Innovative Systems Design and Engineering
ISSN 2222-1727 (Paper) ISSN 2222-2871 (Online)
Vol.5, No.5, 2014

Catalytic Conversion of Wastewater from Starch Industry to Levulinic Acid

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Abstract

Levulinic acid is known as versatile building block for the production of energy and various petrochemical products. In this present work, levulinic acid was produced by dehydration and rehydration of sugar-rich wastewater containing H_2SO_4 from starch industry. This study proposed feasibility of utilizing waste water that obtained from nano-crystalline process of starch factory as resource for the production of levulinic acid without catalyst adding. The influence of reaction time and reaction temperature to yield of levulinic acid were investigated. It was found that the highest yield of levulinic acid was 91.41 mol % at 140 °C with the reaction time of 240 min.

Keywords: Levulinic acid, wastewater, renewable, energy

1. Introduction

At present, the hydrocarbon fossil is the main resource of energy and various petrochemicals-based organic chemical products in the world, for example, textile, lubricant, resin, polymer, fertilizer, asphalt, which are the modern products in the 21st century. However, the demand for hydrocarbon consumption is increased as results of population and economic development. This raises serious issues about the balance of energy markets, as well as the rising price of fossil fuel. In addition, the concerning of high carbon emission, which cause global warming problem, is considered. Due to these reasons, it requires to develop and use of bio-renewable resources, which is green and sustainable, to replace hydrocarbon from fossil for bulk chemical and fuels productions.

However, in Thailand, there are several kind of bioresource such as agricultural waste, weed, and waste water which contain natural carbon, cellulose, hemicellulose, lignin or sugar. Recently, the production of biofuels and chemicals from biomass via bio-refinery concept can be converted via many processes such as mechanical, biological, and thermal processes to several energy forms and valuable chemical. Among these bioresource, the waste water from starch industry is one of the most interest resource to convert to valuable chemical (Levulinic acid) which is the part of promising top-twelve building blocks from lignocellulosic biomass(Werpy, Petersen et al. 2004).

Generally, the starch industry produces a significant amount of waste water from the process, especially in the nano-crystalline unit, the ratio of product per waste water is 1:51.This waste water consists of high sugar and acid content, which must be treated before venting out from the industry. Therefore, the utilization of this sugar-rich waste water as the feedstock for chemical production would be very benefit to the industry in terms of the value chain as well as the environment.

Levulinic acid is a well-known of organic acid with excellent potential for production of conventional liquid fuel. Levulinic acid has been identified as part of promising top-twelve building blocks from lignocellulosic biomass(Werpy, Petersen et al. 2004), as result of two reactive functional groups, ketone and carboxylic that consist in molecule. In addition, levulinic acid also is versatile building blocks chemical for numerous industrial application (Klass 1998, McKendry 2002, Huber, Iborra et al. 2006). Levulinic acid (LA) has been employed as a precursor for the production of 5-methyl-2-pyrrolidone, diphenolic acid, δ-aminolevulinic acid, succinic acid, γ-valerolactone, butanone, pyrrolidones, methyl vinyl ketone, methyltetrahydrofuran, levulinate esters, diesel, gasoline, and jet fuel etc.

Conventionally, Levulinic acid is produced from biomass via acid catalyzed degradation of hexose by using mineral acid as catalyst. The information from previous studies (Haworth and Jones 1944, Harris and Feather 1973, Harris and Feather 1974, Harris and Feather 1975, Horvat, Klaić et al. 1985) hint the production of LA

react through 2 steps, firstly dehydration of hexose to 5-hydroxymethyl-furfural (HMF) which is intermediate product and subsequently hydrated in second step to form LA (Girisuta 2007). This research aims to investigate the possibility of utilizing waste water from nano-crystalline starch production process as the raw material for levulinic acid production.

2. Methodology

2.1 Experimental procedure

The waste water obtained from nano-crystalline starch production process in starch industrial. A 500 ml autoclave reactor made of 316L stainless steel was used for this experiment. The reactor was filled with waste water 240 ml at room temperature and deoxidized by bubbling with high purity nitrogen for 30 min. The reactor was placed in a constant temperature oven (±1 °C with set point). At different reaction temperature (120-220 °C) and time (240-360 min), reactors were taken from the oven and quenched into an ice-water bath to stop the reaction. The samples were taken out of the autoclave reactors and filtrated by using a 0.22 µm cellulose acetate filter for separated the insoluble humins from products. The filtrate was subsequently analyzed using High Performance Liquid Chromatography (HPLC).

2.2 Analytical methods

The acid (H2S04) concentration of waste water was determined by titration technique, which using NaOH as titrant. Potassium hydrogen phthalate (KPH) was used as the primary standard for evaluating really concentration of titrant. Phenol red was used as indicator in all analyzes.

The concentrations of glucose in waste water and the liquid products from hydrothermal process were analyzed with an HPLC system. The HPLC (Shimadzu, Japan) system composed of a Bio-Rad Organic Acid column Aminex HPX-87H, a refractive index and UV-Vis detectors (210 nm). The mobile phase consisted of aqueous sulphuric acid (5 mM) in water which was set at a flow rate of 0.6 cm3/min. The column was operated at 45 °C. The analysis for a sample was complete in 60 min. Each component in the sample was identified by comparing with the retention time of those pure compounds. And the concentrations of each component in the sample were analyzed using calibration curves achieved form standard solution with exactly know concentration.

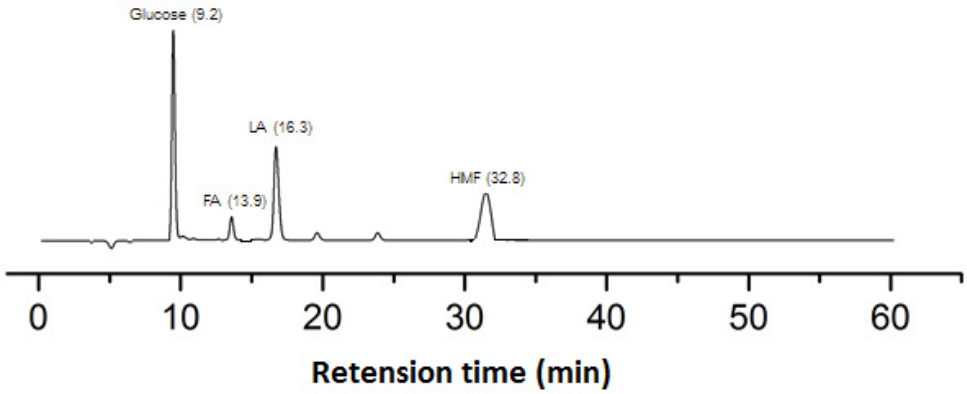

Figure 1.Typicall HPLC chromatogram of product sample after hydrothermal.

3. Results and discussion

Firstly, the wastewater from nano-crystalline starch production process was investigated by titration and HPLC techniques to determine the H_2SO_4 concentration and glucose concentration. By the titration technique, H_2SO_4 concentration is constant at 2.87 M in each lot of waste water, while the glucose concentration in waste water varies between 48.30 to 65.20 g/L.

The chemical composition of product sample, obtained from the hydrothermal process at various time and temperature, is shown in HPLC chromatogram (Figure. 1). The HPLC chromatogram consists of glucose (RT=9.2 min), formic acid (RT=13.9 min), levulinic acid (RT=16.3 min), and HMF (RT=32.8 min).

For the effect of reaction temperature, the hydrothermal process of wastewater was carried out in various

temperatures (120-220°C) for 240 minutes. It was found that HMF as intermediate and humin as by-product were observed at every reaction temperatures studied. The result of product sample on the yield of levulinic acid and conversion of glucose is shown in Fig 2. The result indicates that the glucose conversion increases with rising of the reaction temperature (up to 100% conversion at 160°C), whilst the selectivity or yield of levuinic acid decreased with raising the reaction temperature from 140-220°C. Furthermore, the amount of humin formation increases with the raising of reaction temperature (the result does not show). Analogously, Chang et al. (CHANG, MA et al. 2006) reported that the activation energy for the HMF formation is 86.33 $kJ.mol^{-1}$, levulinic acid formation is 56.95 $kJ.mol^{-1}$ and humin formation is 209.5 $kJ.mol^{-1}$. This report is evident that more reaction temperature result in a lower yield of levulinic acid because higher temperature resulting in higher energy to form humin. However, the yield of levulinic acid at temperature 180°C is not in the same trend since it is slightly higher than yield of levulinic acid at 160°C. This is due to the fact that the initial concentration of glucose at 160°C is slightly higher than at 180°C and the previous studies, Girisuta et al. (Girisuta, Janssen et al. 2006) have already shown that the lower initial concentration of glucose results in a high yield of Levulinic acid. However, at reaction temperature of 120°C, the glucose conversion and levulinic acid formation was dramatically dropped because the energy is not enough for complete converting glucose to levulinic acid under this operating conditions (at 120°C and 240 minutes). Tarabanko et al (Tarabanko, Chernyak et al. 2002) reported the similar phenomena that the yield and reaction rate of levulinic acid formation increased with the rising reaction temperature at moderate temperature.

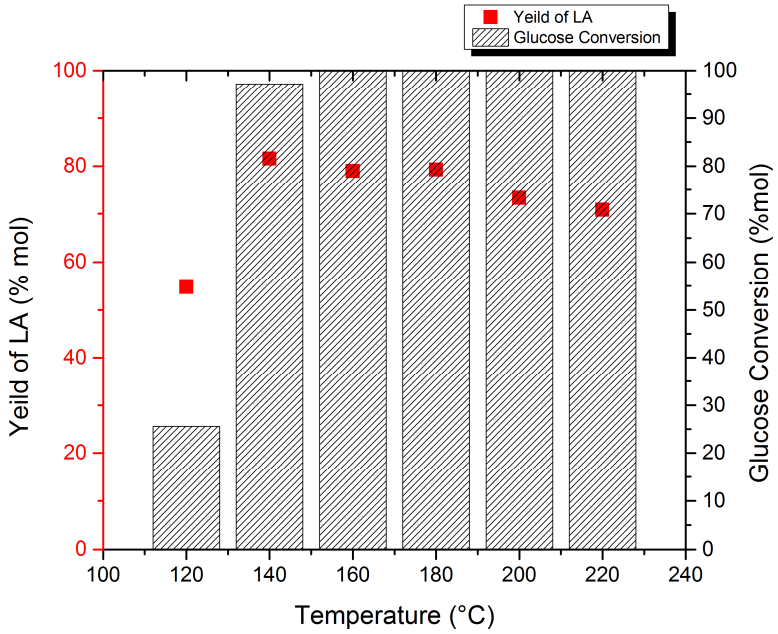

Figure 2. Influence of temperature on conversion of glucose and yield of levulinic acid.

The effect of reaction time is shown in Figure 3. It can be seen that the yield of levulinic acid increases with increasing reaction time, while the glucose concentration steadily decreases to nearly 50% initial content at the reaction time of 360 min.

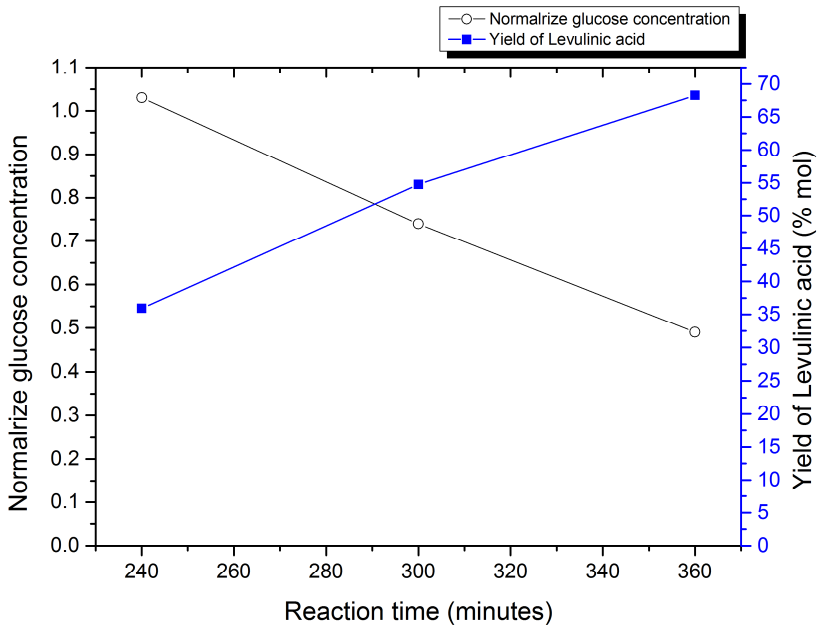

Figure 3. Influence of reaction time on conversion of glucose and yield of levulinic acid at 120 °C

4. Conclusion

The wastewater from nano-crystalline starch production process has great feasibility and potential as resource for the production of levulinic acid because it contains high sugar and acid concentrations. From the study, it was found that the selectivity and yield of levuinic acid slightly decreased with raising reaction temperature. At low reaction temperature, the reaction required longer time to accomplish the glucose conversion and levulinic acid formation. The optimal conditions of levulinic acid production from waste water were achieved at 140 °C for 240 min, which resulted the highest levuinic acid yield of 91.41 % mol.

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