Optimization of Deep Eutectic Solvent Pretreatment of Oil Palm Empty Fruit Bunch Incorporated Assistive Heating Methods

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ABSTRACT

One of the most underutilized biomasses wastes in Malaysia is oil palm empty fruit bunch (EFB). Lignin presented in EFB was found to contain the highest energy content compared to hemicellulose and cellulose. Therefore, EFB can be the sources of lignin extraction to generate profit for the oil palm industry. Deep eutectic solvent (DES) has emerged as a new green solvent in biomass fractionation field as it has impressive delignification efficiency and low toxicity. Many researchers had delignified biomass using DES with conventional oil bath heating. The conventional method for delignification is energy-intensive and involving long pre-treatment time. Hence, this study aims to achieve effective extraction yield while reducing energy usage to extract lignin from oil palm empty fruit bunch (EFB) using DES with aid of microwave heating (MAE) and ultrasonic irradiation (UAE). The feasible extraction scheme was used to investigate parameters include water content in DES, irradiation duration, and heating method power. The crucial parameters affecting MAE pre-treatment was found to be microwave power and duration. As for UAE pre-treatment, ultrasonic amplitude and water content in DES plays a significant role on delignifying EFB using DES. In addition, the models developed for both pre-treatments are identified to be significant and thus the optimized pre-treatment conditions can be obtained. This finding is anticipated to generate an effective DES pre-treatment with integration of assistive heating techniques. From regression analysis, the optimized condition for UAE pre-treatment is at 75% amplitude for 8 min 38s, resulting in an 13.20% of lignin removal from EFB. As for the MAE pre-treatment, 56.30% of delignification efficiency was achieved using optimized condition at 300 W for 2 min 42 sec.

Keywords: Deep eutectic solvent, Oil palm empty fruit bunch fractionation, Assistive heating techniques.

1 Introduction

As the world's natural resources are depleting, there has been an increase in interest in renewable energy in recent decades to ensure the sustainability of our ecosystem. The development of biofuels from lignocellulosic biomass had drawn the greatest attention for its potential to replace fossil fuels [1]. The sources for lignocellulosic biomass are oil palm empty fruit bunch (EFB), switchgrass, corncob, and etc [2]. Cellulose, hemicellulose, and lignin make up the majority of the lignocellulosic biomass [3]. As lignin contains larger energy contents than hemicellulose and cellulose, biomass research has moved into lignin valorization, which is profitable for biorefining companies [4].

Although lignin is extremely valuable as a raw material for many useful compounds, valorization techniques faced challenges such as difficulty in catalytic processing due to presence of interunit linkages and ineffective extraction of lignin from biomass [4], [6], [7]. Thus, pre-treatment process is needed to separate the lignin from biopolymer by breaking the biomass recalcitrance. However, the conventional pre-treatment process using chemicals such as acid and alkali trigger the production of enzymic inhibitors, which are undesirable

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for downstream processes. Hence, green solvent such as deep eutectic solvent (DES) was introduced to replace acid and alkali in chemical pre-treatment as it is environmentally friendly and biodegradable.

Despite that oil bath heating had been reported to be efficient in lignin removal, this pre-treatment method was energy-intensive as it required to be conducted at high temperature of 120 ℃ – 200 ℃[8], [9]. Henceforth, this study is proposed to incorporate process intensification techniques in DES pre-treatment of EFB to minimize the process time and energy usage without compromising the effectiveness of DES fractionation of biomass.

In this research, EFB was delignified using DES incorporating with ultrasonic and microwave irradiation separately. The operating conditions of assistive heating techniques were optimized using Design Expert Box Behnken Design. The parameter investigated includes microwave power and duration, ultrasonic amplitude and duration, and water content in DES. Equations for the design models were provided to ease the prediction of DES delignification efficiency.

2 Materials and Methods

2.1 Material Preparation

Oil palm empty fruit bunch (EFB) obtained from a local plantation was washed with water before being oven dried overnight at 40°C. Before use, the dried EFB was granulated and sieved to the desired mesh size (0.7 mm) using a granulator (Rapid, Sweden).

2.2 Synthesis of DES

Choline chloride was chosen as the hydrogen bond acceptor and lactic acid as the hydrogen bond donor in synthesizing of DES. The molar ratio of HBA to HBD at 1:15 was applied to achieve the best lignin extraction [11]. Choline Chloride: Lactic Acid (CC-LA) at the stated ratio was combined in a water bath at 80°C until the DES mixture become homogeneous. An appropriate volume of deionised water was added to the pure DES to prepare aqueous solution with 0 wt.- 20 wt.% of water.

2.3 DES Pre-treatment of EFB with incorporation of microwave and ultrasound irradiation

0.3 g of extractive-free oil palm empty fruit bunch (EFB) was pre-treated using 3 g of DES at 10 wt.% solid loadings. When DES was used in ultrasound-assisted extraction (UAE) pre-treatment of EFB, the mixture was sonicated using a sonication probe (Q500 Sonica Sonicator) at selected amplitudes and durations. In microwave-assisted extraction (MAE) pre-treatment, the mixture was put inside a microwave oven (Samsung Oven) at various powers and heating time.

After pre-treatment, the mixture was then separated into two parts using filter paper, namely solid fraction (SF) and liquid fraction (LF). Ethanol and water were added into LF with a molar ratio of 1:2 to form LF2 solution. After that, LF2 was then subjected to centrifugation and separation to obtain extracted lignin.

2.4 Experimental Design and Regression Analysis

Design Expert Response Surface Methodology (RSM) Box-Behnken Design was used to conduct regression analysis to optimize the operating conditions of microwave and ultrasonic irradiation. The influencing parameters investigated for MAE pre-treatment are water content in DES (0, 10, and 20%), microwave duration (1.5 – 3.5 minutes), and microwave power (250 – 350 W). Furthermore, the independent variables studied for UAE pre-treatment are water content in DES (0, 10, and 20%), ultrasound irradiation duration (5 – 10 minutes), and ultrasonic amplitude (50%, 75%, and 100%). The range of the pre-treatment conditions for both UAE and MAE pre-treatment were selected based on that obtained from the preliminary results.

Delignification efficiency of EFB (%) as the response of the experiment, Y was fitted into a second order polynomial equation as mentioned in Equation (1) [12]. The significance of the model was evaluated with the assistance of Analysis of Variance (ANOVA).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 \qquad (1)$$

where x_i, x_j = coded independent variable; β_0 = intercept effect; β_i = linear effect; β_{ij} = linear-by-linear interaction; β_{ii} = quadratic effect.

2.5 Characterization of Fractionation Products and DEEL Yield

2.5.1 DEEL Yield

The yield of DEEL can be acquired using Equation (2).

$$DEEL\ Yield\ (\%) = \frac{Mass_{DEEL}}{Mass_{lignin\ in\ raw\ EFB}} \times 100\% \qquad (2)$$

2.5.2 Solid Fraction Recovery

The EFB solid fraction was the remaining EFB after delignification was carried using DES with assistive technologies. The higher the mass loss of EFB, the better the performance of delignification as the biomass dissolution is greater. The SF recovery was found by using Equation (3).

$$SF\ Recovery\ (\%) = \frac{Weight_{SF}}{W_{raw\ EFB}} \qquad (3)$$

Where $Weight_{SF}$ = Weight of solid fraction, $W_{raw\ EFB}$ = Weight of raw EFB

3 Results and Discussion

3.1 Analysis of Variance (ANOVA) for MAE of Lignin Pre-treatment

The optimum operation condition of MAE pre-treatment was generated based on the Design Expert software with Box-Behken Design (BBD) as Design of Experiment (DoE). The factors were optimized namely microwave power (W), microwave irradiation duration (mins), and water content in DES (wt.%).

Equation (3.10) was used to fit the delignification efficiency (response Y) and a second polynomial equation was obtained for MAE of lignin pre-treatment using Design Expert v 8.0.7.1 software. The equation in term of coded factors for MAE of lignin pre-treatment was established in Equation (4). The model was reduced by removing insignificant model terms such as the term AC to enhance the precision of the models. The positive and negative sign before the coded factor indicated their relative impact towards the response in which a positive coded factor enhances the response and a negative coded factor reduces the response.

$$Y = 55.86 + 6.46\,A + 6.40\,B - 5.84\,C - 37.40\,BC - 0.008\,A^2 - 14.36\,B^2 - 1.78\,C^2 \qquad (4)$$

where, Y = Delignification efficiency (%), A = Microwave Power (W), B = Microwave duration (min), C = Water content in DES (wt.%).

According to Equation (4), an increased in microwave power and microwave duration would improve the delignification efficiency of DES. Conversely, the increasing water content in DES would reduce the amount of lignin extracted. The addition of water would lower the acidity of DES causing a lower solubility of lignin in DES. Thus, the delignification efficiency was reduced [13].

From regression analysis, the significance of the model matches the lack of fit test p values at a 95% significant level ($p>0.05$) [14]. Model terms A, B, BC, A2, B2, and C2 are significant with p values less than 0.05. Water content in DES (Term C) factor with smallest coded factor (1.36) and largest Probability F-value (0.33) in the MAE coded factor equation has the least influence on delignification efficiency. Besides, the model was significant as it has a high F-value of 33.92 while the lack of fit model was interpreted to be insignificant indicating that the model was fit with the actual results. The R-Squared value of 0.98 further confirms the MAE model theoretical delignification efficiency has a high correlation with the experimental results.

3.2 Analysis of Variance (ANOVA) for UAE of lignin Pre-treatment

The ultrasonic amplitude (%), ultrasonic duration (mins), and water content in DES (wt.%) were set to optimized in DES pre-treatment incorporated UAE. Through ANOVA analysis, the equation of coded factors for UAE of lignin pre-treatment can be expressed as in Equation (5).

$$Y = 13.0 + 1.1\,A + 0.2\,B - 0.6C + 70.0A\,C - 3.9A^2 - 2.1\,C^2 \qquad (5)$$

where, Y = Delignification efficiency (%), A = Ultrasonic amplitude (%), B = Ultrasonic duration (min), C = Water content in DES (wt.%).

For DES pre-treatment of EFB using UAE, ultrasonic amplitude, duration, and water content in DES were crucial factors affecting the delignification efficiency of DES. An increase in the amplitude of ultrasound increased the rate of lignin removal, as a substantial amount of vapor pressure was formed where the microbubbles expanded and collapsed. This impacted the surface of EFB and damaged the biomass structure (Ong et al., 2019). Similar to MAE, water addition to DES would lower the pH and the weaker ionic strength of DES resulted in a lower amount of lignin removal [15]. Model terms A, C, AC, A^2, and C^2 are considered to be significant as their p values are < 0.05. Ultrasonic amplitude and water content in DES are among the significant factors affecting the delignification efficiency of DES. Similar to the MAE of the lignin pre-treatment model, the UAE pre-treatment model has a high correlation between the predicted lignin removal efficiency and the experimental data as the R-Squared value is 0.94.

3.3 Optimized MAE and UAE Pre-treatment of EFB

The preferred condition for DES pre-treatment of EFB using MAE and UAE were determined by using the mathematical optimization of Design Expert.

The optimized condition for DES incorporated MAE pre-treatment of EFB was 300W, 2 mins 42 sec, and 9.30 wt.% water content in DES with a prediction of lignin removal of 57.10%. The validation experiment based on the optimized condition yielded a lignin removal of 56.60% with a minor deviation of 0.48% between the predicted and experimental values.

On the other hand, the optimized UAE pre-treatment condition was 75% sonication amplitude, 8 mins 38s duration with a 4.2 wt.% water in DES. A disparity of 0.42% between the predicted (12.90%) and experimental (13.30%) values is equally commendable as that in the MAE pre-treatment. The predicted versus actual delignification efficiency of MAE and UAE pre-treatment is displayed in Figure 1.

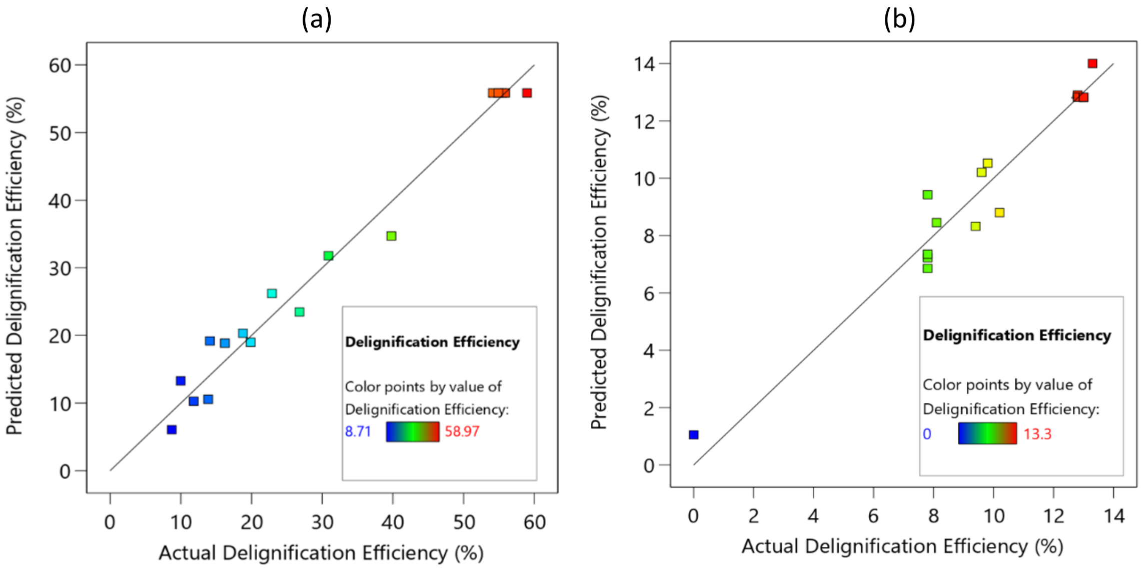

Figure 1: *The predicted versus actual delignification efficiency of (a) MAE and (b) UAE pre-treatment*

3.4 Remaining lignin in pre-treated residue and solid recovery

The effect of different assistive heating techniques on the amount of remaining lignin in the pre-treated EFB and the solid recovery is illustrated in Figure 2.

It can be observed that UAE pre-treated EFB has the highest amount of remaining lignin while UAE pre-treated EFB has the least, signifying that MAE is comparatively better than UAE for DES pre-treatment of EFB.

As for the EFB recovery after pre-treatment, the result is tally with the remaining lignin composition in EFB. This is because high lignin removal rate results in a major weight loss of pre-treated solid [16].

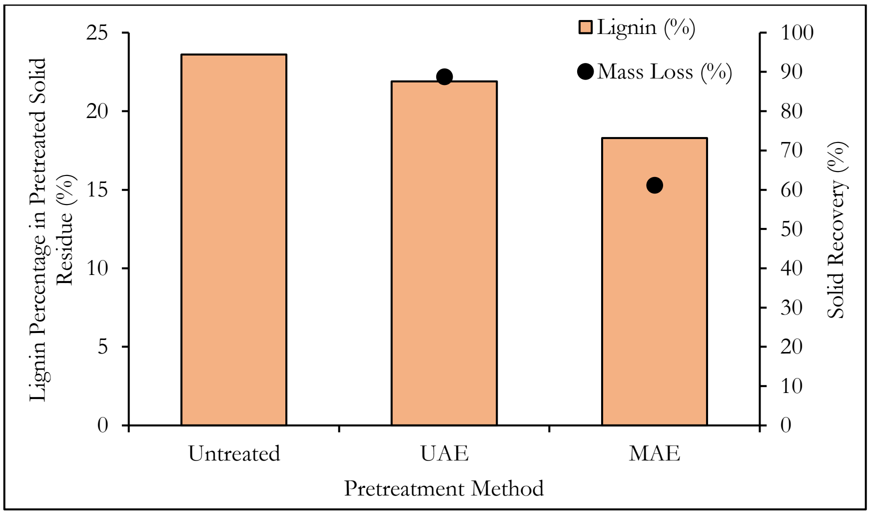

Figure 2: *Lignin percentage in pre-treated biomass (%) and solid recovery (%)*

4 Conclusions

This study verifies that DES pre-treatment of EFB with incorporation of assistive heating techniques results in an efficient and effective removal of lignin from biomass. To reduce pre-treatment duration, assistive

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heating techniques such as microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE) was imposed in the pre-treatment as an alternative for conventional oil bath heating method which takes 8 hours to delignify EFB. Though regression analysis, important DES pre-treatment parameters of each assistive heating method was identified. The important factors of MAE pre-treatment are microwave power and duration while ultrasonic amplitude and water content in DES are crucial variables for UAE Pre-treatment. Furthermore, the theoretical model for both UAE and MAE pre-treatment developed are significant, indicating the high correlation between theoretical and experimental delignification efficiency. With the optimized conditions obtained from ANOVA, 56.60% of lignin was successfully removed from EFB using MAE pre-treatment at 300 W for 2 min and 42 s. As for the UAE pre-treatment, 13.30% of delignification efficiency was achieved at 75% amplitude for 8 min and 38 s.

5 Declarations

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5.3 Competing Interests

The authors declare that they have no known competing financial interests.

5.4 Publisher's Note

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