با محلول سود (M ۱– ۰/۵) نیز بررسی گردید. ذرات ریز گرچه ســطح تمــاس بیــشتری بــا اســید دارشتند، ولی در زمان واکنش کافی ذرات درشت نیز بهمان غلظت بازدهی قنــد رســید. غلظــت اسـید و دمــای واکنش موجب افزایش نرخ بازدهی و سرعت واکنش شد. بنابراین نرخ بازدهی قنــد بــه غلظــت اســید و دمــای واکنش بستگی داشت. با زمان واکنش ۴۰ دقیقه و با ۵ درصد الیاف نخل فاقد میوه و با غلظت اسید ۱۵، ۲۰، ۲۵ و ۳۰ درصد HCl الیاف لیگنو سلولزی به ترتیب به درصد تبدیل ۶۰، ۳۶، ۶۵ و ۸۰ درصد رسـید. غلظــت قنــد الیاف درمان شده با محلول سود (M ۰/۵) موجب افزایش ۳۵ درصد غلظت قند محلول گردید.

1. INTRODUCTION

Malaysia is one of the palm oil producers around the world. But the residue of the palm oil has still not been completely used. In past decades the palm oil residues became the most abundant biomass

resources. The annual rate of production of palm oil in Malaysia was estimated to be more than twelve million tones [1]. The lignocellulosic residues can be used as solid fuel for steam generation. Presently the palm oil residues are burned in the field, which causes major air pollution. Palm oil fiber, which is only partially used as boiler fuel to produce steam for electricity generation with its heating value of 4420 kcal/kg (dried weight) and palm oil kernel process, has its remaining portion left with low commercial value [2]. Total biomass produced by palm oil industries, about 10 % was counted as the crude palm oil. While others remaining as the lignocellulosic wastes are present as trunks, fronds, palm pressed fiber and empty fruit bunches [1]. It was reported that about 27 % of total weight of the fresh fruit bunch would be the crude oil whereas the other portion left was the solid wastes; 23 % EFB, 14-15 % fibre, 6-7 % kernel and 6-7 % shell [3]. It has been believed that palm oil trunks yielded about 24-32 % of hydrolysable sugars [4]. Through out the palm oil industry, the fresh fruit bunch was preliminary sterilized prior to the threshing process for fruit and bunch separation. Therefore, the palm oil empty fruit bunch will be obtained after stripping off the fresh fruit bunch. Palm oil EFB consists of about 50 % cellulose, in compare to other sources of biomass such as sugar cane bagasse, rice straw, sorghum straw and corn cobs, palm oil EFB is enriched in cellulose [5]. Table 1 shows the lignocellulosic composition of various sources of biomass, among them; EFB has the highest percentage of cellulose.

Generally, hydrolysis of lignocellulosic material into its corresponding monomer sugar was performed by acid, enzymatic and microbial hydrolysis [6]. Acid hydrolysis is a direct hydrolysis method used for biomass conversion and single stage acid hydrolysis is considered as the simple and single reaction vessel. Typically, a single stage with diluted acid (less than 5 % acid concentration) was used rather than concentrated acid. A rather high temperature is needed to achieve a maximum conversion with in a short residence time. However, implementation of high temperature resulted in product contamination with the presence of soluble derivatives, furfural and hydroxy-methyl furfural, which is generated in the presence of acids from sugars; C_5 and C_6,

respectively [7-9]. In fact, the acid acts as catalyst for the chemical transformation of sugars into toxic compounds at any temperature greater than 50ºC. In acid hydrolysis of cellulose, it was believed that the mechanisms were leading to a scission of glycosidic bonds which initially catalyzed by the action of proton (H^+) existing in the aqueous medium [10]. Since cellulose was proposed to have both amorphous and crystalline structures, the reaction possibly occurs at both the surface of the cellulose particles and amorphous region, leaving the crystalline cellulose structure unaltered [11]. Compared to enzymatic hydrolysis that correlated with porosity, a specific surface area and degree of hydration, the cellulose crystalline structure was of great consideration in the acidic hydrolysis [12]. Beside the orderly crystalline structure in the cellulose molecules, the presence of lignin fraction in the cellulose materials is also responsible in defending the cellulose from hydrolysis agent [13]. Therefore, those barriers offered strong resistance for the conversion of cellulose into glucose.

The effect of acid concentration and temperature did play a significant role towards the hydrolysis reaction. In the kinetic modeling studies of acid hydrolysis, it has been observed that the rate of generation reaction of monomeric sugar from polysaccharides was influenced by temperature and acid concentration [8,9]. Diluted hydrolysis of α-cellulose with high temperature has been investigated by Xiang and his coworkers [14], it was indicated that at above 215°C, the chemical reaction was more sensitive to temperature than the physical factors of cellulose. The physical factors appeared to be eliminated while the true chemical reaction will be a major influential factor in the overall process.

Hydrolysis reaction was generally controlled by hydrogen ion concentration (H^+). At the same time, the cellulose fragment dissolution performed as a function of hydroxyl ion concentration [11]. In their study Xiang and his coworkers [15] have proved that most of the cellulose was dissolved in 65 % of H_2SO_4 or higher. It was indicated that beyond this concentration, the hydrolysis rate was gradually increased with respect to acid concentration. Most of the hydrolysis of lignocellulose may take place with the presence of hydrogen ions. The suitable range of acid concentration should be considered in order to

TABLE 1. Lignocellulose Composition from Different Source of Lignocellulsic Materials.

Sources	Main Components (Percentage by Dry Weight)					References
	Cellulose	Xylan	Hemicellulose	Lignin	Ash	
	(%)	(%)	(%)	(%)	(%)	
Palm Oil EFB	50.4	-	21.9	10.0	0.5	Umikalsom et al., [5]
Sorghum Straw	35.0	19.0	24.0	25.0	-	Herrera et al., [7]
Sugar Cane Bagasse	38.9	20.6	-	23.9	-	Rodriguez-Chong et al., [8]
Corn Cobs	31.7	-	34.7	20.3	-	Rivas et al., [17]
Rice Straw	43.4	20.2	28.0	17.2	11.4	Roberto et al., [18]

reduce the formation of decomposed products [16].

The lignocellulose size was reduced to a very small fine particle powered by using a grinding mill that may increase the surface area and reduce the diffusion problem related to the reactant involved. The milling efficiencies for both knife and hammer mills have been studied and it was found that the product size distribution in the processes was highly feedstock and mill-type dependence [19]. Meanwhile, the use of vibratory ball milling prior to dilute acid hydrolysis process yields substantial increases in its reaction rate. In the acid hydrolysis of hardwood cellulose, the effect of particle size was assessed by kinetic and modeling results. As the chip size was increased, the maximum attainable glucose was decreased and this effect was significant as the temperature and the acid level were raised [20]. The effect of the ratio of liquid to solid has been studied by [16] peat hydrolysis. The liquid to solid ratio was investigated by Lavarack and his coworkers [21] where as the solid to liquid ratio were reduced, the rate of decomposition of xylose would also been reduced as the xylose produced within the hydrolysate was also diluted. In the concentrated hydrolysis of corn cobs, the feed of solid concentration lower than 5 % was considered to improve the conversion of the reducing sugar. The use of 2, 5 and 10 % of solid concentration resulted in maximum conversion of 90, 70 and 65 %

reduced sugar, respectively [22].

In most lignocellulosic wastes, due to the presence of cellulose crystallinity, the chemical attack on the cellulose is retarded. Therefore, chemical pretreatment was necessary to increase the susceptibility of lignocellulose for hydrolysis reaction. Chemical treatment may accelerate the rate of reaction and the extent of cellulose hydrolysis. Sodium hydroxide, NaOH was employed in order to enhance the digestibility of lignocellulose due to the swelling and disrupting of the crystalline structure of cellulose [23]. Sodium hydroxide acts as an intracrystalline swelling agent for both crystalline and amorphous celluloses [24]. In the pretreated biomass with NaOH solution, the sequential actions that involved will be

- The hemicellulose solubilization,
- The increase of cellulose and hemicellulose digestion activity and
- The improve of cellulose and the hemicellulose digestion rate [25].

In this research, a palm oil empty fruit bunch was used as raw material in an acid hydrolysis process. The cellulose fibers from palm oil EFB were converted to sugars, which can be used for ethanol fermentation. The EFB residue contains nearly 50 percent cellulose [26]. From batch acid hydrolysis, experiments for 4 different parameters; solid size,

HCl concentration, solid to liquid ratio and temperature were carried out and the total reduced sugar was formed as the final product. All experiments were conducted with caution to obtain optimum conditions for hydrolysis reaction and maximum liberated sugar concentration. The purpose of this research was to obtain fermentable sugar from renewable sources for production of ethanol as a bio-fuel.

2. MATERIAL AND METHOD

Palm oil EFB was obtained from the FELCRA palm oil milling plant in Seri Iskandar, Perak as a partially dried raw material. Initially, the fiber was dried. Moisture content of the fiber was determined after 24 hours of drying in a drying cabinet at 100°C. Destruction of fiber was carried out by the vibratory grinding in a laboratory with the aim of achieving a large surface area of cellulose for hydrolysis reaction for the to acid act as a catalysts. EFB contains 17 % moisture, collected from palm oil mills nearby. The EFB were primarily air and oven dried, grinded (Apex-Mill A 38133, England) and screened to the particle size of less than 1mm. The grinded fiber was subjected to a sieving process. Fractions retained on available screen size were 1mm, 710, 500 and 250 microns used for the experiments. Determination of the fiber composition was accomplished using the Elemental Analyzer, Perkin Elmer Model 2400. The evaluation of data was based on maximum sugar yield resulting from the cellulose fibers.

A preliminary experimental run was carried out in a flask using 10 to 30 % HCl with an incumbent of 5 % at 45°C. Several solid percentages (2 to 10 %) were studied and the soliid was charged into a 250ml Elernmeyer flasks placed in a temperature controlleded water bath. The effect of solid particle size was investigated for the size of 250, 500, 710 and 1000 microns.

The hydrolyzate was collected and neutralized with a sodium hydroxide solution with a pH of 7. It was then further diluted with distilled water (1/10v/v) and filtered through 0.45 μm cellulose membrane before being analyzed. The total reducing sugar produced in the hydrolyzate was analyzed by the colormetric method using the UV-Vis spectrophotometer, (Cecil 1000) at 540nm using a reducing chemical reagent, 3, 5-dinitrosalicylic acid 98 % solution (DNS reagent) [27].

The pretreatment of fibers was carried out using 0.5 M sodium hydroxide solution. The impregnation of alkaline solution was implemented by a heat treatment at 121°C in an autoclave for about 12 minutes. The pretreated sample was neutralized and dried prior to main hydrolysis. Batch studies were conducted at 45°C using hydrochloric acids to catalyze the hydrolysis of cellulose. A 5 percent solid was charged into a 100ml flask contained 10 % HCl, reaction time was set for one hour. The flask was placed in a Water Bath Shaker, Clifton 1050W, Nickel Electric LTD England and the stirrer was used to mix the solid with a speed of 300 rpm. The sample was withdrawn for sugar analysis at 10 minutes intervals. The defined volume of the sample was immediately naturalized to stop the reaction. Then, the diluted sample was filtered through filter paper, Whatman # 1.

For electronic microscopic scanning (SEM), samples were taken from the hydrolyzed untreated and treated fibers. The samples were freeze-dried in the Freeze Drier, EMITECH, model IK750, Cambridge, UK. The sample was fixed on the aluminum stub and coated with gold palladium by Polaron machine model SD515, EMITECH, Cambridge, UK, at 20 nm coating thickness. Finally the sample was examined under SEM using Stereoscan model S360 brand SEM Leica Cambridge, Cambridge, UK. The elemental analysis of samples was conducted by an E.M. unit, University Sains Malaysia, Penang, Malaysia.

3. RESULT AND DISCUSSION

Acid hydrolysis of untreated and pretreated palm oil residues were carried out in several sets of experiments. Batch experiments were conducted using HCl as the reaction catalyst. For maximum monomeric sugar production, four parameters were considered, such as solid particle size, solid percentage, acid concentration and reaction temperature with respect to reaction time. Each parameter was evaluated to determine the optimum

reaction condition for the maximum liberated sugars.

The effect of solid particle size in acid hydrolysis is shown in Figure 1. Four different sizes of solid particles (250-1000microns) were investigated. At early stages of hydrolysis, the smaller particle size may show an increase in sugar concentration. As the smaller particles possession a larger surface area, the particle size lower than 250 microns do persuade the hydrolysis process, but at longer reaction time for all solid particle sizes, the sugar concentration profile may follow through a similar pattern as is shown in Figure 1. The total reduced sugar with respect to most of the particle sizes at 10 % HCl, 5 % solid and 45°C, a sugar concentration of about 16 g/L was obtained. Experiments with very fine powder may possibly caused by the presence of impurities, such as debris and ash produced from the grinding process which was also experienced by Abdul Aziz and his coworkers [28]. For solid particles with a size bigger than 1mm, the penetration of acid was slower and the sugar concentration gradually increased after 15 to 20 minutes. This was due to large particle size and insufficient contact time for the acid to penetrate inside the large solid particles. Hydrolysis of EFB fiber with a solid size of 500 microns resulted in acceptable sugar concentration. The librated sugar concentration was increased with the reaction time. It was observed that a rapid reaction time of about 40 to 60 minutes was adequate for maximum sugar concentration. Small particles have provided more surfaces for acid to contact the solid and acid penetrated faster into the
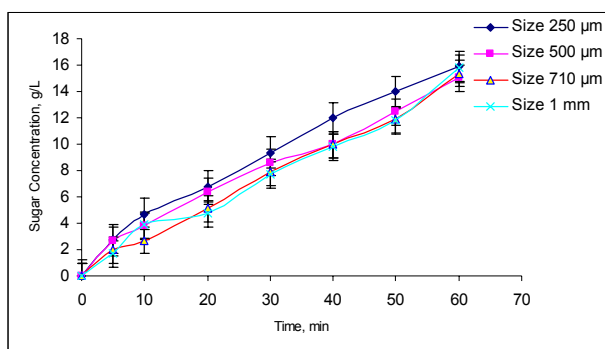
small solid particles. In addition, longer reaction time was necessary if large solid sizes were used. The sugar concentration for acid hydrolysis of 1 mm solid size at 40 min was about 10 g/L. The sugar concentration gradually increased, at 60min, reached to 16 g/L.

Hydrolysis of EFB fiber was carried out at various concentrations of acid; 5 to 30 %, of HCl, with an incumbent of 5 % acid. Merely 36, 60, 65 and 80 % conversion was achieved at reaction time of 60 minutes, 5 % solid with 15, 20, 25 and 30 % of HCl, respectively. As clearly stated by the numbers, the sugar concentration was increased with an increase in the acid concentration that was applicable to the acid, catalyzed the hydrolysis process. The catalyst activity was proportional to H^+ concentration. The more hydrogen ions formed in the solution, the more rapid the hydrolysis process occurred [29,30]. Therefore, the breaking of glucosidic bounds will increase, causing the high conversion of hemicellulose fraction into xylose. Under harsh conditions if high acid concentration was applied, the cellulose fraction would be disrupted and glucose would be generated. In this study, both xylose and glucose concentrations were considered as total reducing sugars. As acid acts as a catalyst, high concentration of acid may speed up the reaction rate while improving the sugar concentration. The experiment was conducted at 45°C with an acid concentration of 10 to 30 % HCl, and with an additional increment of 5 % acid. Figure 2 shows the reduced sugar liberated from acid hydrolysis of 5 % solid EFB at 45°C. The highest sugar
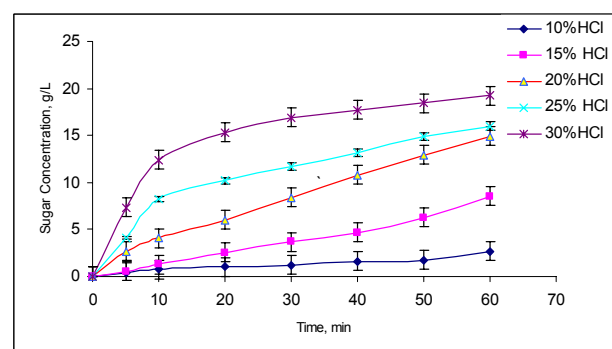

Figure 1. Total reducing sugar with respect to particle size at 10 % HCl, 5 % solid and 45°C.

Figure 2. Total reducing sugar with respect to acid concentration using 0.5mm fiber, 5 % solid at 45°C.

concentration (20 g/L) was associated with high acid concentration and the lowest reduced sugar concentration (2.7 g/L) resulted in 10 % HCl. However, the sugar concentration decreased at high acid concentration at elevated temperatures; the longer reaction time at high temperature may cause deformation of sugar to furfural and hydroxyl methyl furfural. The undesired products, hydroxyl methyl furfural and furfural originate from glucose and xylose decomposition at high temperatures (greater than 55°C) in the presence of acid catalyst, respectively [31].

Figure 3 shows the percentage of solid EFB in acid hydrolysis. Four different percentages of solid EFB (2,5,8 and 10 %) were studied. These conditions coincide with the other researchers' explanation that to a certain percentage of solid concentration of liberated sugar gradually increasing [22]. The lowest percentage of solid resulted in minimum sugar concentration. The concentration of liberated sugar with 10 % HCl at 45°C for 2 and 10 % solid were 7 and 23 g/L, respectively.

The effect of temperature on acid hydrolysis is shown in Figure 4. A temperature range of 35 to 85°C with an incumbent of 10°C was studied. The sugar concentration at low temperatures was low (about 11 g/L). At 45°C, which is a secure temperature, the liberated sugar concentration is about 16 g/L that is about 60 %. At a high temperature of 85°C, the concentration of sugar may increase to 20 g/L. Another words the rate is constant for high temperatures which was higher than the low temperatures since the reaction rate was faster at high temperatures, 85°C. But, at the elevated temperature (greater than 55°C), there is a possibility of decomposition of xylose and glucose to furfural and hydroxyl methyl furfural. However the effect of temperature in kinetic studies of acid hydrolysis has a positive impact. The problem of sugar decomposition needs extensive research to be resolved. The acid hydrolysis data presented in this research focused on positive effects. The negative impact still remains unsolved; it is most probable the problem will be resolved in future research. The high temperature conditions were also experienced by Kim and his coworkers [32] in their hydrolysis study of nitrocellulose (NC). It took only 9 minutes for 90°C to convert the NC to the maximum glucose compared to 63 minutes for
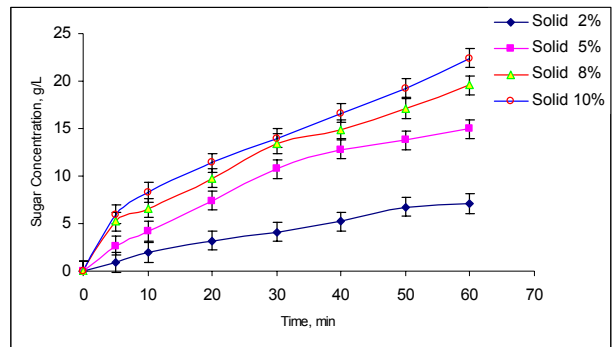

Figure 3. Total reducing sugar with respect to solid percentage at 10 % HCl and 45°C.
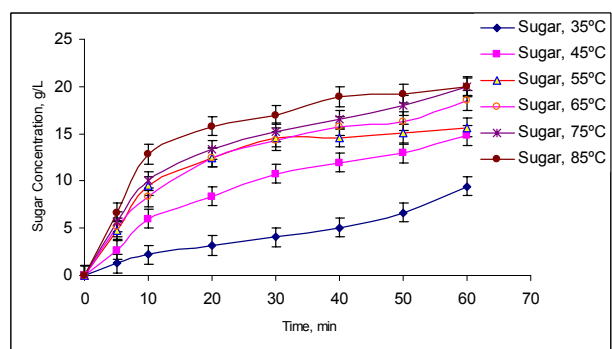

Figure 4. Effect of temperature on total reducing sugar at 10 % HCl and 5 % Solid.

60°C. In addition, [32] it was stated that, temperature did play an important role on the rate of acid hydrolysis reaction. Based on the Arrhenius equation, at high temperatures, the reaction would be faster. Table 2 shows the rate constants and activation energy increase with acid concentration. Table 3 presents the rate constants temperature dependency and the role of acid concentration for 9 sets of experiments. According to Arrhenius law, the rate constants increased as the acid concentrations and temperatures were increased. Beside the higher activation energy showed by its kinetics behavior [15], the high temperature also performed high sugar yield. According to Xiang and his coworkers [14] in their studies, the breakage of hydrogen bonds in hemicellulose and cellulose fraction occurred rather abruptly in response to temperature.

The hydrolysis of the pretreated fibers resulted in about 35 percent more sugar with 5 percent solids using various acid concentrations. It fact, the sugar concentration was observed during the hydrolysis after prior treatment by 0.5M of NaOH solution. Compared to untreated fiber, the hydrolysis of the treated fiber resulted in more than 35 percent of sugar concentration (Figure 5). The hydrolysis reaction was found to be faster with treated fiber. After the NaOH treatment,

hemicellulose fraction of EFB fiber would possibly solubilized. Furthermore, the cellulose fraction swelled and transformed from its crystalline form to the more reactive amorphous form [28]. In addition, it was also understood that lignin might be removed after NaOH treatment leaving carbohydrate fraction reactive towards the acid action [33]. In addition, Umikalsom and his coworkers [5] proved that an increase of reactive cellulose (ready to be attacked by acid) and the

TABLE 2. The kinetic Rate Coefficient and Activation Energy Based on Arrhenius Equation.

Acid Concentration, %	k_i, min^{-1}	E_a, kJ/mol	R^2
10	4.57×10^8	63.78	0.997
20	3.73×10^{12}	74.57	0.998
30	6.32×10^{12}	83.96	0.961

TABLE 3. Kinetic Parameters with Respect to Acid Concentration and Temperature Range of 35-55ºC.

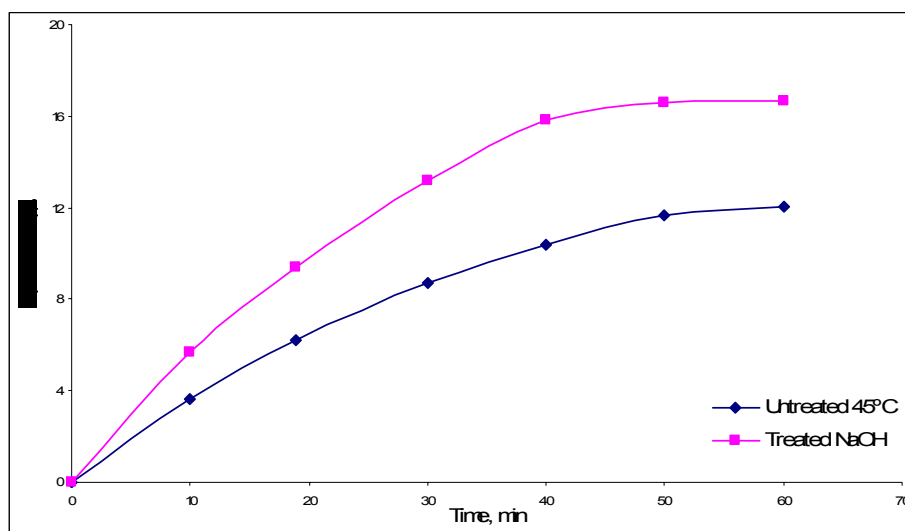| Acid Concentration	k_1 (min^{-1}), at 35ºC	k_1 (min^{-1}), at 45ºC	k_1 (min^{-1}), at 55ºC
10 % HCl	0.007	0.015	0.034
20 % HCl	0.009	0.032	0.112
30 % HCl	0.035	0.138	0.276

Figure 5. Yield of total reducing sugar liberated from treated and untreated EFB fibers, 10 % HCl and 45°C.

reducing of lignin content were not only caused by the pretreatment of NaOH solution itself, but also by autoclaving. Within this chemical treatment of empty fruit bunch fiber, the autoclaving was believed to modify the physical structure of lignin while the NaOH solution acted as an effective intracrystalline swelling agent.

The electronic scanning and images of the treated and untreated palm oil fibers are presented in Figure 6. The surface chemistry reviled that active cites and more extended surfaces were created for the treated fibers and then the reaction of acid hydrolysis made the process act faster on the treated fibers and activated cites. In general, the surface preparation on the treated fibers may result in a higher yield. The uniform action of acid hydrolysis showed the perfect criteria of the treated fibers resulted in higher yield of sugar. In fact, the whole concept of acid hydrolysis of the treated and untreated EFB fibers are presented in SEM and elemental monograms of Figure 6. The hydrolyzed EFB fibers with localized reaction are shown in Figure 6a. The uniform surface area of the treated hydrolyzed fibers is shown in Figure 6b. The elemental analysis for the treated fibers shows about 74.45 wt % carbons. The SEM for hydrolyzed and untreated fiber is shown in Figure 6c. All of the localized sports on the fiber did not contain crystalline product. Figure 6d shows the pretreated fiber electronic scanned image. The SEM for treated and untreated fibers are compared, as the treated fiber shows uniform localized active cites were prepared for further reaction (Figure 6e and 6f).

4. CONCLUSION

From the hydrolysis studies towards palm oil wastes, it was concluded that palm oil wastes show a high potential to be converted to a valuable product, which is monomer sugar. A concentrated acid hydrolysis process was employed in order to perform a moderate reaction condition with ambient temperature and pressure. For a reaction time of 40 minutes, 5 % solid with 15, 20, 25 and 30 percent of HCl, EFB lignocellulose fibers conversion of 36, 60, 65 and 80 % were achieved, respectively. The sugar concentration in the acid

hydrolysis of 10 % solid with 60min reaction time was 22.5 g/L. From the parameters studied, the hydrolysis of EFB present that a better conversion was obtained with 500 micron of particles size compared to the other solid size. It was also concluded that the increase of sugar yield was proportional to both acid concentration and the temperature employed. The reaction rate constant was temperature dependent. In a fast rection, the size of solid particle was inflectional for a short reaction time of less than 30 minutes. In addition, with the prior treatment of EFB with 0.5M of NaOH, the yield of total reduced sugar was observed to increase the sugar concentration. This may be attributed by the solubilization and swelling of hemicellulose and cellulose fraction respectively and exposed the EFB fiber towards the catalytic reagent.

6. REFERENCES

1. Husin, M., Ramli, R., Mokhtar, A., Wan Hassan, W.M., Hassan, K., Mamat, R., and Abdul Aziz, A., "Research and development of oil palm biomass utilization in wood-based industries", Malaysian Palm Oil Board, (2002), 1-5.
2. Hui, Y. H. Ed., "Baily's industrial oil and fat production", 5th edition, John Wiley, New York, Vol. 2, (1996), 309-313.
3. Ma, A. N., Choo, Y. M. and Yusof, B., "Renewable energy from the palm oil industry", Energy REDEC Forum, Langkawi, Malaysia, (1999), 138-146
4. Akmar, P. F. and Kennedy, J. F., "The potential of oil and sago lam trunk wastes as carbohydrate resources", *Wood Science and Technology*, Vol. 35, (2001), 467-476.
5. Umikalsom, M. S., Ariff, A. B., Zulkifli, H. S., Tong, C. C., Hassan, M. A. and Karim, M. I. A., "The pretreatment of oil palm empty fruit bunch fibre for subsequent use as substrate for cellulase production by Chaetomiun globosum kunze", *Bioresource Technology*, Vol. 62, (1997), 1-9.
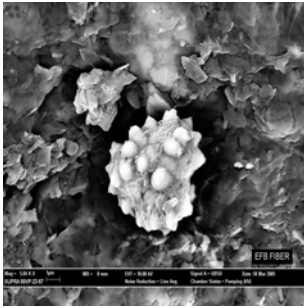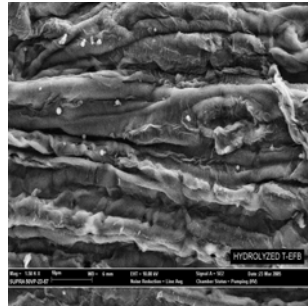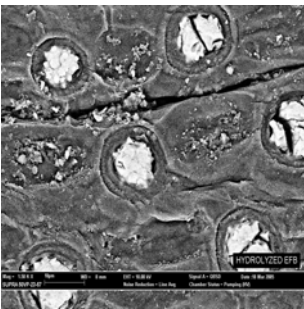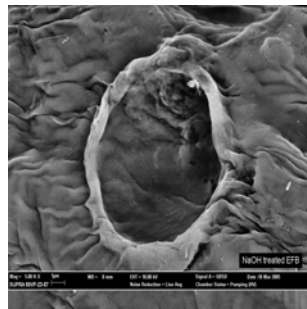
| | | |
| (a) | | (b) |
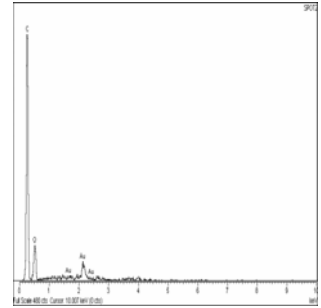
Element	Weight %	Atomic %
C K	74.45	79.51
O K	25.55	20.49
Totals	100.00	

Standard: C   CaCO3   1-Jun-2005 12: 00 AM   O   SiO2   1-Jun-2005 12: 00 AM
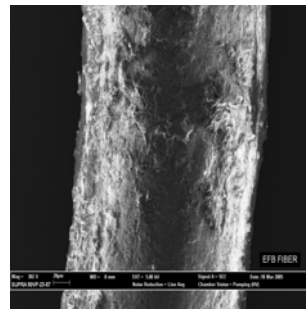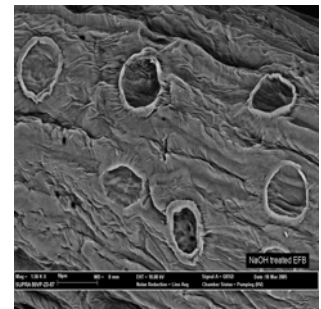
| | | | |
| (c) | (d) | (e) | (f) |
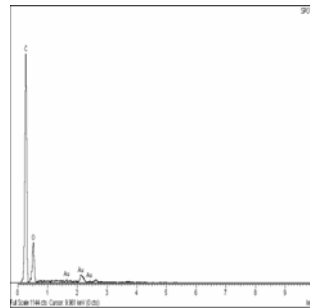
Element	Weight %	Atomic %
C K	72.88	78.16
O K	27.12	21.84
Totals	100.00	

Standard: C   CaCO3   1-Jun-2005 12: 00 AM   O   SiO2   1-Jun-2005 12: 00 AM

Figure 6. Electronic scanning microscopic pictures of untreated, treated and hydrolyzed fibers and elemental analysis of the sample fibers, (a) Hydrolyzed EFB Fibers, Magnified 5000, (b) Hydrolyzed Treated EFB Fibers, Magnified 1500, (c) Hydrolyzed EFB Fibers, Magnified 1500, (d) NaOH Treated EFB Fibers, Magnified 5000, (e) EFB Fibers, Magnified 300, (f) NaOH Treated EFB Fibers, Magnified 1500.

6. Humprey, A. E., "The hydrolysis of cellulosic materials to useful products, in Brown, R. D. and Jurasek, L. ed.", Hydrolysis of cellulose: mechanism of enzymatic and acid catalysts, advances in chemistry series 181, Washington, D. C., (1979).

7. Herrera, A., Téllez-Luis, S. J., Ramírez† J. A. and Vázquez, M., "Production of xylose from sorghum straw using hydrochloric acid", *Journal of Cereal Science*, Vol. 37, (2003), 267-274.

8. Rodríguez-Chong, A., Ramírez, J. A., Garrote, G. and Vázquez, M., "Hydrolysis of sugar cane bagasse using nitric acid: A kinetic assessment", *Journal of Food Engineering*, (2003), 1-10.

9. Aguilar, R., Ramírez, J. A., Garrote G. and Vázquez, M., "Kinetic study of the acid hydrolysis of sugar cane bagasse", *Journal of Food Engineering*, Vol. 55, (2002), 309-318.

10. Fengel, D. and Wegener G., "Wood: Chemistry, Ultrastucture", Reactions, New York, (1984).

11. Ladisch, M. R., "Hydrolysis, in Kitani, O. and Hall, C. W. ed.", Biomass Handbook, Gordon and Breach Science Publishers, New York, (1989).

12. Paquot, M., Thonart, P., Faucart, M. and Mottet, A., "Improvement of pretreatment and technologies for enzymatic hydrolysis of cellulose from inductrial and agricultural refuse and comparison with acidic hydrolysis, in Ferrero, G. L., Ferranti, M. P. and Navaeau, H. ed.", Anaerobic digestion and carbohydrate hydrolysis of waste, Elsivier Applied Science Publishers, USA, (1984).

13. Franzidis, J. and Poteous, A., "Review of recent research on the development of a continuous reactor fro the acid hydrolysis of cellulose, in Klass, D. L. and Emert, G. H. ed.", Fuels from biomass and wastes, Ann Arbor Science, USA, (1981).

14. Xiang, Q., Kim, J. S. and Lee, Y. Y., "A comprehensive kinetic model for dilute-acid hydrolysis of cellulose", *Applied Biochemical Biotechnology*, Vol. 105, No. 108, (2003a), 337-52.

15. Xiang, Q., Lee, Y. Y., Pettersson, P. O. and Torget, R. W., "Heterogeneous aspect of acid hydrolysis of α-cellulose", *Applied Biochemistry and Biotechnology*, Vol. 105, No. 108, (2003b), 505-513.

16. Yan, Y., Li, T., Ren, Z. and Li, G., "A study on catalytic hydrolysis of peat", *Bioresource Technology*, Vol. 57, (1996), 269-273.

17. Rivas, B., Domínguez, J. M., Domínguez, H. and Parajó, J. C., "Bioconversion of posthydrolysed autohydrolysis liquors: An alternative for xylitol production from corn cobs", *Enzyme and Microbial Technology*, Vol. 31, (2002), 431-438.

18. Roberto, I. C., Mussatto, S. I. and Rodrigues, R. C. L. B., "Dilute-acid hydrolysis for optimization of xylose recovery from rice straw in a semi-pilot reactor", *Industrial Crops and Products*, Vol. 17, (2003), 171-176.

19. Himmel, M., Tucker, M., Baker, J., Rivard, C., Oh, K. and Griohmann, K., "Comminution of biomass; hammer and knife mills, biotechnology and bioengineering symposium 15th, in scott, C. D. ed.", *Seventh symposium on biotechnology for fuels and chemicals*, Interscience Publications, USA, (1985).

20. Abasaeed, A. E., Lee, Y. Y. and Watson, J. R., "Effect of transient heat transfer and particle size on acid hydrolysis of hardwood cellulose", *Bioresource Technology*, Vol. 35, (1991), 15-21.

21. Lavarack, B. P., Griffin, G. J. and Rodman, D., "The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose", glucose and other products, *Biomass and Bioenergy*, Vol. 23, (2002), 367-380.

22. Clausen, E. C. and Gaddy J. L., "Concentrated sulfuric acid process for lignocellulosic materials to sugars", *United States Patent*, Vol. 5, (1993), 188-673.

23. Moriyama, S. and Saida, T., "Continuous pretreatment and enzymatic saccharification of lignocellulosics, in Young, R. A. and Rowell, R. M. ed.", Cellulose: Structure, modification and hydrolysis, John Wiley and Sons, Canada, (1986).

24. Millet, M. A., Effland, M. J. and Caulfield, D. F., "Influence of cellulose materials-acid vs. enzymatic, in young, R. A. and rowell, R. M. ed.", Cellulose: Structure, modification and hydrolysis, John Wiley and Sons, Canada, (1986).

25. Lin, K. W., Ladicsh M. R., Schaefer D. M., Noller, C. H., Lechtenberg, V. and Tsao, T. S., "Review on effect of pretreatment on digestibility of cellulosic materials", *AIChE Symposium Series 207*, Vol. 77, (1981), 102-106.

26. Najafpour, G. D. and Tee Chooi, B., "Acid hydrolysis of palm oil residues", *Proceedings of the 14th Symposium of Malaysian Chemical Engineers*, SOMCHE, (2000), 469-476.

27. Miller, G. L., "Use of dinitrosalysilic acid reagent for determination of reducing sugar", *Analytical Chemistry*, Vol. 3, No. 31, (1959), 426-428.

28. Abdul Aziz, A., Das, K., Husin, M. and Mokhtar, A., "Effect of physical and chemical pre-treatments on xylose and glucose production from oil palm press fibre", *Journal of Oil Palm Research*, Vol. 14, No. 2, (2002), 10-17.

29. Mosier, N. S., Ladisch, C. M. and Ladich, M. R., "Characterization of acid catalytic domains for cellulose hydrolysis and glucose degradation, *Biotechnology and Bioengineering*, Vol. 6, No. 79, (2002), 610-618.

30. Nikitin, N. I., "The chemistry of cellulose and wood", Jurusalem, (1966).

31. Larsson, S., Palmqvist, E., Hahn-Ha¨gerdal, B., Tengborg, C., Stenberg, K., Zacchi, G. and Nilvebrant, N., "The generation of fermentation inhibitors during dilute acid hydrolysis of softwood", *Enzyme and Microbial Technology*, Vol. 24, (1999), 151-159.

32. Kim, B. J., Hsieh, H. N. and Tai, F. J., "Anaerobic digestion and acid hydrolysis of nitrocellulose", CERL Technical Report 99/45, US Army Corps of Engineers, Construction Engineering Research Laboratories, (1999).

33. Lim, K. O., Ahmad Din, F. H. and Vizhi, S. M., "A note on the conversion of oil-palm trunks to glucose via acid hydrolysis", *Bioresource Technology*, Vol. 59, (1996), 33-35.