Effect of Hydrochloric Acid Concentration on the Conversion of Sugarcane Bagasse to Levulinic Acid

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Abstract. Levulinic acid is a new green platform chemical used to the synthesis of a variety of materials for numerous applications such as fuel additives, polymers and resins. It can be produced using renewable resources such as biomass like sugarcane bagasse which are cheap and widely available as waste in Indonesia. In this study, sugarcane bagasse was hydrolyzed using hydrochloric acid with a solid liquid ratio 1:10. The effects of hydrochloric acid concentration at temperature of 180 ºC and reaction time of 30 min were studied. The presence of levulinic acid in product of hydrolysis was measured with gas chromatography (GC). It was found that the highest concentration of levulinic acid was obtained at 1 M hydrochloric acid in 25.56 yield%.

1. Introduction

In Indonesia the presence of biomass waste is very abundant. So far, the biomass is used for energy, such us oil palm empty fruit bunch (EFB) which converted to bio-oil [1], ulin wood which converted to bioenergy through pyrolysis process [2], sugarcane bagasse which converted to bioenergy by pyrolysis-gasification process [3] and utilize municipal solid waste (MSW) as the energy source [4]. Actually, biomass waste can be converted into platform chemicals like levulinic acid which has higher value.

Levulinic acid or 4-oxopentanoic acid is an organic compound which has ketone carbonyl group and acidic carboxyl groups. These functional groups turn levulinic acid into the building block for the synthesis of several organic compounds, such as: methyltetrahydrofuran (MTHF) for fuel additive, δ-amino levulinic acid (DALA) for herbicide, and diphenolic acid as a substitute for bisphenol in a polymer manufacture [5].

Traditionally, hexose sugar was the most convenient industrial route to produced levulinic acid [6]. Recently, the utilization of biomass and agricultural wastes for production of levulinic acid has been increased as research topic, since it would give low-cost material which widely available. Chang *et al* investigated wheat straw as a raw material for levulinic acid production and 19.86% yield of levulinic acid was obtained [7].

Levulinic acid can be produced from biomass by acid hydrolysis along with heating at high temperature. In this condition, biomass will be decomposed into glucose, then glucose is converted into hydroxy methyl furfural (HMF) which then produces levulinic acid as the main product and formic acid as a by-product [8].

One of the potential biomass sources to be processed into levulinic acid which is widely available in Indonesia is bagasse, which is a residue from the sugarcane industry. According to Association of Indonesian Sugar Experts (IKAGI), every year 11.38 million tons of bagasse is produced in Indonesia. Today, the utilization of bagasse is limited to animal feed, fertilizer (compost) material, pulp, and boiler fuel in sugar factory [9]. Like biomass in general, bagasse consists of polysaccharide which can be converted into a product or chemical compound which can be used to support production process of other industrial sectors. The polysaccharide in bagasse consists of cellulose (53.75%), hemicellulose (20.98%) and lignin (17.56%) [10]. High cellulose and hemicellulose contents are potential for processing into levulinic acid through hydrolysis.

The reaction of levulinic acid formation from biomass is a very complex series of reactions because it goes through several intermediate reaction stages and side reactions, such as humin formation. In certain condition, the more common reaction is side reactions such as lactone and humin formations, product repolymerization and intermediate repolymerization. Therefore, there should be an ideal reaction condition to obtain levulinic acid as a dominant product. According to Yan *et al*, factors which may influence reaction outcome includes acid concentration, temperature and reaction time [11]. Therefore, this paper will study the effect of hydrochloric acid concentration on levulinic acid yield.

2. Materials and Methods
2.1 Materials
The raw material used in this work is sugarcane bagasse collected from a local industry (PG Madukismo, Yogyakarta, Indonesia). It was air dried, milled, screened to select the fraction of particle size of less then 1 mm, homogenized in a single lot.
Hydrochloric acid 37% was purchased from Merc and levulinic acid 98% was purchased from Sigma Aldrich.
2.2 Methods
The hydrolysis reaction were carried out in a tube glass screw cap with an internal diameter of 13 mm and a length of 70 mm. Sugarcane bagasse and hydrochloric acid with ratio 1:10 placed in the tube. A series of tube was placed in oil bath and heated for (0-50) min at temperature of 180 °C. The oil bath temperature was monitored using thermocouple, with deviations maintened within ±1 °C. Insoluble humins, formed during the decomposition reaction, were separated from the solution by paper filtration. The liquid product was sampled and analyzed using a gas chromatography (GC).
2.3 Analysis
The composition of liquid phase was determined using a GC system by using a column HP-5/SH-Rxi-5Sil with He as carrier gas. The yield of levulinic acid was expressed in term of weight percent yield which calculated from a calibration curve plotting concentration of levulinic acid standart against areas obtained under the GC curve. The following formula was used for calculating the yield of levulinic acid

$$\text{Yield levulinic acid (wt\%)} = \frac{\text{weight of levulinic acid (g)}}{\text{weight of substrat feed (g)}} \times 100\%$$
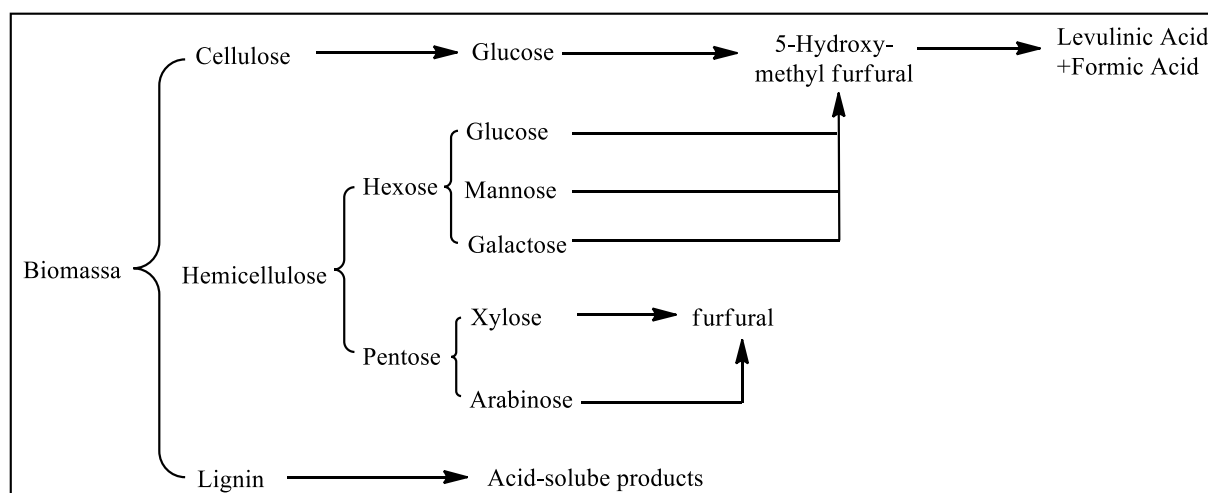
3. Results and Discussion
3.1 Sugarcane bagasse composition
Sugarcane bagasse is lignocellulose biomass whose main composition is cellulose, hemicellulose and lignin. Table 1 shows the test result of cellulose, hemicellulose and lignin contents in the bagasse which used in this study. The method to determine bagasse composition was Chesson's method. The result shows that bagasse contains high cellulose and hemicellulose. Both can be converted into glucose which is an intermediet in the production of levulinic acid. Thus, glucose to be conferted to 5-HMF and then to levulinic acid as the final product. The conversion of a typical lignocellulosic biomass to levulinic acid is shown in Figure 1.

Table 1. Component of sugarcane bagasse.

Compound	Value (%)
Cellulose	41.9
Hemicellulose	23.9
Lignin	21.6
Others	12.6

Figure 1 Simplified reaction scheme for the conversion of lignocellulosic biomass to levulinic acid [12]

3.2 Composition of the liquid product

Sugarcane bagasse was hydrolyzed with hydrochloric acid at 180 °C for 30 min, and after the reaction the products were analyzed by GC to measure the chemical compositions. The retention time of the standard sample of levulinic acid was at 10.380 min according to Figure 2.
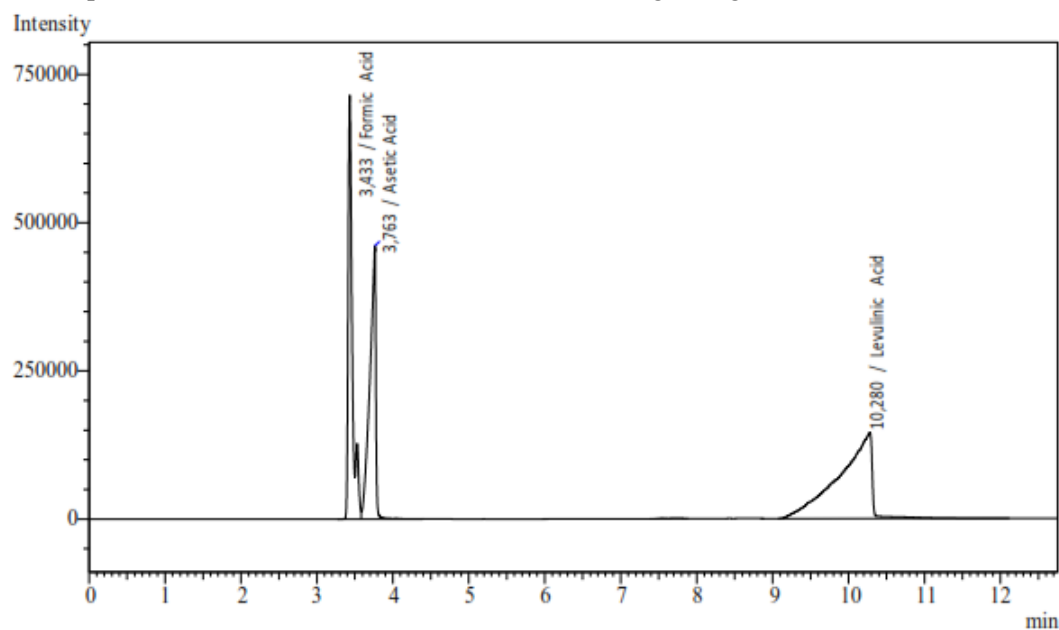

Figure 2 Representative GC profile of the standard samples

Figure 3 show the GC profiles of the products obtained from hydrolysis sugarcane bagasse. This shows that the peak for levulinic acid was determined at the retention time of 10.280, on the basis of the GC analysis of the standard sample. Besides levulinic acid, there were formic acid and acetic acid as by-product.
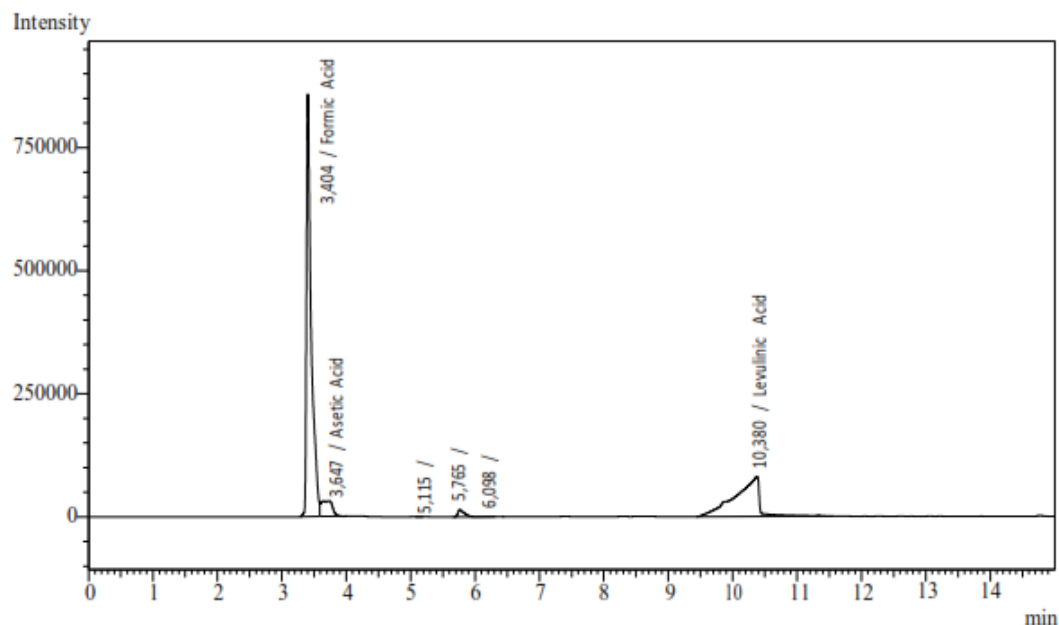

Figure 3 Representative GC profile of the liquefaction fraction from hydrolysis sugarcane bagasse

3.3 The effect of reaction time on levulinic acid yield
Figure 4 shows the effect of reaction time on the conversion sugarcane bagasse to levulinc acid with the concentration of hydrochloric acid of 1 M and temperature of 180 °C. This result show that the amount of levulinic acid increasing very fast during the 30 minute. Afterward it was observed that only a slight rise occurred after 30 min of reaction time. This happened because side reactions started to occur when the degradation products were exposed to high temperatures for a prolonged period of time.
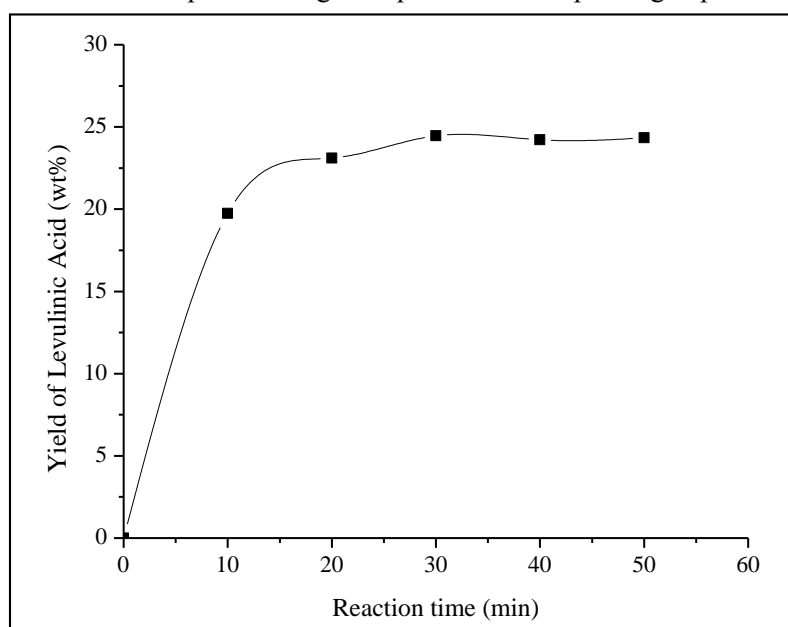

Figure 4 Effect of reaction time on yield levulinic acid

3.4 The effect of hydrochloric acid concentration on levulinic acid yield

Hydrochloric acid was selected to be acid catalyst because it is affordable and easily ionized, so it is more effective for the hydrolysis process of bagasse into levulinic acid. The effect of of hydrochloric acid concentration on the sugarcane conversion to levulinic acid was investigated in concentration range of 0.25-1M. Reaction was performed for 30 minutes at 180 °C and ratio of solid to liquid 1:10. Figure 5 shows effect of HCl concentration on yield levulinic acid.
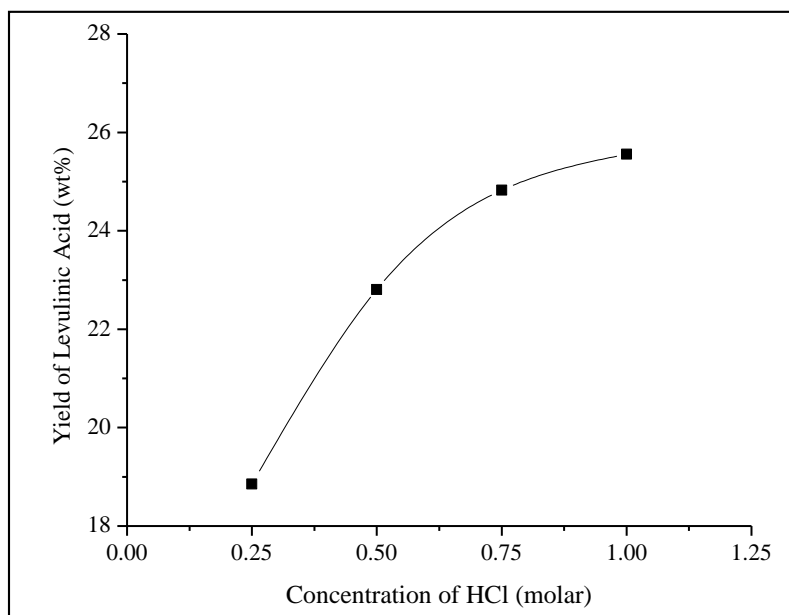

Figure 5 Effect of HCl concentration on yield levulinic acid

From Figure 5, we notice that the highest conversion was achieved at 1 M concentration of hydrochloric acid with yield of levulinic acid of 25.56 wt%. The result of this work showed that levulinic acid yield will increase as the concentration of hychloric acid catalyst increases until optimum condition was reached. Afterward, increasing catalyst concentration only has small effect on levulinic acid yield. Higher HCl concentration causing side reactions that may negatively affect the rate of hydrolysis cellulose to levulinic acid. Similar result with Fang and Hanna observed that higher sulfuric acid concentration also significantly increased the levulinic acid yield. Yield of levulinic acid was positively correlated with mineral acid concentration, which greatly boosted the yield of levulinic acid by the higher rate of hydrolysis of carbohydrates to organic acids [12].

4   Conclusion

Levulinic acid can be produced by hydrolysis reaction of sugarcane bagasse using hydrochloric acid catalyst. The conversion of bagasse into levulinic acid was affected by the concentration of hydrochloric acid as the catalyst. The yield of levulinic acid increased at higher consentration of hydrochloric acid. Maximum yield of levulinic acid (25.56wt%) was obtained at the concentration of hydrochloric acid of 1 M at 180 °C and reaction time of 30 minutes.

Acknowledgments

References

[1]   Pradana YS and Budiman A 2015 *Journal of Engineering Science and Technology* **10** pp 1-8
[2]   Widiyannita AM, Cahyono RB, Budiman A, Sutijan and Akiyama T 2016 *AIP Conference Proceedings* 1755
[3]   Daniyanto, Sutijan, Deendarlianto, and Budiman A 2016 *Journal of Engineering and Applied Sciences* **11** pp 9974-9980
[4]   Sudibyo H, Majid AI, Pradana, YS, Budhijanto W, Deendarlianto, and Budiman A 2017 *Energy Procedia* **105** pp 263-269
[5]   Morone A, Apte M and Pandey RA 2015 *Renewable and Sustainable Energy Reviews* 546-565
[6]   Fang Q and Hanna MA 2002 *Industrial & Engineering Chemistry Research* **81** 187-192
[7]   Chang C, Cen P and Ma X 2007 *Bioresource Technology* **98** 1448-1453
[8]   Baugh KD and McCarty PL 1998 *Biotechnology and Bioengineering* **31** 50-61
[9]   Setiati R., Wahyuningrum D, Siregar S and Marhaendrajana T 2016 *Jurnal Penelitian dan Pengabdian Masyarakat* pp 257-264
[10] Widyawati, Niken L and Argo B 2014 *Jurnal Teknologi Pertanian* **15** pp 1-6
[11] Yan L, Yang N, Pang H and Liao B 2008 *Journal Clean* **36** 158-163
[12] Girisuta B 2007 Levulinic acid from lignocellulosic Biomass *PhD Thesis* University of Groningen Netherlands