Analysis and design of low gas emission of ethanol fuel from ionic liquid-assisted pretreatment of biomass

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Abstract. The growth of gas emissions (GE) in the environment that stirred climate change, has correlated with the decline of fossil fuels. Generally, GE was produced by burning fossil fuels such as gasoline in the combustion engine. Gasoline has higher air toxic emissions than ethanol. Hence, the investigation of ethanol has gained attention. On the other hand, biomass has become a renewable source of ethanol. However, due to the rigid structure of biomass, biomass pretreatment is needed before the hydrolysis and fermentation process. Recently, growing attention has been devoted to applying ionic liquids (ILs)-assisted pretreatment despite the high-cost process. Therefore, in this study, to optimize the ethanol production from biomass, the simulation using SuperPro Designer (SPD) software was conducted. Bagasse as biomass material was treated by IL, namely choline acetate (ChOAc), with the range of ratio IL/biomass of 0–1.5. The developed SPD model was validated with published data. The results indicated that the minimum ratio of IL/biomass was 1.3. When in the hydrolysis performed at high-loading after 72 h reaction time, the glucose and xylose concentrations were 49 g/L and 13 g/L, respectively. When the fermentation process was conducted, the initial mixed sugar solution concentration was 23 g/L of glucose and 6 g/L of xylose. Then, the ethanol concentration was 15 g/L at 24 h, which was 89% of the theoretical ethanol yield. To conclude, the developed SPD model not only could support to optimize the biomass refinery into low GE of ethanol but also could reduce large cost experimental.

1. Introduction
Increased environmental pollution and climate change have occurred due to increased levels of harmful exhaust gases such as carbon dioxide and plumbum (Pb) [1]. The exhaust gas is the result of fossil energy such as gasoline, petroleum, and others. On the other hand, fossil energy is the most important source in supporting human activities in various sectors. However, fossil energy reserves experience scarcity due to continuous exploitation [2]. Therefore, we need an energy source that is environmentally friendly and renewable. One of the alternative sources of environmentally friendly renewable energy is a source of biomass energy.

Biomass comes from various kinds of plants. The characteristics of carbon dioxide exhaust gas produced by biomass can reduce emissions [3]. On the other hand, biomass is very abundant in various sectors such as agriculture, plantation, animal husbandry, and other bio-sourced sectors [4]. The utilization of biomass into bioethanol through three stages is pretreatment, enzymatic saccharification, and fermentation [5]. Among the three stages, pretreatment plays an important role. This role is related to the structure of the biomass, which is very difficult to degrade.
Lignocellulosic biomass is a biopolymer consisting of cellulose, hemicellulose and lignin, and small amounts of protein, pectin, ash and extractives [4][6]. Lignin and hemicellulose are plant walls of lignocellulosic biomass that are difficult to break down. Therefore, the pretreatment process is needed so that the wall is broken. So that in the enzymatic saccharification process, the enzyme can access cellulose [5][7]. The product of the enzymatic saccharification process is fermentable sugar. Then, ethanol was obtained from the fermentable sugar by using fermentative microorganisms at the fermentation process [8].

Currently, the most effective pretreatment process in biorefinery is the use of ionic liquids (ILs). ILs have been shown to dissolve cellulose [8][9]. However, high IL prices and heavy experimental processes have made the cost of this process uneconomical. Therefore, this research aims to optimize bioethanol production in the biorefinery process through process simulation with SuperPro Designer (SPD) software. The biomass refinery process was concretely modelled by three stages, such as pretreatment, enzymatic saccharification, and fermentation. The simulation includes a pretreatment, low loading enzymatic saccharification, high loading saccharification, and fermentation. Then, simulation results in this study were validated with experimental data that had been carried out [8]. SPD software has a good process structure, especially biochemical processes, specific compounds, and complete units. SPD software used in this study was SPD version 9.5 [10].

2. Material and simulation method

Figure 1 shows the outline 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 stages, namely enzymatic saccharification and fermentation, were also simulated concerning the experimental research [8].

In the simulation pretreatment stage, 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.

The enzymatic saccharification stage was carried out in a vessel procedure reactor (P-7/R-102). Experimental conditions were the mixing process of cellulose, hemicellulose and lignin with 5 mL of Ctec2 enzyme (enzymatic low-loading (10 g/L) and 9 mL of water (enzymatic high-loading (100 g/L) operated at a constant temperature of 50 °C for 72 h. Enzymatic low-loading (g/L) of water was replaced using a phosphate buffer of 20 g. The sugar solution was centrifuged in a centrifugation device (P-8/CF-101) to remove supernatants. The filtration process used a microfiltration device (P-11/MF-101) to remove micro-size supernatants before entering the fermentation stage. The fermentation stage was operated by a fermentation reactor (P-7/FR-101). The fermentation process of a sugar solution with yeast will produce ethanol. In detail, the terminology and function of each component in the outline in Figure 1 are specified in Table 1.
Figure 1. The outline of biomass biorefinery process in SuperPro Designer software

Table 1. Reactor block description in the simulation

| Superpro Designer Name | Description |
|------------------------|-------------|
| Shredding              | P-1/SR-101-Shredding of biomass (250-500 µm) |
|                        | P-5/MX-101-Mixing water and Ionic Liquid |
| Mixing                 | P-2/MX-102-Suspension of IL/biomass ratio of 0-1.5 |
|                        | P-12/HX-102-Heating the suspension at 110 °C |
| Heating                | 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 procedure       | 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 Procedure       | 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 and discussion

3.1. Model validation at low loading saccharification
In order to check the developed model's accuracy, the simulation was validated with the published data of the experimental investigation of IL-assisted pretreatment of bagasse into ethanol [8]. During their research, Ninomiya et al. [8] have studied experimentally the minimum amount of cholinium ionic liquid (IL), ChoAc, for pretreatment of bagasse to achieve the sufficient enzymatic saccharification and co-fermentation from the obtained sugars. The authors [8] 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.

![Figure 2: Validation of IL/biomass ratio on saccharification percentage at low-loading [8]](image)

Figure 2 shows a good agreement between experimental and simulated values. However, a slight discrepancy was observed, and the mean error for all tested values is 5.5% [10]. Because the error value was smaller than the simulation that has been done, the IL/biomass ratio of 1.3 simulations had been carried out. The result showed that the cellulose saccharification percentages at an IL/biomass ratio of 1.3 were 84%. Meanwhile, hemicellulose saccharification percentages at an IL/biomass ratio of 1.3 was and 82%. These simulation results indicated that pretreatment at an IL/biomass ratio of 1.3 could replace the IL/biomass ratio of 1.5.

3.2. Model validation at high loading saccharification
In the enzymatic high-loading saccharification process, the simulation data was in glucose and xylose concentration data, as shown in Table 2. In the experiments, glucose and xylose concentrations increased with elapsed time, reaching 56 g/L and 14 g/L at 72 h, respectively [8]. The cellulose and hemicellulose
saccharification percentages were 95% and 65% at 72 h, respectively. The average error value was 1.59%. This error value was much smaller than the error value from previous studies [10].

| IL/Biomass ratio | Experiment (g/L) | Simulation (g/L) | Error (%) |
|------------------|------------------|------------------|-----------|
|                  | Glucose | Xylose | Glucose | Xylosa | Glucose | Xylose |
| 1.5              | 56.00   | 14.00  | 56.42   | 14.34  | 0.75    | 2.43   |
|                  |         |        |         |         |         |        |
|                  |         |        |         |         |         | The mean error (%) 1.59 |

The simulation results also showed that at the IL/biomass ratio of 1.3, the glucose concentration was 49 g/L, while the xylose concentration was 13 g/L. Therefore, the IL/biomass ratio of 1.3 had potential to be an alternative way for the IL/biomass ratio of 1.5.

3.3. The fermentation of IL/Biomass ratio of 1.3
Figure 3 shows the fermentation simulation results of various IL/biomass ratios that were not experimentally carried out except for the ratio 1.5. The simulation results showed that the ethanol concentration obtained by IL/biomass ratio 1.3 was close to the ethanol concentration value of the IL/biomass ratio 1.5. The ethanol concentration IL/biomass ratio 1.3 was 15 g/L at 24 h of reaction time. The theoretical ethanol yield was 89%. Meanwhile, the IL/biomass ratio of 1.5 was 15 g/L at 48 h of reaction time [8]. Therefore, the IL/biomass ratio 1.3 had the potential to cut production costs through a faster fermentation process than the IL/biomass ratio 1.5.

4. Conclusion
This paper predicted the bioethanol generation prospect of IL-assisted pretreatment 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 stages, namely pretreatment, enzymatic saccharification, and fermentation. The simulation includes a pretreatment, low loading enzymatic saccharification, high loading saccharification, and fermentation. The developed model was successfully validated with published experimental results of cholinium ionic liquid assisted pretreatment 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 results indicated that the minimum ratio of IL/biomass was 1.3. Moreover, when in the hydrolysis performed at high-loading after 72 h reaction time, the glucose and xylose concentrations were 49 g/L and 13 g/L, respectively. When the fermentation process was
conducted, the initial mixed sugar solution concentration was 23 g/L of glucose and 6 g/L of xylose. Then, the ethanol concentration was 15 g/L at 24 h, 89% of the theoretical ethanol yield. The developed SPD model strongly to not only support optimizing the biomass refinery into low GE of ethanol but also could reduce large cost experimental. Therefore, this study suggests minimizing the low production costs of the biomass refinery into GE ethanol so that the operating time of the combustion engine is also relatively short. Thus, the reduction of GE, which is harmful to the environment that can cause climate change, will also be reduced.

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