Process Optimization of Deep Eutectic Solvent Pretreatment of Coffee Husk Biomass

Sukunya Areeya[1], *Marttin Paulraj* Gundupalli[2], *Babu* Dharmalingam[3], *Baranitharan* Paramasivam[4], *Prapakorn* Tantayotai[5], *Patchanee* Yasurin[6], and *Elizabeth Jayex* Panakkal[1,*]

[1] Biorefinery and Process Automation Engineering Center, Department of Chemical and Process Engineering, The Sirindhorn International Thai-German Graduate School of Engineering, King Mongkut's University of Technology North Bangkok Bangkok, Thailand
[2] Food and Nutritional Science Department, Faculty of Agricultural, Life and Environmental, Sciences, Agricultural, University of Alberta, Edmonton, AB, Canada
[3] College of Engineering Guindy, Anna University, Chennai, India
[4] Department of Mechanical Engineering, Saveetha School of Engineering, SIMATS, Chennai, India
[5] Department of Microbiology, Faculty of Science, Srinakharinwirot University, Bangkok, Thailand
[6] Department of Food Biotechnology, Faculty of Biotechnology, Assumption University, Bangkok, Thailand

Abstract. The increased processing of coffee beans has generated huge amount of coffee husk, which are improperly disposed. Inappropriate disposal of coffee husk has led to release of toxic compounds to the environment causing serious environmental concerns. To mitigate the impact of improperly disposed coffee husk, it is suggested for valorisation of the coffee husk. Hence, this study has focussed on identifying the potential of coffee husk in maximizing the sugar yield from it which can be converted to value added product. Deep eutectic solvent (DES) involving choline chloride and lactic acid (ChCl:LA) mixed at 1:4 molar ratio was studied to investigate the effect of DES pretreatment on coffee husk to produce reducing sugar in the hydrolysis process. Pretreatment conditions of the biomass were optimized for biomass loading (5-20%, w/w), temperature (70-120 ^{o}C), and duration (60-240 min) using Response Surface Methodology (RSM) for obtaining maximum yield of reducing sugar. The RSM model predicted an optimal pretreatment condition of biomass loading with 20% (w/w), pretreated at 120 ^{o}C for 231.80 min to achieve maximum sugar yield (30.522%). The pretreatment effect on biomass composition was analyzed using the Van Soest method, which showed an increase in the cellulose content along with the hemicellulose removal when compared with the native biomass. Moreover, evaluation of chemical structural changes also confirmed the effectiveness of DES pretreatment. Thus, the current study would illustrate the potential of coffee husk to produce value-added compounds from it.

Keyword. Biofuels, Biorefinery, Coffee husk, DES pretreatment, Lignocellulosic biomass

1 Introduction

Coffee husk is the major residual produced during coffee bean processing because a major portion of the coffee fruit accounts for its husk (43.2%) and the bean contributes 38.9% of its weight [1]. After the coffee processing, the coffee husk is mostly inappropriately disposed, leading to severe environmental problems due to the presence of various harmful organic compounds like caffeine, tannins, and polyphenols. Furthermore, the burning of the coffee husk will lead to the release of greenhouse gases and particulate matter [2]. Via the wet processing method, a lower heating value (LHV) of 16.60 MJ kg^{-1} was noted in coffee husks, which was closer to the LHV of sugarcane bagasse (17.70 MJ kg^{-1}). However, it was higher than LHV reported from the rice husk (13.39 MJ kg^{-1}) [3]. In addition, coffee husks have high volatile content, low ash content, and high carbon content, which is suitable for their thermochemical conversion processes [1]. Hence, valorization of this agro-waste to valuable products like biofuels and other platform chemicals, would reduce the negative environmental impact and follows the concept of circular economy [4,5].

However, the complex structure of coffee husk, composed of amorphous polymers with complicated interactions between cellulose, hemicellulose, and lignin, presents recalcitrance to the biomass, thereby preventing chemical and biological degradation [6]. Primarily, the drying process is carried out to reduce the costs of storage and transportation and since the drying process prevents the deterioration of materials, it expands the life of coffee husk biomass [1]. Subsequently, the particles are reduced in size to attain a standard size for the densification step that can probably increase the energy density of biomass and its calorific value [1].

The primary purpose of pretreatment is disaggregating or disrupting interactions within the

* Corresponding author: elizabeth.jayex@gmail.com

lignocellulosic complex structure [7]. The method of thermochemical conversion used in the pretreatment determines the efficiency of the pretreatment. Moreover, it also helps in reducing the particle size of lignin and the crystallinity of cellulose, thus increasing the surface area and pore volume to facilitate enzymatic accessibility and microbiological digestibility [8].

Owing to the unique characteristic of deep eutectic solvents (DES) as a green and environment-benign solvent, along with its other properties of low volatility, non-toxicity, high thermal stability, and less inhibitor generation has led to prefer DES over other pretreatment methods [9]. DES is formed by mixing a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) [10]. It is well known for its ability to dissolve lignin from the lignocellulosic biomass as the chloride ions cause the disruption of β-O-4 aryl ether bonds resulting in delignification [11]. Besides, DES can also remove hemicellulose because of the proton dissociation while cellulose is retained in biomass [10,12]. Choline chloride (ChCl) as HBD, especially combined with organic acid (as HBA) has higher lignin removal capability and cheaper cost than other HBA [9]. In addition, it is also reported in pretreatment of various types of biomasses [13].

Previously reported studies have used ChCl combined with lactic acid (LA) in different molar ratios. ChCl/LA in a ratio of 1:10 has reported the high recovered lignin (72.3%) for pretreated masson pine [14]. A glucose yield of 87.09% was achieved by ChCl/LA (1:4) pretreatment for Napier grass [15]. Moreover, ChCl as HBD was also investigated to pretreat Bambara groundnut haulm by combining with various HBA, namely acetic acid, formic acid, LA, glycerol, and urea. The highest sugar recovery (94.8%) was achieved by ChCl/LA pretreatment [16]. Consequently, this study has used ChCl as HBD and LA as HBA.

A study on Ethiopian Arabica coffee husk has carried out pretreatment with NaOH (10% w/w) to determine the influence of alkaline pretreatment on coffee husk [17]. The study showed that the alkaline pretreatment could decrease the recalcitrant polymer, hemicellulose, and lignin, and slightly increase the cellulose content. Another study on the pretreatment of coffee husk with ozone utilized the hydrolysate for production of biogas and preserved the solid phase rich in cellulose for 2G ethanol production [8]. The study revealed that two-stage anaerobic digestion (AD) could produce more methane than single-stage AD. Moreover, the addition of activated carbon in powder form significantly increased the methane yield and energy recovery. The physical pretreatment, namely steam explosion, of coffee husk was also carried out for biogas production through anaerobic digestion [6]. The energy production of methane and electricity from the pretreated coffee husk, using a combined heat and power co-generation system (CHP) was more when compared with the untreated coffee husk. The combination of biological pretreatment and physical pretreatment, with white-rot fungi *Pleurotus ostreatus* (PL) and steam explosion on coffee husk revealed that the combined pretreatment could achieve the highest overall yield of 26.93 g reducing sugars/100 g biomass [2].

The present study has focused to investigate the effectiveness of DES pretreatment on coffee husk under the determination of the optimal pretreatment conditions via Box-Behnken design from the Response Surface Methodology (RSM). The experimental data were used to analyze the prediction of pretreatment condition and response variables by using multiple regression analysis based on maximized sugar yield. The effectiveness of pretreatment in the structural changes was further analyzed by Fourier Transform Infrared (FTIR) spectroscopy and the Van Soest methods.

2 Materials and methods

2.1 Raw materials

Coffee husk was obtained from Chiang Mai Province, Thailand. To remove the moisture content, the coffee husk was dried at 60 ºC overnight. In the subsequent process, it was pulverized by a blender to reduce the particle sizes and screened by a 20 mesh-sized aluminum sieve to obtain coffee husk with uniform size.

Deep eutectic solvent (DES) for pretreatment was prepared by mixing Chlorine chloride (ChCl) and Lactic acid (LA) in a ratio of 1:4 w/w and heating at 60 ºC, with continuous stirring at 100 rpm for 10 min. The transparent DES formed was stored within a desiccator to prevent moisture absorption.

2.2 RSM experiment design

Box-Behnken design from the Response Surface Methodology (RSM) was applied via design-expert 7.0.0 to achieve the objective of the optimization [18-20]. The model used three boundary conditions consisting of biomass loading (X_1) varying between 5-20% (w/w), temperature (X_2) from 70-120 ºC, and time (X_3) between 60-240 min. The design has suggested 17 runs varying the boundary conditions at different levels (Table 1). The model was further optimized depending on the maximum sugar yield (Y) obtained from the model. The pretreated samples were hence enzymatically hydrolyzed to evaluate the sugar yield (%) for prediction of the optimal pretreatment condition.

2.3 Deep eutectic solvents pretreatment

DES pretreatment was performed according to the conditions depicted in Table 1 using a stirring mantle. The pretreated solids were washed with distilled water several times until the pH of wash liquid was neutral. The pretreated solids were separated from the wash liquid by using Whatman No. 1 filter paper through vacuum filtration. The pretreated solids were then dried in a hot-air oven at 60 ºC overnight and further stored in desiccator for future use.

2.4 Enzymatic hydrolysis

The untreated and pretreated coffee husks were hydrolyzed with a solid loading of 2.5% (w/v) in 50 mM citrate buffer along with the commercial CTec2 enzyme (20 FPU/g biomass) [21,22]. The hydrolysis reaction was done at 50°C, in an orbital shaker with 150 rpm for 72 h. The reaction in the mixture was stopped by heating the mixture at 95 ºC for 10 min in a water bath. The liquid fraction was separated by filtration with Whatman No. 1 filter paper and further taken to analyze the reducing sugar using high-performance liquid chromatography (HPLC) [15].

2.5 Determinations of reducing sugar and biomass composition

Reducing sugar analysis was performed using high-performance liquid chromatography (HPLC) (Perkin Elmer Flexar LC) equipped with Brownlee Amino 5 µm column (150×4.6 mm) and a refractive index detector (RID). The mobile phase used for the analysis was water and acetonitrile (25:75) at a flow rate of 1 mL/min. The biomass composition for both untreated and pretreated coffee husks was analyzed by using the Van Soest method [23,24] to calculate cellulose, hemicellulose, and lignin composition in the sample. All experiments were repeated at least three times.

2.6 Fourier Transform Infrared (FTIR) spectroscopy analysis

FTIR spectroscopy was performed on both untreated and pretreated coffee husk samples using Spectrum 2000, Perkin-Elmer, USA with a resolution of 4 cm^{-1} from 400 cm^{-1} to 4000 cm^{-1}.

3 Results and discussions

3.1 Optimization of DES pretreatment by Box Behnken Design (BBD)

RSM is an important method in the Design of Experiments (DoE) for achieving the optimization of experimental conditions. It is a dependable optimization technique by applying both mathematical and statistical tools, which can demonstrate the correlation between the independent variables and the response variables [25]. Interpreting the interactions of these variables in an optimization approach with the RSM method consumes less time than experimental trials [26,27]. Box-Behnken design [28] is one of the RSM to achieve an appropriate response variable. It is integrating the 2^k Factorial Design and the incomplete block design, moreover, the Analysis of Variance (ANOVA) technique and the Lack-of-Fit test are used to estimate the accuracy of the fitted model [29]. Seventeen experimental conditions of DES pretreatment for coffee husk were conducted through RSM based on Box-Behnken design using design-expert 7.0.0 trial with reducing sugar yield (Y) as response variables. The reduced sugar yield obtained for each run is depicted in Table 1.

Table 1. Experimental design using BBD for pretreated coffee husk biomass.

Run	Biomass loading (%, w/w)	Temperature (ºC)	Time (min)	Sugar yield (%)
1	5	120	150	22.494
2	20	120	150	26.628
3	12.5	95	150	26.265
4	5	70	150	23.769
5	20	95	240	28.778
6	12.5	70	240	25.055
7	12.5	70	60	17.352
8	12.5	95	150	29.165
9	12.5	120	60	20.488
10	5	95	240	18.371
11	12.5	95	150	24.350
12	20	95	60	21.771
13	20	70	150	32.126
14	5	95	60	26.191
15	12.5	120	240	25.722
16	12.5	95	150	25.970
17	12.5	95	150	21.794

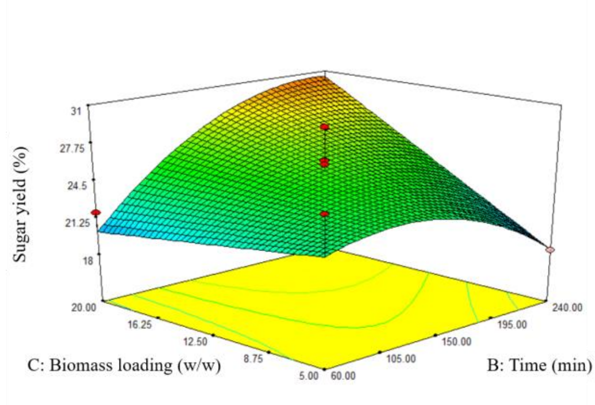
The release of maximum reducing sugar is optimized by using multiple regression analysis to experimental data. ANOVA based on the backward quadratic model, which is most fit in this study, is shown in Table 2. The ANOVA analysis revealed the significance of the model with an F-value of 5.28 (p-value <0.05). Figure 1 depicts a three-dimensional plot of the effects of three independent variables, such as biomass loading, temperature, and time, on sugar yield for the saccharification process of pretreated coffee husk. The figure shows that the reducing sugar yield increased according to the increase of biomass loading and time, but the temperature is not affected on reducing sugar yield. The results of RSM based on the Box-Behnken design indicated that optimal pretreatment conditions are 20% biomass loading, pretreated at a temperature of 120 ºC for a time period of 231.80 min to achieve the predicted reducing sugar yield (30.522%). The regression equation describing the relation between predicted reducing sugar yield (Y) and three independent variables consisting of biomass loading (X_1), temperature (X_2), and time (X_3) is shown as follows.

$$Y = 21.77782 + 0.054643X_3 - 0.51577X_1 + 5.49149\times 10^{-3}X_3X_1 - 3.54826\times 10^{-3}X_3^2 \quad (1)$$

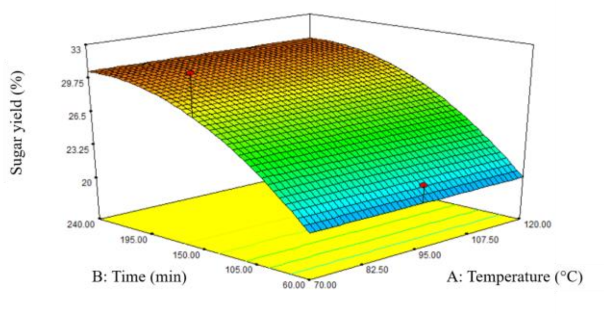
Table 2. ANOVA analysis from RSM experiments.

Source	Sum of square	DF	Mean square	F value	Prob > F
Model	151.00	4	37.75	5.28	0.0109
B-Time	18.37	1	18.37	2.57	0.1349
C-BL	42.68	1	42.68	5.97	0.0310
BC	54.96	1	54.96	7.69	0.0169
B2	34.99	1	34.99	4.89	0.0471
Residual	85.79	12	7.15		
Lack of Fit	56.50	8	7.06	0.96	0.5550
Pure Error	29.29	4	7.32		
Cor Total	236.76	16			0.0109

*BL = %Biomass loading



(a)



(b)

Fig. 1. Three-dimensional plot of the effects of (a) biomass loading and time on sugar yield at optimal temperature (120 °C) and (b) temperature and time on sugar yield at optimal biomass loading (20%).

3.2 Effect of DES Pretreatment on coffee husk compositions

Van Soest and Wine method [8,24] is used to estimate the cell wall components of cellulose, hemicellulose, and lignin [30]. The components of both native and pretreated coffee husk are shown in Table 3. In this study, DES pretreatment has resulted in increasing the cellulose content from 39.91% to 43.16% in addition to the increased lignin content. It could be the acidic DES pretreatment at a higher temperature for a prolonged time that could have led the lignin to redeposit onto the biomass surface, leading to increased lignin content in the pretreated coffee husk [31]. Furthermore, the results also show that the hemicellulose in the untreated coffee husk was completely removed after pretreatment with DES. With the DES pretreatment process, cellulose increased as same as lignin, but lignin was inconsistent with the FTIR results. A previous study on the pretreatment of Ethiopian Arabica coffee husk with alkali (NaOH) has enhanced the cellulose content from 53.2% to 56.58% along with hemicellulose and lignin removal [12]. Another study on the H_2SO_4 pretreatment of coffee husk has also resulted in enhanced cellulose content coupled with hemicellulose removal [27]. A similar trend was observed in the present study which had enhanced cellulose content with removal of hemicellulose.

Table 3. The components of untreated coffee husk and pretreated coffee husk.

Biomass composition (%)	Untreated coffee husk	Pretreated coffee husk
Cellulose	39.91	43.16
Hemicellulose	4.04	0.00
Lignin	21.51	33.09

3.3 Biophysical Characterization of Coffee husk biomass

FTIR analysis generally demonstrates the bond rupture and the stretching vibrations which correlate with the structural integrity of lignocellulosic biomass [32]. Generally, the components of biomass are the compounds of esters, alkene, aromatics, alcohol, and ketones [33]. The FTIR results of untreated and pretreated coffee husk are represented in Figure 2. The peak near 3337 cm^{-1} presents in both untreated and pretreated biomass was ascribed to –OH stretching of hydrogen bonds, mainly assigned to the cellulose [26,34]. The peak of 2355 cm^{-1} was attributed to the aliphatic and alkyl groups within the cellulose and the methyl, methoxy groups in hemicellulose and lignin respectively [2]. The intensity of this peak has been decreased in the pretreated biomass, which may be due to the hemicellulose removal. The sharp peak at 1727 cm^{-1} denoted the C=O stretching of acetyl or carboxylic acid that was associated with hemicellulose, which decreased after the pretreatment process [26,35]. The peak of 1610 cm^{-1} is assigned to the C=C stretching vibration together with the asymmetric-stretching vibration in the aromatic ring of COOH that refers to the relation of cellulose, hemicellulose, and lignin [36,37]. The sharp peak at 1155 cm^{-1} implies the presence of β-O-4 linkages referred to as an entry point for lignin valorization [38]. FTIR study implies that the pretreatment with ChCl:LA (1:4) has caused significant changes in the chemical structure of coffee husk.

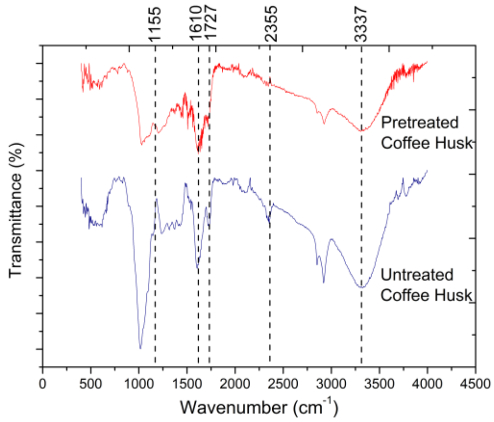


Fig. 2. Fourier-transform infrared spectroscopy (FTIR) spectra of untreated and pretreated coffee husk biomass.

4 Conclusion

The present study has focused on the optimization of pretreatment conditions for coffee husk using RSM. The mathematical model has predicted the optimal pretreatment conditions to be biomass loading of 20% (w/w), pretreatment at a temperature of 120 °C, for a duration of 231.80 min to obtain the maximum sugar yield. Under this optimal condition, the pretreatment was able to remove hemicellulose from the biomass thereby exposing more cellulose for the enzymatic hydrolysis. The chemical structural changes in biomass after pretreatment also confirm the effectiveness of DES pretreatment on the coffee husk. Thus, this study suggests an optimal pretreatment condition for the acidic DES pretreatment of coffee husk that can further ease the valorization of coffee waste to produce value-added products in the biorefinery industry.

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