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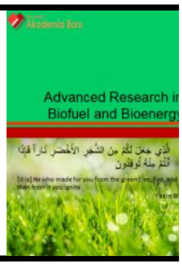

Ethanol Production Prediction in Various Biomass Species Pretreated by Cholinium Ionic Liquid at SuperPro Designer Software

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ABSTRACT

This research aims to optimize ethanol production from various biomass species pretreatment by choline acetate (ChOAc), a biocompatible cholinium ionic liquid (IL). The biomass types are bagasse, empty fruits bunch (EFB), and oil palm frond (OPF). Therefore, the ethanol biorefinery process is simulated by using the SuperPro Designer (SPD) software. The simulation contains pretreatment, enzymatic saccharification, and fermentation process. The developed SPD model was then validated with published data of the cholinium (IL)-assisted pretreatment of bagasse in the IL/biomass ratio of 1.5 (g/g). Further, the influence of ionic liquid-assisted pretreatment of various biomass was investigated. The obtained results indicate that an IL/biomass ratio of 1.5 is suitable and sufficient for obtaining a maximum ethanol yield. Moreover, after 72 h of enzymatic saccharification at high-loading, the glucose concentrations of bagasse, EFB, and OPF were 56.42 g/L, 64.13 g/L, and 45.88 g/L, respectively. Furthermore, the xylose concentrations of bagasse, EFB, and OPF were 14.34 g/L, 14.19 g/L, and 18.52 g/L, respectively. In the subsequent co-fermentation from a mixed sugar solution containing glucose, xylose, and ethanol concentrations at 24h from bagasse (26.65 g/L, 6.67 g/L, 15.52 g/L), EFB (28.95 g/L, 6.41 g/L, 15.34 g/L), and OPF (20.85 g/L, 8.42 g/L, 15.11 g/L), which was 85%, 99.85%, 97.64% the theoretical value for the sugar-based ethanol yield. To conclude, the implementation of SPD simulation on biomass refinery into ethanol has a considerable potential to secure the cost of ethanol process production and future experimental process demand.

Keywords:
Ionic liquid; choline acetate; biomass; SuperPro designer; simulation

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1. Introduction

Fossil energy is one of the essential components to support all human activities in various sectors. However, according to the depletion of fossil energy resources and global warming issues, renewable energies have gained attention for the past few decades [1,2]. A particular interest due to their carbon neutral type of energy has been focused on utilizing lignocellulosic biomass for biofuel production, namely the second generation of ethanol [3,4]. According to their carbon neutral, biomass comes from various plants, so the resulting exhaust gas of carbon dioxide can reduce emissions by about 80% [5]. Moreover, biofuel's utilization and conversion into bioethanol is a promising strategy for providing biofuel with low emission gas shortly [5,6].

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Lignocellulosic biomass is the most abundant biopolymer in nature. It consists of cellulose, hemicellulose, and lignin and small amounts of protein, pectin, ash, and extractives [7]. Converting lignocellulosic biomass into bioethanol generally occurs in three main process, namely the pretreatment process, the enzymatic saccharification process, and the fermentation process [8]. Lignocellulosic biomass covered by plant walls, namely lignin, and hemicellulose, which are difficult to break down [3] . Therefore, it is necessary to have a pretreatment process that can break down these walls[9-11]. In the subsequent, the enzymes can access cellulose to be converted into fermentable sugar. Currently, the pretreatment process can be done in several ways; one of the most effective ways compared to conventional methods is using ionic liquids (ILs), which have been proven to dissolve cellulose [12,13]. However, the experimental research process using IL requires a relatively high cost due to the price of IL itself [14,15].

Therefore, to reduce the high-cost biomass refinery process into ethanol and to optimize ethanol production, simulation using SuperPro Designer (SPD) software is an important step. SPD has an acceptable process arrangement, which is part of this software's advantages, especially in biochemical processes, specific compounds, and complete units [16,17]. The previous study reported that the comparison between the experiment and SPD simulation's results was not much different, namely error around 8.4% [18]. Hence, in this study, we investigate ethanol production's prediction from various biomass species by using SPD software. The various biomass species, namely bagasse, empty fruits bunch (EFB), and oil palm frond (OPF) was pretreated by choline acetate (ChOAC), a biocompatible ionic liquid at an IL/biomass ratio of 1.5. The developed SPD model was then validated with experimental data that has been published [19]. As a result, the simulation error value was justified. The error value has to lower than the previous result, i.e., 8.4%. Furthermore, the developed SPD model could be used as a reference for better preparation before conducting heavy experimenting.

2. Methodology

2.1 Process Overview

Figure 1 shows the basic diagram developed for the biomass refinery process simulation into ethanol based on the literature's available data [19]. The first process corresponded to biomass pretreatment, including shredding, mixing, heating, cooling, washing, and separation. The pretreatment process was followed by a second process corresponding to the enzymatic saccharification process. This latter was composed of a mixing and vessel reactor. Then, the third process corresponded to the fermentation process, in which sugar solution was separating and was fermented using yeast as fermentative microbial. Finally, each of these processes would be validated to determine the error of the simulation process's data. The error obtained did not exceed 8.4%; this referred to the previous simulation research [18].

2.2 Process Description in the SuperPro Designer

Figure 2 shows the process flow diagram of simulation modelling regarding experimental methods carried out with slight modifications, namely minimizing the IL/biomass ratio. In the pretreatment, 10 g of bagasse mixed with IL, namely choline acetate (ChOAc) of 0–15 g. Thus, the ratio between IL/biomass obtained is 0-1.5 (g/g). The next simulation steps, namely enzymatic saccharification and fermentation, were also simulated concerning the experimental research [19].

In the simulation pretreatment process, bagasse was crushed and sieved by a shredding device (P-1/SR-01) with a size of 250-500 μm. Bagasse was mixed with ChOAc IL with IL/biomass ratio 0-1.5

in a mixer (P-2/MX-102). The mixture would then be heated at a temperature of 110 ˚C for 5 h on a heating device (P-12/HX-102). After that, the suspension was cooled back to 25 ˚C in the cooling device (P-13/HX-103). The next process was washing to separate IL from pretreated bagasse in the washing device (P-3/WSH-101). The sample was dried at 90 ˚C in a heating device (P-4/HX-101). The pretreatment stage ended when the pretreated bagasse entered the reactor (P-6/R-101) to be changed and analyzed the composition to proceed to the enzymatic step.

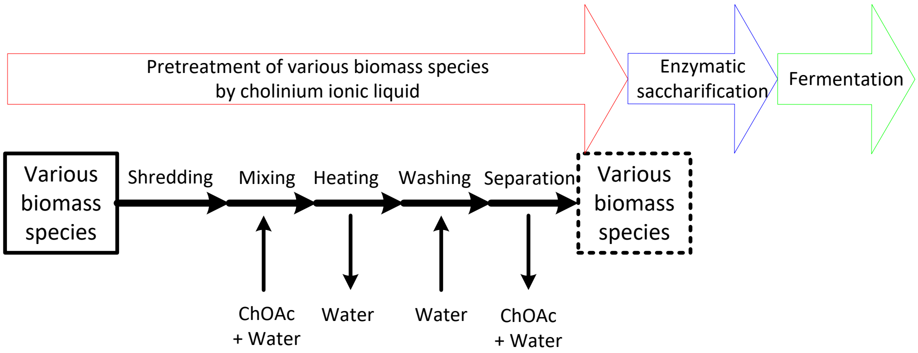

Fig. 1. The basic diagram process of biomass refinery into ethanol production

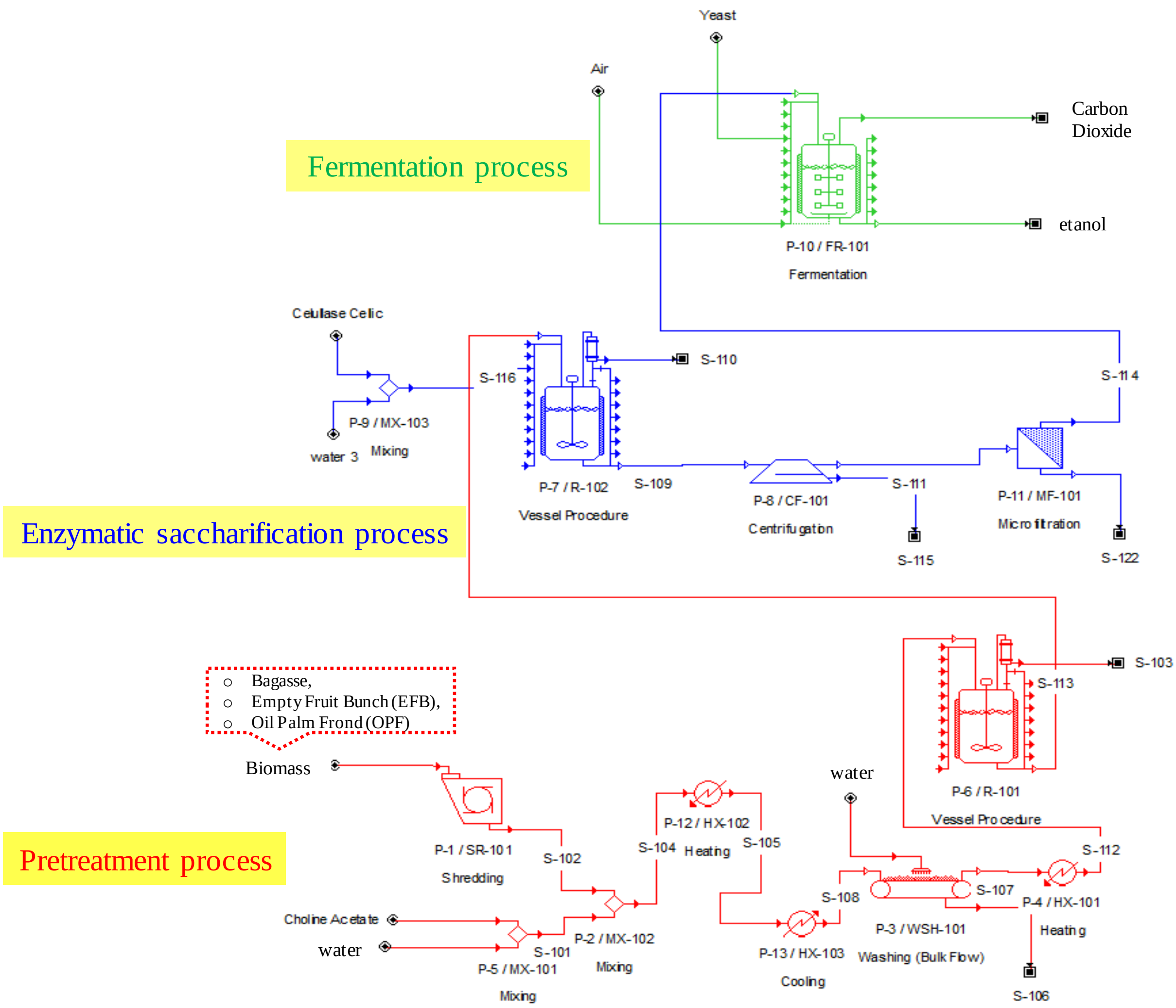

Fig. 2. Process flow diagram of biomass biorefinery process in SuperPro Designer software

Table 1
The reactor block description in the simulation

Superpro Designer Name	Description
Shredding	P-1/SR-101-Shreding of biomass (250-500 µm)
Mixing	P-5/MX-101-Mixing water and *Ionic Liquid* P-2/MX-102-Suspension of IL/biomass ratio of 0-1.5
Heating	P-12/HX-102-Heating the suspension at110 ˚C P-4/HX-101-Drying of pretreated bagasse at 90 ˚C
Cooling	P-13/HX-103-Cooling of pretreated bagasse at 25 ˚C
Washing	P-3/WSH-101-Washing and separation of pretreated bagasse
Vessel reactor	P-6/R-101-Chemical reaction to analysis of composition of pretreated bagasse
Mixing	P-9/MX-103-Mixing cellulase cellic, phosphate buffer (at low-loading) and water (at high-loading)
Vessel reactor	P-7/R-102-Chemical reaction to obtain the fermentable sugar
Centrifugation	P-8/CF-101-Removing the supernantant
Microfiltration	P-11/MF-101-Filtration of fermentable sugar solution
Fermentation	P-10/FR-101-Fermentation process at 30 ˚C for 72 h of reaction time

3. Results

3.1 Model Validation of Effect of IL/Biomass Ratio on Recovery Percentage and Composition of Various Biomass Species

To guidance investigate the developed model's accuracy, the compositional analysis of the various biomass species was conducted according to the NREL method [20]. Figure 3 shows the composition of various biomass species pre-treated at an IL/biomass ratio of 1.5. The cellulose, hemicellulose, lignin, and ash contents were approximately 40%, 20%, and 30% for bagasse. EFB contains 59.7% cellulose, 22.1% hemicellulose, 18.1% lignin and 0.1% ash. For OPF, 30.4% cellulose, 40.4% hemicellulose, 21.7% lignin, and 7.5% ash were examined. These results indicate that EFB contains a higher percentage of cellulose among biomass species.

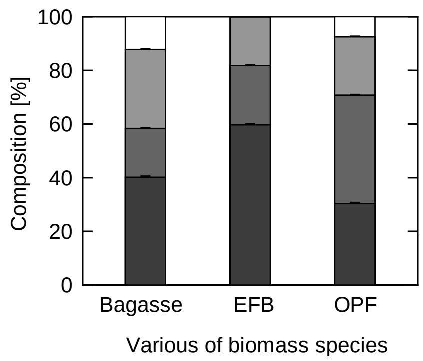

Fig. 3. Content of cellulose (bottom of stacked bar), hemicellulose (middle of stacked bar), lignin (top of stacked bar) in various of biomass species pretreated with ChOAc at IL/biomass ratio of 1.5. The error bars indicate the standard deviation from three independent experiments

Figure 4 shows a good agreement between experimental and simulated values. However, a slight discrepancy was observed, and the mean error for all tested values is 5.8%. This error value was much smaller than the error value from previous studies [18].

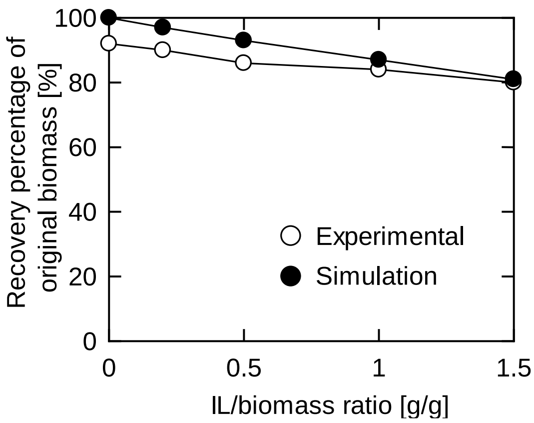

Fig. 4. Validation of IL/biomass ratio on recovery percentage

3.2 Model validation Enzymatic Saccharification at low loading

To validate the simulation, the developed model's accuracy was verified with the published data of the experimental investigation of IL-assisted pre-treatment of bagasse into ethanol. During, their research, the authors [19] showed that the minimum IL/biomass ratio was found to be 1.5. At low loading (10 g/L) of enzymatic saccharification, the IL/biomass ratio of 1.5 achieved the cellulose and hemicellulose saccharification percentages are 95% and 93%, respectively. Table 2 shows that the mean error for all tested values is 1.73%.

Table 2
The error values of enzymatic saccharification at low-loading

IL/Biomass Rasio	Experiment(%)		Simulation (%)		Error (%)	
	Glucosa	Xylosa	Glucosa	Xylosa	Glucosa	Xylosa
1.5	95	93	96.57	94.68	1.66	1.80
		Mean error (%)			1.73	

Figure 5 shows the simulation result of EFB and OPF in the enzymatic saccharification at a low-loading process. According to the result obtained in Figure 3, it is observed that the composition affects the amount of cellulose and hemicellulose percentage, particularly at OPF.

3.3 Model Validation Enzymatic Saccharification at High-Loading

In the enzymatic high-loading saccharification process, the simulation data was in glucose and xylose concentration data, as shown in Table 3. The average error value was 1.59%. This error value was much smaller than the error value from previous studies [18].

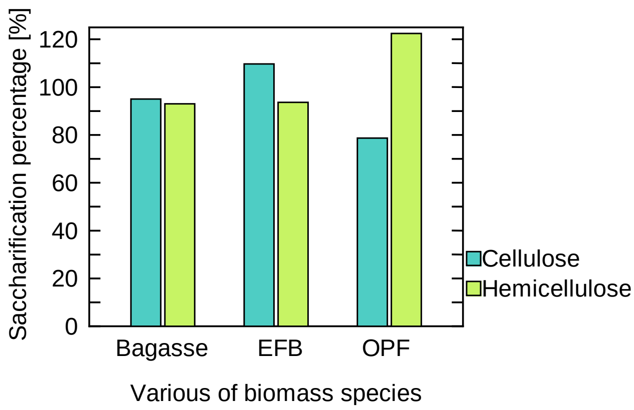

Fig. 5. The saccharification percentage at low-loading for various of biomass species pretreated with ChOAc at IL/biomass ratio of 1.5

Table 3
The error values of enzymatic saccharification at high-loading

IL/Biomass Rasio	Experiment(%)		Simulation (%)		Error (%)	
	Glucosa	Xylosa	Glucosa	Xylosa	Glucosa	Xylosa
1.5	56.00	14.00	56.42	14.34	0.75	2.43
	Mean error (%)				1.59	

Figure 6 shows the simulation result of EFB and OPF in the enzymatic saccharification at a high-loading process. After 72 h of enzymatic saccharification at high-loading, the glucose concentrations of bagasse, EFB, and OPF were 56.42 g/L, 64.13 g/L, and 45.88 g/L, respectively. According to the result obtained in Figure 3, it is observed that the composition affects the amount of cellulose and hemicellulose percentage, particularly at OPF.

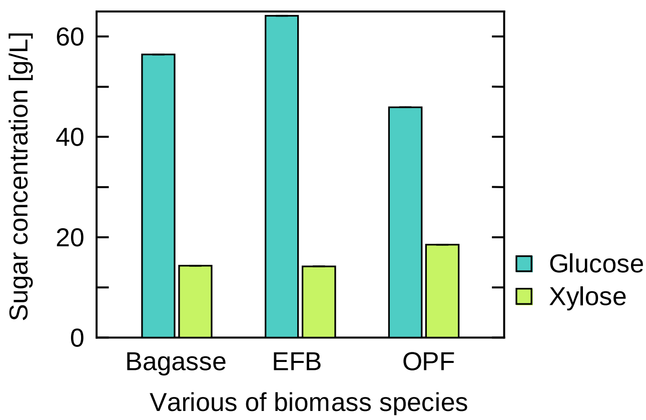

Fig. 6. The sugar concentration during enzymatic saccharification at high-loading for various of biomass species pretreated with ChOAc at IL/biomass ratio of 1.5 at 72 h reaction time

3.4 Model Validation Ethanol Production in the Fermentation Process

In the fermentation process, the simulation data was in glucose and xylose concentration data, as shown in Table 4. The average error value of glucose, xylose, and ethanol concentration was 1.3%, 3.29%, and 3.47%, respectively. This error value was much smaller than the error value from previous studies[18].

Table 4
The error values of ethanol production

Parameter	Glucosa (g/L)		Xylose (g/L)		Ethanol (g/L)	
Condition	Experimental	Simulation	Experimental	Simulation	Experimental	Simulation
Value	27	26.65	7	6.77	15	15.52
Mean Error (%)	1.3		3.29		3.47	

Figure 7 shows the simulation result of the subsequent co-fermentation from a mixed sugar solution containing glucose, xylose, and ethanol concentrations at 24h from bagasse (26.65 g/L, 6.67 g/L, 15.52 g/L), EFB (28.95 g/L, 6.41 g/L, 15.34 g/L), and OPF (20.85 g/L, 8.42 g/L, 15.11 g/L), which was 85%, 99.85%, 97.64% the theoretical value for the sugar-based ethanol yield. Thus, an IL/biomass ratio of 1.5 is the recommended experimental procedure for each biomass species for both bagasse, EFB, and OPF pre-treated with ChoAc, respectively.

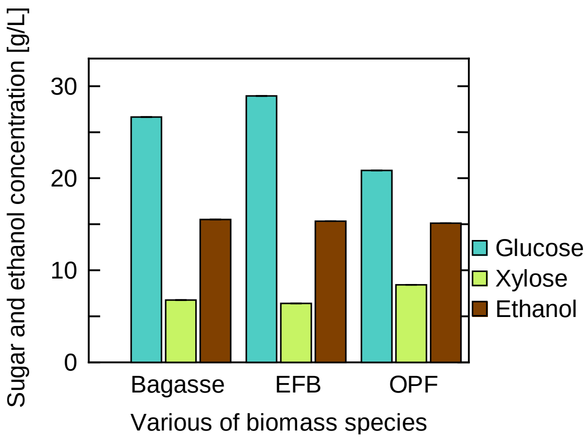

Fig. 7. The sugar and ethanol concentration during subsequent fermentation for various of biomass species pretreated with ChOAc at IL/biomass ratio of 1.5 at 24 h reaction time

4. Conclusions

In this paper, we predict the bioethanol generation prospect of IL-assisted pre-treatment of biomass in biorefinery based on optimum IL/biomass ratio of 0-1.5 employing SPD software. The biomass refinery process was modelled by three processes, namely pre-treatment, enzymatic saccharification, and fermentation process. The simulation contains a pre-treatment, low loading enzymatic saccharification, high loading saccharification, and fermentation step. The developed model was successfully validated with published experimental results of cholinium ionic liquid assisted pre-treatment of bagasse. Then, an optimization investigation on IL/biomass ratio was carried out. The study results showed that the mean error for all tested values was 4.34%. The obtained results indicate that an IL/biomass ratio of 1.5 is suitable and sufficient for obtaining a maximum ethanol yield. Moreover, after 72 h of enzymatic saccharification at high loading, the glucose concentrations of bagasse, EFB, and OPF were 56.42 g/L, 64.13 g/L, and 45.88 g/L, respectively. Furthermore, the xylose concentrations of bagasse, EFB, and OPF were 14.34 g/L, 14.19 g/L, and 18.52 g/L, respectively. In the subsequent co-fermentation from a mixed sugar solution containing glucose, xylose, and ethanol concentrations at 24h from bagasse (26.65 g/L, 6.67 g/L, 15.52 g/L), EFB (28.95 g/L, 6.41 g/L, 15.34 g/L), and OPF (20.85 g/L, 8.42 g/L, 15.11 g/L), which was 85%, 99.85%, 97.64% the theoretical value for the sugar-based ethanol yield. To conclude, the implementation of SPD simulation on biomass refinery into ethanol has a considerable potential to secure the cost of ethanol process production and future experimental process demand.

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