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Simulation of Furfural and Levulinic Acid Production from Lignocellulosic Biomass

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ABSTRACT

Furfural and levulinic acid are chemicals that can be produced from lignocellulosic biomass. In this research, mass balance simulation of furfural and levulinic acid production at scale of 100 tons of biomass/year was examined. This research using various models of kinetic reaction and biomass to solvent ratio from lignocellulosic biomass raw materials consisting of cellulose, hemicellulose, lignin, ash, and water composition of 35%, 30%, 25%, 3%, and 7%. The kinetic models used in this research were separate kinetic models and simultaneous model (model-3). The separate kinetic models were divided into two models which separate kinetic model 1 (model-1) and separate kinetic model 2 (model-2). SuperPro Designer 9.0 software was used to calculate mass balance simulation. From the research, it was found that variations in kinetic reaction model affected furfural and levulinic acid production. Higher biomass to solvent ratio produced higher furfural and levulinic acid production. The highest furfural produced from simulation process was kinetic reaction model-2 with a biomass to solvent ratio of 1:30 and 0.67 liter furfural/hour. While the highest levulinic acid produced from the simulation process was kinetic reaction model-1 with a biomass to solvent ratio of 1:30 and 2.37 liter levulinic acid/hour.

***Keywords*:** furfural, levulinic acid, lignocellulose, mass balance.

1. INTRODUCTION

Indonesia as an archipelagic country with potential for various plantation commodities has many potential sources of lignocellulosic biomass. Several plantation commodities that are widely processed include oil palm, cassava, rubber, coffee and so on. The potential of this biomass cannot be separated from the contents in the biomass itself such as lignin, hemicellulose and cellulose. These three types of materials have potential to be processed into various high-value chemicals. Furfural and levulinic acid are products that can be obtained from hemicellulose and cellulose hydrolysis process.

Furfural can be produced from biomass through hydrolysis process of hemicellulose containing xylose. Furfural has many applications in various chemical industries like health industry and electrode materials [1,2]. One of the furfural derivative compounds is furfuryl alcohol which consumes 62% of the world furfural market [3]. Furfuryl alcohol can be produced from furfural hydrogenation reaction with various solid catalysts [4-7].

The hydrolysis process of biomass compounds containing glucose can produce levulinic acid. Levulinic acid can be converted into various compounds such as 5-bromolevulinic acid, ɣ-valerolactone (GVL), 2-methyltetrahydrofuran, valeric acid levulinate esters, methyl pyrrolidone, and others [8]. Many studies have been carried out on the production of ɣ-valerolactone as a potential biofuel from levulinic acid using solid catalysts [9-17]. In 2022, global consumption of levulinic acid reached 3,436.9 tons and is expected to increase every year [18]. The high consumption of levulinic acid is due to the wide use of levulinic acid in the food industry, polymers and various chemical compounds [19-21].

Fulfilling the need for furfural and levulinic acid must be obtained from renewable materials, namely biomass. Biomass

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hydrolysis method using acid catalyst is one of the processes that can be carried out to convert hemicellulose and cellulose into furfural and levulinic acid. Miranda, et al. have examined simulation 8 kilotons of levulinic acid production from sugarcane bagasse biomass as raw material [22].

Besides that, several studies have examined simulation of levulinic acid and furfural production from biomass, especially discussing techno-economics. Gozan, et al. examined techno-economics of levulinic acid production from Sorghum bicolor [23]. Rahman, et al. examined the techno-economics of levulinic acid, formic acid and furfural production from empty oil palm fruit bunches [24]. Mohammed, et al. examined techno-economics of furfural and glucose production from empty oil palm fruit bunches [25]. Sato, et al. examined the techno-economics of levulinic acid production using formic acid co-product as catalyst [26].

In this paper, we examine simulations of mass balance calculations for furfural and levulinic acid production from lignocellulosic biomass on a factory scale using various reaction kinetics models and SuperPro Designer 9.0 software.

2. RESEARCH METHODS

Mass balance calculations for furfural and levulinic acid production plants from lignocellulosic biomass were carried out using SuperPro Designer 9.0 Academic License simulation software. The factory capacity used in the mass balance calculation process was 100 tonnes of lignocellulosic biomass/year that the composition of lignocellulosic biomass consists of cellulose, hemicellulose, lignin, ash and water were 35%, 30%, 25%, 3% and 7%. The furfural and levulinic acid production process consists of a biomass hydrolysis process to produce furfural-levulinic acid and furfural-levulinic acid purification process.

The biomass hydrolysis process to produce furfural and levulinic acid simultaneously was carried out using a sulfuric acid catalyst with a concentration of 0.5M at 170^{o}C. The ratio between biomass-acid solution and furfural-levulinic acid kinetic model were the independent variables used in this research. Variations in the ratio between biomass and acid solution were 1:10, 1:20 and 1:30. Meanwhile, reaction kinetic model used in furfural and levulinic acid production consists of 3 reaction kinetic models, namely Model-1 is a separate kinetic model 1 according to research by Dussan, et al. [27], Model-2 is a separate kinetic model 2 according to research by Gozan, et al. [28], and Model-3 is a simultaneous kinetic model according to the research of Gozan, et al. [28]. Separate kinetic model was a kinetic model where levulinic acid and furfural was produced from two different fractions, namely glucan and xylan fractions. Meanwhile, simultaneous kinetic model was a kinetic model where levulinic acid and furfural come from same source which is lignocellulose biomass. These three models were used in this research because they were able to produce kinetic parameters for levulinic acid and furfural production from lignocellulose biomass using sum of square error calculations between experimental data and kinetic model. Various kinetic models scheme can be seen in Table 1.

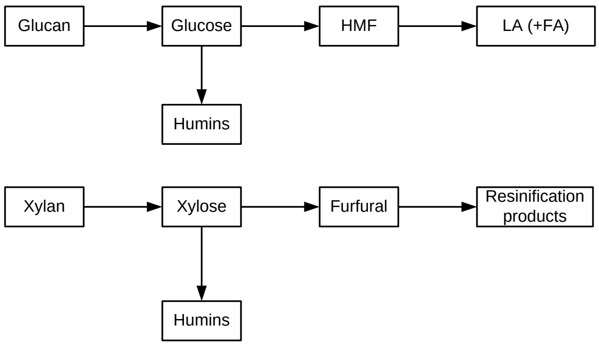
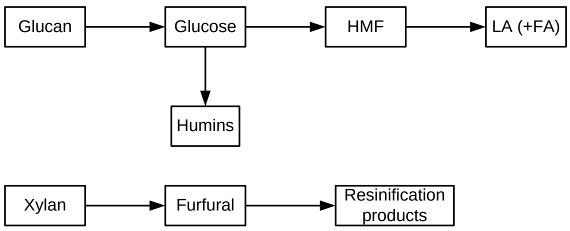
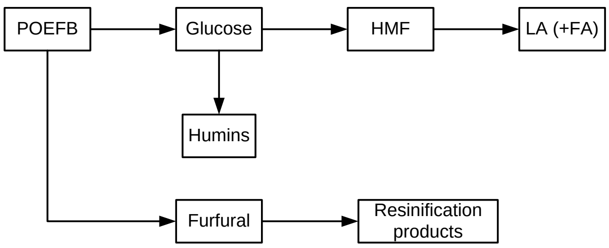
The flowsheet for furfural and levulinic acid production process can be seen in Figure 1. In the beginning, biomass will enter the grinder (GR-101) to reduce the lignocellulose biomass size which was then mixed with sulfuric acid solution according to variations in the mixer (MX-101). The mixture then enters the reactor (R-102) to produce levulinic acid and furfural at 170^{o}C. The product from the reactor in the form of gas will be condensed in the condenser (HX-101) to become liquid. Meanwhile, the output products of the reactor in the form of liquids and solids will enter clarification (CL-101) to separate liquid and solid products. Liquid product from the condenser will enter three distillation columns. The purifying step of furfural and levulinic acid from biomass hydrolysis was carried out using a distillation process based on Nhien, et al. [29]. The first distillation column (C-101) will separate water, the second distillation column (C-102) will separate formic acid, and the third distillation column (C-103) will separate furfural. The clarification output divided into liquid and solid product, where the liquid product will enter the fourth distillation column (C-104) to separate levulinic acid, while the solid product from clarification will enter the washing stage (WSH-101) to wash lignin and humins as solid residue from the reaction.

3. RESULTS AND DISCUSSION

Furfural and levulinic acid production from various kinetic models and biomass-acid solution ratios can be seen in Table 2. The effect of various kinetic models from the simulation results showed quite different results according to Table 2. In general, Table 2 showed that higher biomass-acid solution ratios used will produce higher hydrolysis products (furfural, levulinic acid, formic acid, and lignin-humins). This indicated that the hydrolysis process was more effective if the amount of solvent used was higher. This is in accordance with research by Dong, et al. [30].

The amount of furfural in model-1 and model-3 were lower compared to model-2. This can be happened because model-1 and model-3 used a more complex model than model-2. Based on model-1, xylose will be converted to furfural and humins. This model caused the furfural production lower than other kinetic models. On the other hand, model-3 predicted that furfural and levulinic acid were produced from a single unit of biomass namely Palm Oil Empty Fruit Bunches (POEFBs) [28]. The fundamental difference between model-1 and model-3 in furfural production that in model-3, furfural was directly obtained from the hemicellulose fraction without xylose and humins production according to Table 1.

Table 1. Kinetic model scheme.

Kinetic Model	Scheme	Reference
Model-1 (Separate kinetic model 1)		[27]
Model-2 (Separate kinetic model 2)		[28]
Model-3 (Simultaneous kinetic model)		[28]

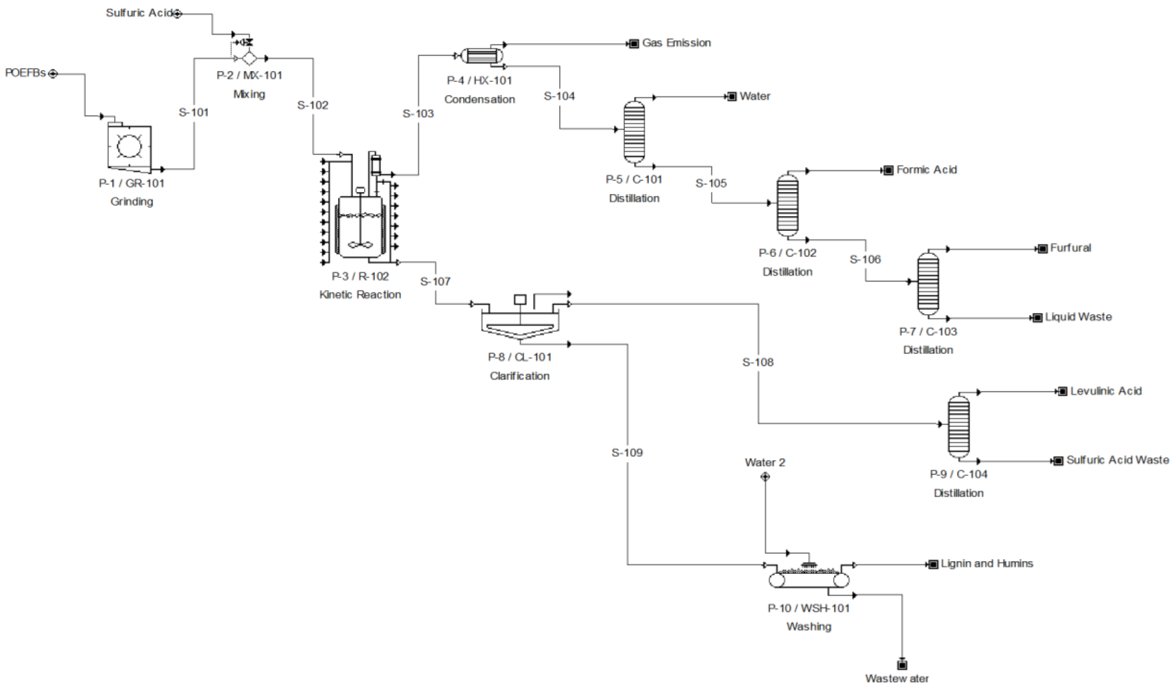


Figure 1. Furfural and levulinic acid production flowsheet.

Table 2. Simulation results of furfural and levulinic acid production.

Parameters	Model–1			Model–2			Model–3		
	Biomass:Solvent Ratio								
	1:10	1:20	1:30	1:10	1:20	1:30	1:10	1:20	1:30
Furfural (l/h)	0.23	0.44	0.66	0.24	0.46	0.67	0.23	0.45	0.66
Levulinic Acid (l/h)	2.33	2.35	2.37	0.69	0.71	0.73	0.63	0.66	0.68
Formic Acid (l/h)	607.08	607.27	607.46	175.17	175.36	175.55	161.48	161.67	161.86
Lignin and Humins (l/h)	3.19	3.19	3.19	3.26	3.26	3.26	3.33	3.33	3.33

The simulation on levulinic acid production according to Table 2 showed that model-1 was the kinetic model with the largest amount of levulinic acid production compared to model-2 and model-3. This could be due to model-1 originating from the study of Dussan, et al. [27], examining the production process of furfural and levulinic acid using higher temperatures (150^{o}C – 200^{o}C) than model-2 and model-3 (150^{o}C – 170^{o}C). Yield of levulinic acid tends to increase with increasing reaction temperature in the range of 150 – 230^{o}C [31].

Formic acid was the most produced product according to Table 2. This could be due to all the kinetic models used in this study produce formic acid as a final product. The use of high temperature around 170^{o}C in the reactor will degrade furfural into resinification products where formic acid is the most dominant product [32-36]. In addition, a lot of lignin as a raw material component that was not hydrolyzed and humins as a by-product of the hydrolysis process were produced as by-product according to Table 2.

4. CONCLUSION

In this research, a mass balance simulation was investigated for furfural and levulinic acid production at a factory scale of 100 tons of biomass/year using various models of reaction kinetics and biomass-acid solution ratios from lignocellulosic biomass. From the research results, it was found that the amount of furfural and levulinic acid produced was influenced by the reaction kinetics model where the greater biomass-acid solution ratios used would produce higher furfural and levulinic acid. The highest furfural produced from the simulation process using model-2 with biomass-acid solution ratios of 1:30 was 0.67 l/hour. While the highest levulinic acid produced from the simulation process using model-1 with biomass-acid solution ratios of 1:30 is 2.37 l/hour.

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