Autoclave-assisted weak acid pretreatment of oil palm empty fruits bunches for fermentable sugar production

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Abstract. Pretreatment of oil palm empty fruit bunches (OPEFB) catalyzed by weak acids (oxalic, formic, and citric acid) in an autoclave under moderate condition is one of the appropriate pretreatment alternatives to recover reducing sugar both from cellulose and hemicellulose. This sugar can be fermented to be various bioprocess products. In this study, the effect of weak acid concentration (1–5\% for oxalic acid; 5–20\% for formic and citric acid), pretreatment temperature (115–125°C), time (60–90 min), and solid loading (5–10\%) was investigated. To improve total reducing sugar yield, residual solid after pretreatment was subsequently hydrolyzed by Cellic CTec2. With the increasing weak acid concentration, pretreatment temperature, and time, more reducing sugar was obtained in spent liquor of pretreatment. On the contrary, the increase of solid loading declined the reducing sugar yield. After residual solid was enzymatically hydrolyzed, the amount of reducing sugar significantly elevated for nearly all weak acids, except 5\% oxalic acid pretreatment. However, the pretreatment by 5\% oxalic acid gave the maximum yield of total reducing sugar at 125°C for 60 min and using 5\% solid loading. The reducing sugar obtained in spent liquor and hydrolysate at this optimum condition was 0.245 g/g OPEFB and 0.352 g/g OPEFB, respectively.

Keywords: pretreatment, autoclave, weak acid, OPEFB, reducing sugar

1. Introduction
Oil palm empty fruit bunches (OPEFB) categorized as biomass feedstock are solid waste generated from palm oil factories. Indonesia as the world’s largest producer of palm oil certainly produces this waste in high amounts. The increase rate of OPEFB production in Indonesia has reached up to 34,280 tons/hour indicating that OPEFB is abundantly available in Indonesia [1,2]. The abundance of OPEFB amount contributes to the environmental issue, so this must be immediately coped with. One of the best alternative solutions to tackle this problem is the conversion of OPEFB to a variety of added-value products.

The major component of OPEFB consists of cellulose (21.9–35.3\%), Hemicellulose (10–22.1\%) and lignin (4.3–17.7\%) [1,3,4]. In particular, cellulose and hemicellulose can be either chemically or biologically hydrolyzed to reducing sugar such as glucose, xylose, mannose, arabinose, and galactose.
This sugar is subsequently fermented by several types of microorganisms to form bioprocess products, for instance, bioethanol and xylitol. Thus, OPEFB is highly potential to be used as the raw materials for producing marketable products.

Direct hydrolysis without any prior treatment could lead to the ineffective degradation of lignocellulose. Consequently, the lower yield of reducing sugar was obtained. Thus, before hydrolysis, the pretreatment process had to be conducted to degrade the recalcitrant structure of lignin. The objective of pretreatment was chiefly to break lignocellulose structure to ease the accessibility of enzymes in hydrolysis [6,7]. The pretreatment method commonly used just focused on cellulose degradation to produce glucose such as steam explosion and alkaline pretreatment. This pretreatment type deconstructed and removed lignin without considering another valuable constituent, hemicellulose [6].

The alkaline use for pretreatment is aimed to dissolve lignin, decline cellulose crystallinity, and increase enzyme digestibility [10,11]. The solid phase rich in cellulose is subsequently hydrolyzed to glucose while the liquor containing degraded lignin, phenolic compounds, and sugar oligomer of hemicellulose is discarded. The removal of liquor is because the separation between phenolic compounds and sugar oligomer is unfeasibly conducted. On the other hand, hemicellulose is more easily degraded with a less severe process. If the pretreatment is performed in high pressure and temperature, xylose and arabinose formed will be dehydrated to be furan [10], an inhibitor for the subsequent process. Hence, to minimize the amount of hemicellulose wasted the proper pretreatment method for recovering all reducing sugar from OPEFB must be evaluated.

According to [11], autohydrolysis was the best pretreatment technique to acquire all reducing sugar from OPEFB cellulose and hemicellulose. This process was initiated with the deionization of water to be hydrogen ion. This ion degraded hemicellulose structure including the cleavage of acetyl group and dissolved to liquid. As a consequence, the presence of such an acetyl group catalyzed the degradation of hemicellulose structure [13]. From this theory, it is summed up that acid existence could accelerate the process to release hemicellulose from OPEFB. Therefore, acid pretreatment accompanied by heat is the most appropriate alternative for reducing sugar production [9]. Additionally, this pretreatment also could reduce energy consumption [14].

Various type of acid pretreatment assisted with heating has been considerably reported. The type and concentration of pretreatment, however, influenced the yield of reducing sugar. Both strong acid and weak acid with high concentrations caused the formation of furan [10]. Hence, this work used weak acids as the solvent assisted by the heat to decompose lignocellulose and obtain all reducing sugar. The types of weak acid used in this work were oxalic acid [13], formic acid, and citric acid [14]. Pretreatment temperature, time, and solid loading were also investigated in this work.

2. Materials and methods

2.1. OPEFB preparation

In this study, oil palm empty fruit bunches (OPEFB) was provided from PT Condong Garut, West Java, Indonesia. Preparation of OPEFB was initiated with washing and was followed by drying using oven drying at 60 °C for 1 day. Dried OPEFB was milled using a disc mill and subsequently sieved to obtain OPEFB with particle size below 80 mesh [17]. The composition of the OPEFB particle was then analyzed following the method of [18]. The OPEFB used in this study contained cellulose (48.55 ± 7.64%), hemicellulose (28.06 ± 0.41%) and lignin (23.39 ± 8.05%).

2.2. Autoclave-assisted pretreatment

The OPEFB (5–10 gram) was soaked and mixed with 100 ml of the weak acid in a 300-mL flask until all parts of OPEFB was wet. The types of weak acid used in this work oxalic acid (1–5%, w/v), formic acid (5–20%, v/v) and citric acid (5–20%, w/v). The OPEFB was heated in the autoclave at 115–125°C and then the temperature was maintained constant for 60–90 minutes. Pretreated OPEFB was cooled to room temperature. Two fractions formed, spent liquor and residual solid, were then
separated by filter cloth. The spent liquor was directly analyzed to determine total reducing sugar concentration following the DNS method [19] while the residual solid was dried at 80 °C for 24 hours.

2.3. Enzymatic hydrolysis of residual solid
Three grams of residual solid and 29 mL of citrate buffer (0.2 M, pH 5) was dissolved in 100-mL flasks. To maintain the contaminant-free sample the solid in the flask was sterilized at 121°C for 15 minutes. One mL of Cellic CTec2 was then added to the OPEFB. The OPEFB hydrolysis was performed using rotary shaker incubator (ω = 150) rpm at room temperature for 72 hours. After incubation, the total reducing sugar of hydrolysate was quantitatively determined using the dinitrosalicylic (DNS) method [19]. The yield was calculated following equation below:

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Yield = \frac{\text{Reducing sugar concentration (g/L)} \times \text{Working Volume (L)}}{\text{Initial OPEFB (g)}}
\]  

The significance of the data was statistically analysed by a one way analysis of variance (ANNOVA with \( \alpha = 0.05 \)). The tool to compute the data was IBM SPSS Statistic 25.0.

3. Result and discussion

3.1. Effect of different weak acid types and concentration on reducing sugar yield
The influence of weak acid types and concentration on reducing sugar yield was shown in figure 1. The highest reducing sugar yield for spent liquor was obtained when the pretreatment was conducted using 5% oxalic acid (0.11 g/g-OPEFB). This result showed that stronger weak acid was able to degrade more cellulose and hemicellulose in OPEFB than the solution with lower acidity level, formic and citric acid for this study. Nevertheless, after residual solid was enzymatically hydrolyzed, the yield of reducing sugar at 5% oxalic acid pretreatment was the lowest of the other pretreatment solution types (0.19 g/g-OPEFB). This indicated that nearly all cellulose and hemicellulose had been moved to spent liquor and converted to reducing sugar or its oligomer during the pretreatment process. Just a little portion of those was retained in residual solid. Moreover, stronger acid could extract more cellulose and hemicellulose to liquor, and their amount still could be increased with higher concentration.
Figure 1. Yield of reducing sugar in different types and concentration of weak acid (T = 115 °C, t = 60 minutes, 10% solid loading). The different superscript letters indicated that the mean value differed significantly (p < 0.05).

To increase the yield the enzymatic hydrolysis of pretreated OPEFB was carried out by Cellic CTec2. The result showed that the OPEFB pretreated using 20% formic acid gave the highest yield for residual solid hydrolysate (0.27 g/g-OPEFB). The use of 20% formic acid could increase the accessibility of enzyme in degrading solid, so more reducing sugar was released to the hydrolysate. Besides, the amount of cellulose and hemicellulose in OPEFB degraded to spent liquor during pretreatment was higher than citric acid pretreatment, but it was lower than oxalic acid pretreatment with a concentration above 3%. After the yield of spent liquor and residual solid hydrolysate was added up, the yield of pretreatment both using 3%, 5% oxalic acid and 20% formic acid was not significantly different (p > 0.05) with the yield of 0.31 g/g-OPEFB, 0.30 g/g-OPEFB, and 0.31 g/g-OPEFB, respectively. Pretreatment using these three weak acid types gave the highest yield as compared to the other types.

Apart from weak acid types, the concentration of each weak acid also affected the yield of reducing sugar obtained. The change of concentration caused significant variations in the reducing sugar yield (p < 0.05). The increase of oxalic acid concentration could improve pretreatment performance shown by the increase of the yield from 0.28 g/g-OPEFB for 1% oxalic acid to 0.31 g/g-OPEFB for 3% oxalic acid. However, when the concentration was gone up to 5%, no significant difference was observed (p > 0.05). On the other hand, the increase of concentration for both formic acid pretreatment and citric acid pretreatment was also significantly influenced by the yield (p < 0.05). The more concentration was used, the higher yield was obtained.

The pattern of reducing the sugar amount released from OPEFB was different between oxalic acid and the other types of weak acid. After the spent liquor was analyzed, the more concentration could increase the yield for all weak acid types. This result showed that concentration influenced the yield during pretreatment. After residual solid hydrolysate was analyzed, the decrease of yield occurred with the increase of concentration, particularly for oxalic acid. Conversely, for the other types of a weak acid (formic and citric acid), the increase of concentration could elevate the yield of reducing sugar in
the residual solid hydrolysate. According to [20] High concentrations of weak acids could break down lignocellulose, so the digestibility of enzymes in OPEFB degradation improved. Several studies had been reported concerning the effect of weak acid pretreatment on the yield of reducing sugar from biomass. According to [21], the use of the highest concentration provided high sugars as in the study of bagasse pretreatment. Pretreatment of durian seed waste also provides increased yield when acid concentration is increased [22]

3.2. Effect of different temperature on total reducing sugar yield
The other influencing factors evaluated in this study was the pretreatment temperature increase from 115 °C to 125 °C. The evaluation was conducted was only the lowest and highest concentration for each weak acid type. According to figure 2, overall, pretreatment temperature could change the yield of total reducing sugar from spent liquor and residual solid significantly \((p < 0.05)\). However, several pretreatment types did not give significant change, for instance, 1% oxalic acid and 5% citric acid. Temperature gave an insignificant effect to the yield \((p > 0.05)\) when the pretreatment was conducted using these both acid types. On the contrary, for the other weak acid types, the increase of total reducing sugar yield increased significantly with the increase of temperature. The highest yield was reached up to 0.48 g/g-OPEFB using 5% oxalic acid pretreatment at 125 °C for 60 minutes.

The increase of temperature ranging from 115 °C to 125 °C during 5% oxalic acid pretreatment could escalate the yield of reducing sugar by 0.18 g/g-OPEFB. This result also was the highest increase as compared to the other pretreatment types. The significant increase of this pretreatment type occurred to spent liquor which was from 0.11 to 0.31 g/g-OPEFB. Contrarily, the increase in temperature could decrease the yield in residual solid. However, when the pretreatment was carried out at lower oxalic acid concentration (1%), the yield relatively remained constant. This trend was led to more cellulose and hemi cellulose moved to spent liquor during pretreatment and remained the lower amount of those in residual solid OPEFB when the temperature was raised at higher weak acid concentration [23,24]. However, an insignificant increase in the yield occurred at the lower concentration of weak acids.

The same pattern was also shown in citric acid pretreatment. A significant increase and decrease of the yield for spent liquor and residual solid hydrolysate, respectively, took place only at the highest citric acid concentration (20%). However, there was no effect of temperature on the yield for 5% citric acid, the lowest concentration in this study. In contrast to oxalic and citric acid pretreatment, formic acid pretreatment showed the increase of the yield in the residual solid with the increase of temperature. At the lower concentration of formic acid, the effect of temperature was not significantly affected on the yield in spent liquor, but vice versa for higher formic acid concentration. This was because formic acid pretreatment was possible to bind formic groups in hemicellulose, so pretreatment was conducted effectively [25, 26].
3.3. Effect of different pretreatment time on total reducing sugar yield

The effect of pretreatment time on reducing sugar yield had been investigated in this study. The pretreatment duration range used was from 60 to 90 minutes. Figure 3 showed that at the lowest concentration of weak acid, the extension of time showed a positive effect shown by the increase of reducing sugar yield. However, the decline of oxalic acid and citric acid yield occurred in the highest concentration (20% formic acid) when the time was extended. The increase of yield at formic acid pretreatment was caused by the longer reaction time to breakdown lignocellulose into reducing sugar [27]. Breaking down the carboxyl groups in hemicellulose took place during pretreatment and the amount increased with the extension of the time, as conducted by [25,28].

Differences result of reducing sugar yield between oxalic and citric acid pretreatment with formic acid pretreatment had been reported in similar studies. A longer time residence in formic acid pretreatment could produce a high amount of reducing sugar [25]. This high amount of reducing sugar was obtained at the same pretreatment temperature and concentration of formic acid. A study on oxalic acid pretreatment on straw showed a decreased yield when the time residence was added [29]. However, there were no specific studies regarding the effect of time residence on citric acid pretreatment to produce reducing sugar.

Although formic acid pretreatment had a positive effect when the time residence was added, the highest yield was obtained by oxalic acid pretreatment. Oxalic acid pretreatment produced the highest amount of reducing sugar at 5% concentration and pretreatment temperature of 125 °C for 60 minutes. In this study, the highest reducing sugar yield was the main objective of the investigation, causing 60 minutes of pretreatment time residence to be used for further investigation.
3.4. Effect of different solid loading use on total reducing sugar yield

Investigation of different solid loading used had been investigated in OPEFB pretreatment to produce reducing sugar. The investigation was carried out using the concentration of weak acid, in each type. In addition, the pretreatment temperature was used at 125°C for 60 minutes according to the results of the previous investigation. Reduced solid loading showed a positive effect due to an increasing reducing sugar. Thus, the addition of solid loading could inhibit the breakdown of lignocellulose into reducing sugar and 5% solid loading could produce more amount of reducing sugar than 10% solid loading[30].

In the spent liquor, the amount of reducing sugar from oxalic and citric acid pretreatment decreased whereas the formic acid pretreatment was increased the reducing sugar yield. However, the amount of reducing sugar in residual solid was increased when the reduction of solid loading was carried out. Although the amount of reducing sugar in the spent liquor of formic acid pretreatment was increased, the residual solid still provided a large amount of reducing sugar than residual solid of 10% solid loading. A large amount of reducing sugar produced by formic acid pretreatment (in 5% solid loading) caused the easier degradation of the carboxyl groups in hemicellulose[28]. Generally, the reduction of solid loading in pretreatment could increase the amount of reducing sugar yield[31]. Figure 4 showed that the reduction of solid loading increased reducing sugar yield. The highest reducing sugar was obtained by 5% oxalic acid pretreatment in 5% solid loading. The result indicates oxalic acid pretreatment provided the highest reducing sugar yield in each investigation.
Figure 4. Comparison of difference solid loading use on total reducing sugar yield using the highest weak acid concentration and the best pretreatment condition (T = 125 °C and t = 60 minutes). The different superscript letters indicated that the mean value differed significantly (p < 0.05).

3.5. Comparison the result of this study with other similar studies

Table 1 showed the results of several similar studies with a variation of the pretreatment methods. The result of this study provided reducing sugar yield in the range of the results in other studies. In addition, this study provided an easy and inexpensive method to use compared to other studies in table 1. Then, the use of weak acid was not dangerous and easier to waste remediation than the study was used a strong acid as in [32,33].

In this study, the pretreatment temperature and time residence were compared to other similar studies. The use of low temperatures with time residences less than one hour provided a high amount of reducing sugar as in the result of [35,37,39,40]. Thus, the use of pretreatment temperature was considered as low-cost pretreatment methods even though the time residence was longer than the study of [33,34,36,38,41].

The reduction of solid loading in this study showed an increase in reducing sugar and could compare with other similar studies. Less solid loading in this study could effectively to produce reducing sugar than the results of studies was used 25–50% solid loading [33,36]. Thus, the results of this study provided an advantage as ease, low cost and effectiveness process than other similar studies.
Table 1. Comparison of this study result with other related study.

| Raw materials       | Pretreatment type                              | Condition | Xylose (g/g raw material) | Glucose (g/g raw material) | Reference |
|---------------------|------------------------------------------------|-----------|---------------------------|----------------------------|-----------|
|                     |                                                 | T (°C)    | t (min)                   | Solid loading              |           |
| Quercus mongolica   | 4% sulfuric acid, supercritical water hydrolysis| 121       | 105                       | 14%                        | 0.211     | 0.509     | [28]        |
| Wheat straw         | 2% sulfuric acid, thermochemical pretreatment   | 180       | 10                        | 50%                        | 0.075     | 0.290     | [29]        |
| Pine chips          | 4% sulfuric acid, thermochemical pretreatment   | 178       | 5                         | 50%                        | 0.105     | 0.182     | [29]        |
| Poplar chips        | 3% sulfuric acid, thermochemical pretreatment   | 178       | 15                        | 50%                        | 0.131     | 0.400     | [29]        |
| Cassava residue     | ULA one-step pretreatment                      | 180       | 20                        | 5%                         | 0.411     | NM*       | [30]        |
| Elephant grass      | KOH and glycerol pretreatment                  | 121       | 60                        | 6%                         | 0.138     | 0.190     | [31]        |
| Liriodendrum tulipifera | Dilute acid pretreatment                  | 158       | 13                        | 25%                        | 0.037     | 0.042     | [32]        |
| Eucalyptus urophylla| GLV/diluted acid pretreatment                  | 80        | 60                        | 2%                         | 0.011     | 0.002     | [33]        |
| Wheat straw         | Steam explosion pretreatment                   | 200       | 10                        | 10%                        | 0.117     | 0.354     | [34]        |
| Walnut shell        | Mineral acid and alkali pretreatment           | 121       | 60                        | 10%                        | 0.138     | 0.140     | [35]        |
| Corn stover         | Mineral acid and alkali pretreatment           | 121       | 60                        | 10%                        | 0.711     | 0.360     | [35]        |
| Kenaf               | Alkali pretreatment                            | 121       | 30                        | 2%                         | 0.274     | 0.499     | [36]        |
| Corn straw          | Steam explosion pretreatment                   | 190       | 3                         | 5%                         | 0.056     | 0.370     | [37]        |
| OPEFB               | Autoclave-assisted weak acid pretreatment      | 125       | 60                        | 5%                         | 0.596**   |           | This study  |

* Not measured
** in reducing sugar

4. Conclusion
Several parameters observed in this study such as weak acid types and concentration, pretreatment temperature, time, solid loading was significantly affected by the yield of reducing sugar both in spent liquor and residual solid hydrolysate. High level of acidity of weak acid for instance oxalic acid could produce higher reducing sugar in spent liquor. Because nearly all of cellulose and hemicellulose in OPEFB had been moved to spent liquor, this pretreatment gave the lowest yield in the residual solid hydrolysate. In addition, the more concentration was used, the higher yield was obtained. The increase of pretreatment temperature also could increase the yield for the highest concentration of weak acid (5% oxalic acid, 20% formic acid, and 20% citric acid). On the contrary, the insignificant change occurred when the temperature was increased for the lower concentration of weak acid. The extended pretreatment time from 60 minutes to 90 minutes declined the yield for 5% oxalic acid and 20% citric
acid pretreatment. Besides, 5% solid loading gave the highest yield of reducing sugar up to 0.60 g/g-OPEFB using 5% oxalic acid at 125 °C for 60 minutes.

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