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Effect of Ultrasonication in Organosolv Pretreatment for Enhancement of Fermentable Sugars Recovery from Palm Oil Empty Fruit Bunches

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ABSTRACT

Lignocellulosic biomass has been widely explored as a substrate for biofuel production. In view of the recalcitrant properties of biomass, pretreatment is essential to open up the structure so it could more accessible to hydrolytic reactant for better hydrolysis process to yield fermentable sugars. The study focused on the incorporation of ultrasonication with organosolv pretreatment of palm oil empty fruit bunches (EFB) using ethanol solvent. The results showed that ultrasound-assisted organosolv improved the recovery of reducing sugars from EFB. A maximum amount of reducing sugars 41.3 mg was recovered from EFB under sonication power and temperature of 100% and 50°C, 30% ethanol concentration for a pretreatment duration of 15 min without the presence of sodium hydroxide catalyst. It was higher compared to organosolv pretreatment without ultrasonication and with the presence of sodium hydroxide catalyst. Among the operating variable investigated, sonication power, pretreatment time and ethanol concentration were significantly affecting the pretreatment performance, but not for the pretreatment temperature and presence of catalyst.

1. Introduction

The world is highly dependent on the use of fossil fuel for daily activities, such as transportation, industrial, residential and commercial activities. Fossil fuel is a non-renewable energy source and its usage is causing air pollution as its combustion releases carbon monoxide, carbon dioxide, nitrogen dioxide and volatile organic compounds. These problems instigate the study of renewable energies to replace the use of fossil fuel. Bioethanol is one of the most favorable choice of fuels, because its combustion produces less particulate, nitrogen oxide and volatile organic compounds [1]. Bioethanol can be produced from agricultural crops and wastes. The latter is more favorable in view of its sustainability and economic feasibility. Its utilization also prevents food competition which experience by bioethanol production from agricultural crops.

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In Malaysia, due to fast develop of palm oil industry, large amount of wastes including palm oil fronds, trucks and empty fruit bunches (EFB) are produced. These wastes contribute to 90% of the total palm tree biomass [2]. Among them, EFB contained relatively higher carbohydrates content, and hence it which could be converted to sugars and subsequently bioethanol. Similar to other lignocellulosic biomass, EFB is also recalcitrant to chemical processing in view of the complex structure of three major components of cellulose, hemicellulose and lignin. Therefore, EFB need to be pretreated for better hydrolysis yield.

The purpose of pretreatment is to break down the cell wall barrier and lignin-carbohydrate complexes, as well as reduces cellulose crystallinity, so that hydrolytic reactant can attack the biomass macrostructure and convert it to sugars monomers, and subsequently to bioethanol. Pretreatment process can be categorized into few methods, including chemical, physical, biological and physicochemical. Chemical pretreatment is reported to be more effective in biomass pretreatment [3,4]. Organosolv pretreatment is the most promising chemical pretreatment due to its ability to produce valuable by-products, and ease recovery and recycling of organic solvent used during the pretreatment process [5]. Thus, in long-term production, organosolv will be more economic as compared to other pretreatment methods. Organosolv pretreatment is a pretreatment process that remove lignin or some portion of hemicellulose with the help of organic solvents such as ethanol [6]. With the removal of lignin, the biomass will be more readily converted to fermentable sugars.

All chemical pretreatment processes including organosolv need thermal heating to improve the rate of conversion. Recently, there are few studies on incorporating ultrasonic irradiation to replace conventional thermal heating for enhanced pretreatment [7,8]. Ultrasonic irradiation creates cavitation effect of the hydrolytic reactant to pretreat the biomass. Cavitation effect is created when the acoustic energy achieved by the microbubbles formed from ultrasonic irradiation received sufficient intensity, making the microbubbles unstable and breakdown [9,10]. The irregular breakdown of microbubbles at the solvent solid interface (biomass) produces microjets at high speed towards the biomass surfaces and strong shockwaves with pressure up to 103 MPa, leading to the production of tremendously strong shear forces which able to distribute the solvent into insignificant droplets and improve the effectiveness of the pretreatment process [11].

In this study, the synergistic effect of organosolv pretreatment with ultrasonication on EFB was investigated. The operating conditions including sonication power, temperature, pretreatment time, ethanol concentration, effect of catalyst was evaluated. The pretreatment efficacy was also compared to without any pretreatment and without ultrasonication. The evaluation was made based on amount of reducing sugars recovered from the EFB.

2. Materials and Methods

2.1 *Materials*

EFB collected from Kwantas Oil Sdn Bhd, Malaysia was washed to remove dirt and contaminant, followed by drying in an oven (AX 120, Carbolite, United Kingdom). Dried EFB sample was ground and sieved to particle size of approximately 500 µm. This is to ensure the consistency in results reporting at the later stage. Ethanol (95.0% purity), sulphuric acid (95.0-97.0% purity) and sodium hydroxide were purchased from Friendemann Schmidt, Malaysia.

2.2 *Ultrasound-assisted Organosolv Pretreatment*

Organosolv pretreatment was conducted by adding 10% (w/v) EFB in a test tube containing ethanol solvent. The pretreatment was conducted in an ultrasonic bath (SK7210 HP, Kudos, China) with adjustable power and temperature. Samples were collected throughout the pretreatment. The effect of pretreatment temperature, sonication power, ethanol concentration and presence of catalyst on the pretreatment performance were investigated. The range of investigation of each variable are tabulated in Table 1. The frequency of ultrasonication remained constant at 53 kHz.

Table 1 Investigated variables with their range of studied

Variable	Range of investigation
Sonication power (%)	40, 60, 80, 100
Temperature (°C)	25, 50
Ethanol concentration (%, v/v)	10, 20, 30, 40, 50
Type of catalyst	No catalyst, sodium hydroxide

Having had the OPEFB pretreated, the mixture was washed with distilled water for removal of ethanol residual. The mixture was centrifuged (2-6E, Sigma, Germany) and filtered. Pretreated solid residues were oven-dried at 60°C for a day prior to acid hydrolysis. The experiment was repeated by conducting the organosolv pretreatment in water bath (TW 12, Julabo, Germany) at 50°C for comparison basis. All experiments were conducted in duplicate.

2.3 *Acid Hydrolysis*

Pretreated EFB was subjected to acid hydrolysis using low concentrated sulphuric acid (2%, v/v) in a water bath maintained at 50°C for 30 min. After the reaction, the hydrolysate (liquid supernatant) was separated though filtration and the concentration of reducing sugars was determined using 3,5-dinitrosalicylic acid (DNS) assay [12]. The amount of reducing sugars was calculated using Eq. (1):

$$\text{Mass of reducing sugars} = \text{mass of reducing sugars (mg)} \times \text{volume of hydrolysate (ml)} \quad (1)$$

3. Results and Discussion

3.1 *Effect of Sonication Power and Pretreatment Time on Reducing Sugars Recovery from Pretreated EFBs*

Effect of sonication power on the amount of reducing sugars recovered from pretreated EPB is illustrated in Fig. 1. It can be observed that sonication power had a significant effect on the pretreatment performance in terms of reducing sugars recovery during acid hydrolysis of pretreated EFB. At short pretreatment time of 15 min, the higher the sonication power, the higher amount of reducing sugars was recovered. Reducing sugars recovered was more than double when sonication power increased from 40% to 100%. However, this trend was not observed when pretreatment was conducted more than 15 min. A strong interaction between the sonication power and pretreatment time was observed in pretreatment performance.

At ultrasonication power of 40%, reducing sugars yield was the lowest at 15 min (13.3 ± 0.2 mg) but increased with pretreatment time to 36.7 ± 0.3 mg at 2 h. Despite the higher amount of reducing sugars obtained at higher sonication power when short pretreatment duration was applied, declination of yield was observed when pretreatment prolonged and the degree of declination increased with sonication power. At sonication power of 60%, amount of reducing sugars recovered increased drastically to 36.7 ± 0.4 mg for the 30 min of pretreatment and the increment was slowed down and reached plateau at 39.3 ± 0.1 mg when pretreatment extended to 1 h before declination to 36.0 ± 0.3 mg when pretreatment prolonged further to 2 h. The time to attain maximum amount of reducing sugars reduced with increased in sonication power. Maximum yield of 37.4 ± 0.1 mg and 41.3 ± 0.0 mg was achieved at 30 min and 15 min at sonication power 80% and 100% respectively. These yields decreased linearly with pretreatment time.

The results showed that sonication power significantly affects the performance of pretreatment, whereby sonication power intensity found to have positive influence on reducing sugars recovery from EFB subjected that the pretreatment duration was being controlled to avoid unnecessary product degradation at prolonged pretreatment. This is because, sonication power increases the cavitation phenomena of ethanol solvent and thus greater disruption of biomass could be attained [13].

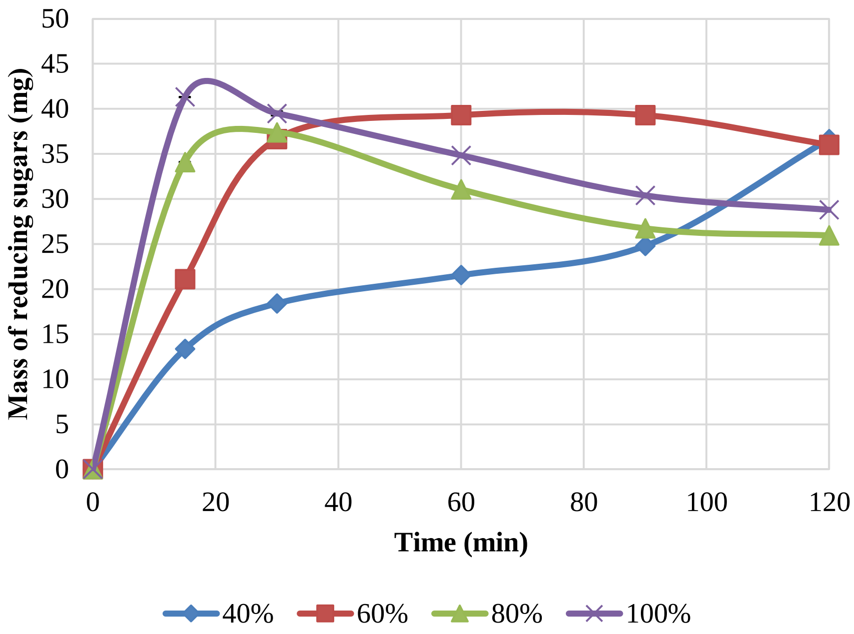

Fig. 1. Reducing sugars recovery from EFB at different sonication powers

3.2 *Effect of Sonication Temperature on Reducing Sugars Recovery from Pretreated EFBs*

To study the influence of sonication temperature on pretreatment performance, ultrasonic bath was set at temperature 50°C and without temperature effect (room temperature, 25°C). The pretreatment performance was determined from the amount of reducing sugars recovered in acid hydrolysis of pretreated EFB. The amount of reducing sugars recovered at both room temperature and 50°C are presented in Fig. 2. When temperature was incorporated during sonication, higher amount of reducing sugars was attained. However, the increment was insignificant compared to sonication conducted at room temperature. Although there were many studies reported that increment in temperature improved the pretreatment process, but the reported temperatures were relatively high at 140°C to 220°C [14,15]. With the low temperature applied during ultrasound-assisted organosolv pretreatment, its effect in reducing sugars recovery became insignificant.

The temperature effect was investigated at 100% sonication power as it gave the highest amount of reducing sugars at shortest pretreatment time of 15 min (Figure 1). Interaction effect of temperature and time on pretreatment performance was studied by extending the pretreatment from 15 min to 1 h. Similar trend was observed at both temperatures, 25°C and 50°C. Maximum amount of reducing sugars was achieved at 15 to 20 min and the yield gradually decreased when pretreatment prolonged to 1 h. This suggested that the insignificant interaction effect between temperature and time on pretreatment performance, which was in contradiction to many reported works [8,16]. Again, the plausible reason for this observation was due to the low temperature of 50°C applied in this work which caused insignificant variation compared to when the reaction conducted at room temperature.

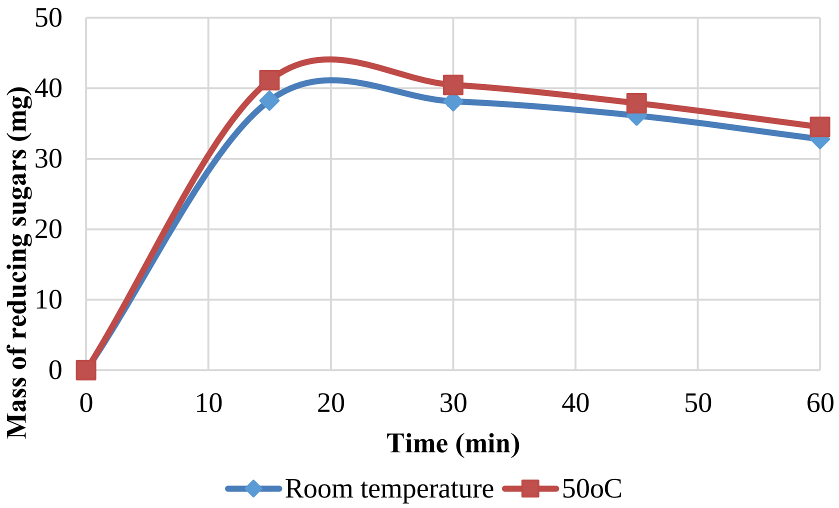

Fig. 2. Reducing sugars recovery from EFB at different sonication temperatures

3.3 *Effect of Ethanol Concentration on Reducing Sugars Recovery from Pretreated EFBs*

In organosolv pretreatment, ethanol was among the most widely used solvent in view of its benign and good solvation properties [17]. The effect of ethanol concentration on the recovery of reducing sugars from EFB was investigated by subjecting the EFB to different ethanol concentrations ranged from 10% (v/v) to 50% (v/v). The mass of reducing sugars attained at different ethanol concentrations is plotted in Fig. 3. It is clearly shown that ethanol concentration of 30% (v/v) gave the highest amount of reducing sugars at 38.3 ± 0.2 mg. Different results were reported by different researchers. For instance, Heringer [18] reported that Loblolly pine gave an optimum reducing sugars yield at 65% of ethanol. Ravindran and his co-authors [19] reported to achieve maximum sugars at 68% ethanol concentration when spent coffee waste was applied, and ethanol concentration of 45% was reported for rice straw by Asadi and Zilouei [20].

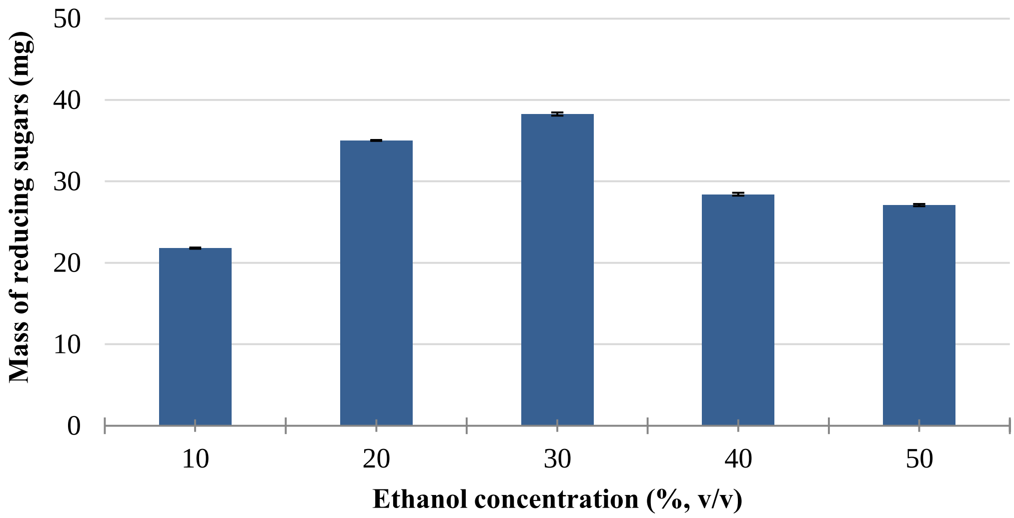

Fig. 3. Reducing sugars recovery from EFB at different ethanol concentrations

The difference in results could be due to the effect of different types of lignocellulosic biomass applied. Different biomass has different composition and bonding within the cellulose-hemicellulose-lignin complex, and hence, they require different concentration of ethanol in breaking the bonds for an effective conversion of biomass to sugars [17]. Hence, study on effect of ethanol concentration on extraction of sugars from biomass is crucial as it varies for different types of biomass. With identified optimum ethanol concentration, the sugars production could be maximized. In this work, 30% of ethanol concentration was reported to be the best in pretreating EFB as it recovered the highest amount of reducing sugars.

3.4 *Effect of Catalyst on Reducing Sugars Recovery from Pretreated EFBs*

In most chemical processes, catalyst is used to lower the operating conditions to improve process safety and economic feasibility. The study was further extended by incorporating 1% (w/v) of sodium hydroxide as catalyst during the pretreatment reaction. Sodium hydroxide was selected as the catalyst as it has been reported to be effective in delignification [21,22]. The amount of reducing sugars recovered from EFB under the influence of sodium hydroxide catalyst and without the catalyst was compared as in Fig. 4. The addition of catalyst during the organosolv pretreatment did not improved the amount of reducing sugars but caused a slight decrement in yield. The finding was also supported by Park and his colleagues [23] where the addition of 1% sodium hydroxide had no effect on biomass pretreatment. Although sodium hydroxide reported to be effective in delignification, its incorporation as a catalyst during organosolv did not exhibit its potential in biomass pretreatment. The is because, the presence of sodium hydroxide will cause considerable sugars degradation at low pretreated biomass [23].

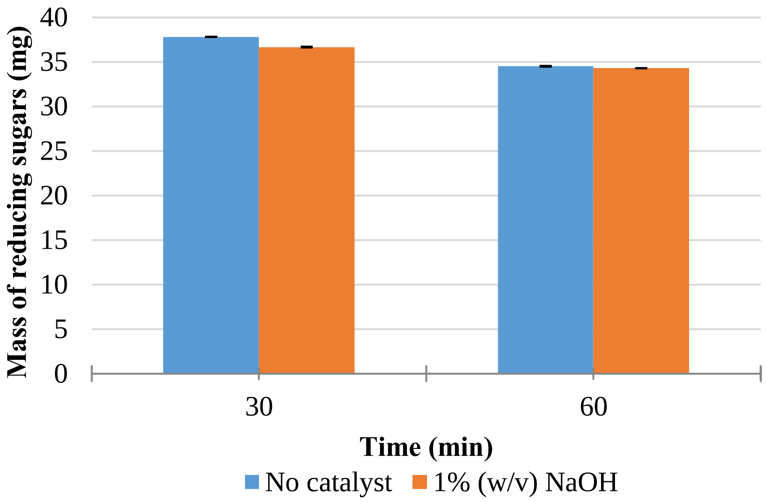

Fig. 4. Reducing sugars recovery from EFB in catalytic and non-catalytic pretreatment

3.5 *Performance Evaluation on Ultrasonication in Organosolv Pretreatment*

In order to investigate the effect of ultrasonic irradiation on organosolv pretreatment, the pretreatment was conducted without ultrasound irradiation but to remain the thermal effect by conducting the reaction at the same temperature of 50°C using a water bath. The amount of reducing sugars recovered over the course of 2 h of pretreatment is illustrated in Fig. 5. It can be seen from the figure that the incorporation of ultrasonication in organosolv pretreatment achieved higher amount of reducing sugars at a relatively shorter pretreatment time of 15 min compared to without ultrasonication. Despite its higher yield, the amount of reducing sugars gradually reduced with pretreatment time. An opposite trend was observed for organosolv pretreatment without ultrasonication, in which the amount of reducing sugars increased gradually with pretreatment time.

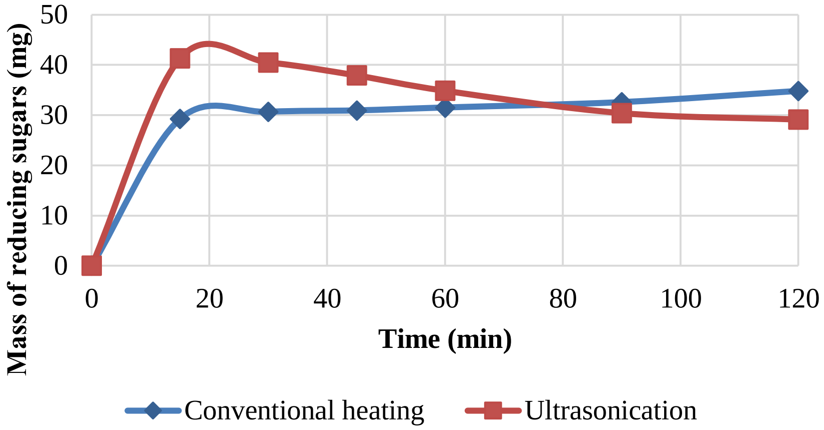

Fig. 5. Effect of ultrasonication in organosolv pretreatment in recovering of reducing sugars from EFB

Although conventional heating with no ultrasonication gave lower amount of reducing sugars, it was still higher than without any pretreatment. Without any pretreatment, acid hydrolysis of EFB produced only 17.2 ± 0.0 mg of reducing sugars. With the incorporation of ultrasonication using organosolv pretreatment, the amount of reducing sugars achieved was higher at relatively shorter time. It is because, ultrasonication works with cavitation, in which the propagation of ultrasound waves allowed the formation and collapse of cavities in the ethanol solvent, which provided better contact between the EFB sample and ethanol solvent, leading to a higher efficiency of pretreatment [9]. Besides, the implosion of cavities enhanced the breakdown of recalcitrance structure of EFB, and hence it was more susceptible to hydrolysis [17]. Hence, ultrasound-assisted organosolv pretreatment could be applied in pretreatment of lignocellulosic biomass to enhance the reducing sugars recovery from the biomass.

4. Conclusion

In this study, the effectiveness of ultrasound-assisted organosolv pretratment of EFB was investigated. Sonication power, pretreatment time and concentration of ethanol solvent were found to affect the pretreatment process leading to different recovery of reducing sugars from EFB. A maximum reducing sugars of 41.3 mg was obtained at sonication power and temperature of 100% and 50^{o}C, at 30% ethanol concentration for a duration of 15 min without the presence of sodium hydroxide catalyst. The study also showed that the performance of ultrasound-assisted organosolv pretreatment enhanced the recovery of reducing sugars from EFB. It not only gave higher reducing sugars but required shorter pretreatment time compared to conventional thermal treatment. These collectively suggested the feasibility of ultrasound-assisted organosolv pretreatment in pretreating EFB to maximize the recovery of reducing sugars from the biomass.

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