



WORKSHOP PROCEEDING



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Development of Renewable Energy for the Mekong Delta – DRE34D

Conversion of Water Hyacinth into Biofuel Intermediate: Combination Subcritical Water and Zeolite Based Catalyst Processes

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ABSTRACT

The production of gamma-valerolactone, a biofuel intermediate, from water hyacinth is reported in this article. Gamma-valerolactone is an attractive platform chemical that can be further converted into a variety of chemical derivatives for wide use in industrial applications. In this study, we employed a combination of solid acid catalyzed and subcritical water processes to convert hemicellulose and cellulose derived from water hyacinth in levulinic acid, and subsequently followed by catalytic hydrogenation of levulinic acid into gamma-valerolactone. Prior to the catalytic conversion of water hyacinth into levulinic acid and gamma-valerolactone, the lignin content in the water hyacinth was removed by alkali pretreatment using sodium hydroxide solution. The maximum yield of levulinic acid was 173.4 mg/gram dried water hyacinth obtained at 40 bar, 200°C, reaction time of 120 min, and in the presence of acid activated zeolite catalyst. The hydrogenation reactions of levulinic acid into gamma-valerolactone were conducted at 160 to 220°C in the presence of mixed catalysts (Pt/TiO₂ and acid activated zeolite). The experimental results indicated that the mixed acid activated zeolite and Pt/TiO₂ catalysts gave good performance on the conversion of levulinic acid into gamma-valerolactone (more than 95% conversion).

Key words: water hyacinth, zeolite, subcritical water.

1. INTRODUCTION

The studies of bio-fuels production from various kinds of oils and other renewable materials have become important and increasing in the terms of quantity or quality. To the present, there are more than ten thousands discussed about the various aspects about biofuels preparation and some of them have been summarized in many recent review papers (Scholey et al., 2016; Thangavelu et al., 2016; Ghadiryanfar et al., 2016; Karmier, 2016). Most of those studies deal with the preparation of biodiesel and bioethanol using various kinds of feedstocks and processes. Some studies employed food resources as the

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feedstocks, while other used unconventional materials as the raw materials for the biofuels production.

Normally, production system of biofuel can be classified into primary and secondary (1st, 2nd, and 3rd generation) depending on processor type, feedstock and stage of development, as depicted in Figure 1.

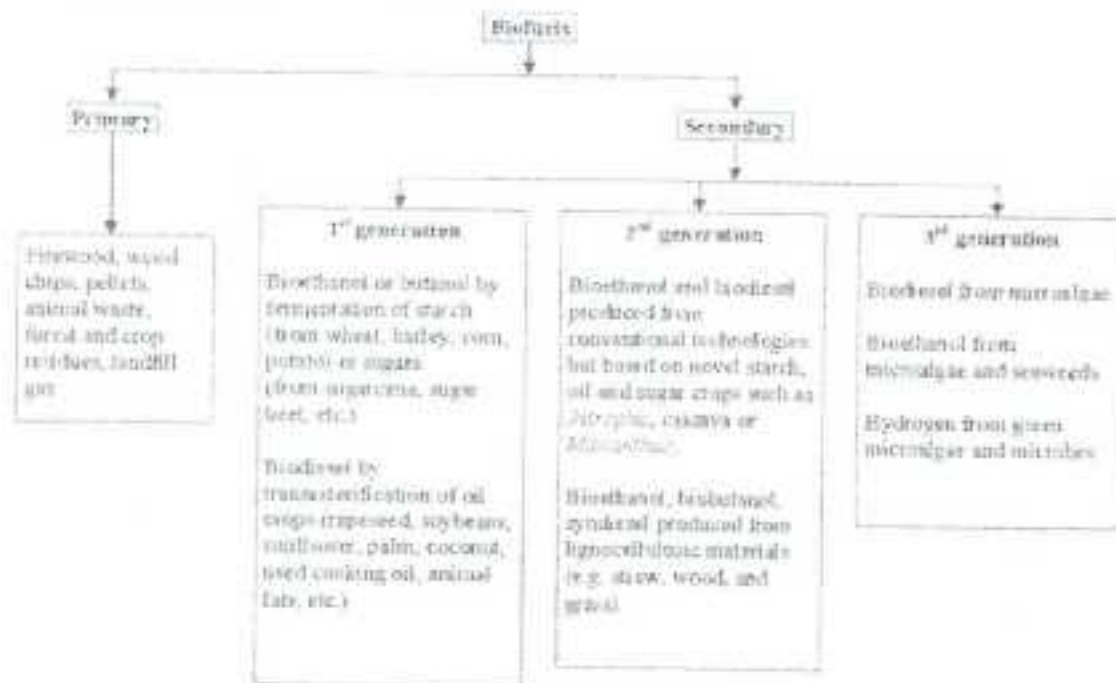


Figure 1. Biofuels classification (adapted from Dragone et al., 2010)

Primary pathway covering fuels that used from unprocessed biomass, while the secondary pathway covering biofuels from processed biomass (like bioethanol and biodiesel) that can be used for vehicles and various industrial processes. The first generation of biofuel is associated with significant economic and environmental issue, where competition between cropland used for food production and biofuel can become intense especially in developing countries with food shortage problem. Furthermore, the intensive use of land with high fertilizer and pesticide applications can cause severe problems environmentally. As for third generation of biofuel which is from microalgae with short harvesting cycle and can produce more yield than traditional crops on area basis is thought as a new alternative in biofuel production history. However scaling up production of biofuel from microalgae can face unsustainable demands on energy, water (1L biofuel: 3650 L water), and nutrients (nitrogen, phosphorus, and CO₂) required for cultivating this particular feedstock. Thus, this option is not currently feasible. Whereas a second generation of biofuels is considered the most viable one considering that lignocellulosic biomass as the main source of this biofuel is abundantly available in Asian

countries and not competing with food production. Typically, resources of this biomass can come from switch-grass, agricultural, forest, and wood processing wastes (i.e. leaves, straw or wood chips), as well as the nonedible parts of corn and sugarcane.

Water hyacinth (*Eichhornia crassipes*), which originally from the Amazon basin, is known as highly problematic invasive plant. With its fast growing, high cellulose and hemicellulose content, this invasive plant is suitable as the precursor for many applications such as carbon fibre production (Soenjaya et al., 2014), super-capacitor electrode (Kurniawan et al., 2015), etc. In this study, we utilized water hyacinth as biofuel intermediate. A combination of subcritical water process and catalytic hydrogenation process was employed to produce gamma-valerolactone from water hyacinth.

2. MATERIAL AND METHODS

2.1 Material

Water hyacinth was collected from swamp and rivers in the outskirts of Surabaya city, Indonesia. Prior to use, the water hyacinth was repeatedly washed with tap water to remove mud, dirt, etc. Subsequently, the clean water hyacinth was cut into smaller size and dried in the oven at 110°C for 24 h. The dried water hyacinth was pulverized into powder (60/80 mesh) using a JUNKE & KUNKEL hammer mill. The proximate and elemental analyses of the water hyacinth were conducted using ASTM E870 and CHNS/O analyzer model 2400 from Perkin-Elmer, respectively.

The natural zeolite from Ponorogo was chosen as the catalyst and catalyst support in this study, and the chemical composition of the zeolite is as follows: SiO₂ (60.14%), Al₂O₃ (12.52%), CaO (2.51%), Fe₂O₃ (2.49%), Na₂O (2.44%), K₂O (1.28%), MgO (0.49%), H₂O (14.40%), and loss on ignition (3.73%). All of the chemical used in this study were obtained as analytical grade from Sigma Aldrich and directly used without any further purification.

2.2 Methods

Prior to use, the powder natural zeolite was treated with 2 N hydrochloric acid solutions to increase its acid property. The acid pretreatment was conducted in round bottom flask equipped with reflux condenser. The pretreatment was carried out at 70°C for 24 h under constant stirring. The acid pretreated zeolite was then repeatedly washed with tap water and calcined at 500°C for 6 h.

In order to expose the cellulose and hemicellulose content in the water hyacinth, the delignification process was carried out using 20% NaOH solution. The delignification process was conducted at 30°C for 24 h under constant stirring (500 rpm). After the process completed, the pretreated water hyacinth was washed with tap water until the pH of water did not change, and subsequently dried in the oven at 110°C for 24 h.

The subcritical hydrolysis of the water hyacinth and the conversion of the resulting sugars into levulinic acid were conducted at several temperatures (160 to 220°C) in the presence of acid pretreated zeolite as the catalyst. The total pressure of the system was maintained at 40 bar by insertion of nitrogen gas. A brief description of subcritical hydrolysis and levulinic acid preparation is as follows: 20 grams of pretreated water hyacinth powder were mixed with 100 mL of reverse osmosis water, and 0.6 gram of acid pretreated zeolite was added to the mixture. Then the reactor was tightly closed, pressurized, and heated to the desired temperature. After the desired temperature was reached, the temperature of the system was maintained at constant temperature for 120 min. Subsequently, the reactor was rapidly cooled to room temperature (30°C). The solid then separated from the liquid by centrifugation at 3000 rpm, and the concentrations of levulinic acid, monomer sugars, organic acids, and hydroxyl methyl furan (HMF), and furfural were determined by high performance liquid chromatography (HPLC) analysis. The productions of gamma-valerolactone from levulinic acid were carried out according to the procedure of Putro et al. (2015).

The characterizations of catalysts were carried out using SEM analysis, XRD diffraction, and nitrogen sorption analysis. Details of the characterization procedures can be referred in our previous paper (Putro et al., 2015). The lignin, hemicellulose, and cellulose content in water hyacinth and pretreated water hyacinth were determined based on the TGA method.

3. RESULTS AND DISCUSSION

The chemical composition, proximate, and ultimate analysis of the raw water hyacinth and the pretreated one are given in Table 1. High cellulose content is an indication that water hyacinth is suitable as the precursor for biofuel intermediate (gamma-valerolactone) production. In general, the lignin, cellulose, and hemicellulose contents of water hyacinth are similar to other biomass product (Putro et al., 2015). The pretreatment of water hyacinth using 2N sodium hydroxide solutions effectively removed some of the lignin content in the raw material as indicated in Table 1. The removal of lignin is necessary since lignin acts as the physical barrier, encapsulating, and confining cellulose and hemicellulose. This complex three dimensional aromatic polymer structure is highly recalcitrant toward biological or chemical processes (Putro et al., 2015), therefore in order to achieve the effectiveness of the hydrothermal hydrolysis process, the removal of lignin before the main process is necessary.

In order to increase the surface acidity of the zeolite, the acid pretreatment of the zeolite using hydrochloric solution was also conducted. The type of zeolite used in this study was mordenite. The acid pretreatment removed some of the exchangeable cations (Ca^{2+} , Fe^{3+} and Al^{3+}) from the framework of zeolite and replaced by H^+ , and dealumination of the structure was also occurred, and as the consequence the acid strength of the zeolite increased from 0.461 mg butylamine/g to 0.743 mg butylamine/g. Figure 2 depicts the surface topography of zeolite and acid activated zeolite. This figure clearly

shows that the surface topography of zeolite after pretreatment using hydrochloric acid is similar with the natural zeolite.

Table 1. Chemical composition, proximate, and ultimate analysis of the raw water hyacinth and the pretreated water hyacinth

Component	Water Hyacinth	Pretreated water hyacinth
Lignin, wt %	23.8 ± 1.5	8.9 ± 0.6
Cellulose, wt %	29.4 ± 1.8	53.3 ± 2.1
Hemicellulose, wt %	24.6 ± 2.2	22.7 ± 1.2
Ultimate analysis, wt % (dry basis)		
Carbon	54.4	55.7
Hydrogen	6.5	6.8
Nitrogen	0.7	0.5
Sulphur	0.1	0.0
Oxygen (by difference)	38.3	37.0
Proximate analysis, wt % (dry basis)		
Fixed carbon, wt %	24.4 ± 1.7	27.3 ± 1.5
Volatile matter, wt %	58.1 ± 2.5	54.1 ± 2.6
Moisture content, wt %	10.9 ± 0.8	10.7 ± 0.4
Ash, wt %	6.6 ± 0.3	7.9 ± 0.3



Figure 2. SEM images of (a) zeolite, and (b) acid activated zeolite

At subcritical condition, the water dissociates into H_3O^+ and OH^- ions, and the presence of these excess ions indicates that at subcritical condition the water can act as an acid or base catalyst. The subcritical hydrolysis of the water hyacinth and the conversion of the

resulting sugars into levulinic acid were conducted either with or without acid-activated zeolite addition and the results are summarized in Table 2.

The presence of excess H_3O^+ and OH^- in subcritical condition make the water more acidic and reactive, therefore at subcritical condition the water has the ability to convert cellulose and hemicellulose into monomeric sugars. Without addition of acid-activated zeolite, the yield of monomeric sugars increased with the increased of reaction temperature (Table 2). By increasing temperature, the dielectric constant of water will decrease, and it increasing the ionization of water into H_3O^+ and OH^- . The hydroxonium (H_3O^+) which act as the proton in the solution subsequently attacks β -1,4-glycosidic bonds as the linking bonds of several monomeric D-glucose units in the long chain polymer of cellulose, and resulting C_6 sugars as the product, while for the hemicellulose it will produce C_5 sugars. With the presence of acid-activated zeolite in the mixture, the system became more acidic, more proton were available in the system (from hydroxonium and H^+ from the surface of catalyst), and the breakdown of linking bonds of both cellulose and hemicellulose also increased and leading to the increase of yield of C_5 and C_6 sugars.

Levulinic acid is a C_5 -chemical with a ketone and a carboxylic group in its structure. This intermediate also known as 4-oxopentanoic acid or γ -ketovaleric acid. During the process, the C_5 sugars were converted into furfural and the later was further degraded into formic acid and other insoluble products (Girisuta et al., 2013), while the C_6 sugars were first dehydrated to HMF (hydroxy-methyl furan) and then converted to levulinic acid. The conversions of C_5 and C_6 sugars into furfural, levulinic acid and other by products are endothermic processes, so the increase of reaction temperature also increases the rate of reaction and leading to the increase of the yield of products as indicated in Table 2. The conversion of HMF into levulinic acid has lower activation energy than the dehydration reaction of C_6 sugars into HMF, therefore as soon as the HMF formed it instantaneously converted to LA. As a result, the yield of HMF in the reaction mixture was always low as indicated in Table 2. At high temperature (above $200^\circ C$), most of the products were further dehydrated into humin, as indicated by much lower yield of all the products when the reaction temperature was increased to $220^\circ C$.

The hydrogenations of levulinic acid into gamma-valerolactone conducted at 160 to $220^\circ C$ in the presence of a mixture of catalyst Pt/TiO_2 and acid-activated zeolite. The pressure of the system kept constant at hydrogen pressure of 50 bars, and reaction time of 6 h. The conversion of levulinic acid into gamma-valerolactone usually occurs into two steps of reaction pathways: the first pathway is the dehydration of levulinic acid into angelica lactone and followed by the reduction of angelica lactone into gamma-valerolactone. The second pathway is the reduction of levulinic acid into 4-hydroxy-pentanoic acid and subsequent dehydration into gamma-valerolactone (Alonso et al., 2010).

The reaction temperature has strong influence on the catalytic activities of the catalyst mixture (Pt/TiO_2 and acid-activated zeolite) as seen in Table 3. The yield of gamma-

valerolactone increased from 77.2 to 158.6 mg/g dried water hyacinth when the temperature raised from 160 to 220°C as indicated in Table 3. The reaction of levulinic acid into gamma-valerolactone is an endothermic process, by increasing temperature; the available energy needed for the reaction also increase and promote faster reaction rate, leading to increase the conversion of levulinic acid into gamma-valerolactone. The formation of MTHF (methyltetrahydrofuran), 1,4-pentanediol and other unidentified compounds was also observed in the GC spectra which indicated that the reduction of gamma-valerolactone into 1,4-pentanediol and subsequently dehydrated into MTHF was also occurred during the process.

Table 3. Hydrogenation of levulinic acid into gamma-valerolactone in the presence of Pt/TiO₂ and acid activated zeolite

Temperature, °C	Conversion of levulinic acid, %	Yield of gamma-valerolactone, mg/gram dried water hyacinth
160	86.5	77.2
180	95.2	102.9
200	97.8	133.4
220	99.6	158.6

4. CONCLUSION

The subcritical hydrolysis of the water hyacinth and the conversion of the resulting sugars into levulinic acid in the presence of acid activated zeolite catalyst were studied. The maximum amount of levulinic acid was obtained at 200°C. The levulinic acid obtained in the subcritical water hydrolysis was used as the material for gamma-valerolactone preparation, and Pt/TiO₂ and acid activated zeolite were used as catalysts. Reaction temperature has strong influence on the conversion of levulinic acid to gamma-valerolactone.

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