

Comparison of Fractionated and Non-Fractionated Eucalyptus in Organic Solvent Subsequence Hydrolysis Reaction to Sugar Production

T. Klamrassamee, V. Champreda, W. Wiyaratn, and N. Laosiripojana

Abstract—Fractionation process of lignocellulosic biomass are a primary step for converting multi-structure biomass to biofuels and other industrial products in integrated biorefinery processes. This research was performed in order to study the effect homogeneous and heterogeneous acid promoter (H_2SO_4 and H_3PO_4 -activated carbon ($AC-H_3PO_4$) respectively) and subsequence hydrolysis reaction in the presence of solid acid catalyst to enhance the yield and purity of sugar production. Clean fractionation (CF), a single-step aqueous-organosolv fractionation and subsequence hydrolysis reaction, of eucalyptus wood chips was studied. The operating of fractionation process contained 16.7% w/v biomass in a ternary mixture of methyl isobutyl ketone:methanol:water (25:42:33) with 5% $AC-H_3PO_4$ and incubated at 180 °C for 60 min and subsequence hydrolysis reaction contained at 200 °C for 5 min. Under these conditions, it was found that the optimized conditions that maximize the yield of sugar production are the hydrolysis of fractionated eucalyptus in the presence of $AC-H_3PO_4$ at 200 °C for 5 min let to 10% (35 % of substrate) glucose yield. Importantly, the great benefits of fractionation prior to the hydrolysis are the achievement of high sugar yield and the capability to separate glucose and xylose in the final product.

Index Terms—Fractionation, homogeneous, heterogeneous, and subsequence.

I. INTRODUCTION

Bio-ethanol is typically produced from starch and sugar, which is called as first-generation bio-ethanol. It is noted that the first generation biofuel is referred to the fuels that mainly produced from food crops. Starch and/or sugar-based ethanol production has been aware for the rising in food prices as well as the potential food crisis in the near future. Currently, many researchers have been developing the technologies to produce second-generation biofuel, which is referred to the fuels that produced from non-food crops. One important resource for second-generation biofuel production is lignocellulosic biomass (or cellulosic biomass), which could be efficiently applied for bio-ethanol production (as called

lignocellulosic ethanol). Since biomass is a very abundant source, from which a wide variety of products can be generated, the best way to utilize its potential is through a biorefinery concept [1]. Alternative to the pretreatment process, the fractionation process is presented as a novel class of pretreatment, which aims not only to improve hydrolysis but also to isolate the core constituents of lignocellulosic biomass (i.e. cellulose, hemicelluloses, and lignin). Regarding the detail of fractionation process, the traditional toxic solvents are generally required to dissolve cellulose, hemicellulose and lignin; nevertheless, the current research and developments widely investigated the possible use of relative harsh process for biomass fractionation. One of the potential green technologies for lignocellulosic biomass fractionation is the use of proprietary solvent mixture, which is called organosolv technology. The first step of this technology is to treat biomass with a proprietary solvent mixture that dissolves the lignins and hemicellulose components. These lignins are high purity and low molecular weight [2], are practically free of sulfur and sodium, which gives low ash content [3]. This can be considered under the broad category of organosolv pulping. The cellulose fraction is produced as an undissolved solid. Clean cellulose is obtained by a wash/dry step. A second separation is then performed on the soluble material to isolate the lignin from the hemicellulose. The lignin fraction is isolated as a solid; the hemicellulose remains in solution. The fractionation steps, another promising procedure to increase the yield of ethanol production is to improve the hydrolysis process by maximizing the yield of sugar production [4], since it is the main reactant for ethanol production.

The main objectives of this research is investigated the fractionated and non-fractionated process (with and without solid acid catalyst) to isolate lignocellulosic biomass (i.e. cellulose, hemicelluloses, and lignin) and subsequence hydrolysis reaction for sugar production.

II. METHODOLOGY

A. Materials

Eucalyptus (*Eucalyptus grandis*) wood chips were obtained from a local pulp mill in Ratchaburi province, Thailand. The wood chip size was in the range of 1.5-2 cm × 1.5-2 cm with 0.25-0.5 cm thickness. The biomass was air-dried and used in the experiments without prior physical processing. Chemical compositions (% lignin, cellulose, hemicelluloses, and ash) were analyzed using the standard NREL method [5]. The starting material contained 45.2 wt% cellulose, 21.1 wt% hemicelluloses, 30.4 wt% lignin, and 3.3

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wt% other content. Analytical grade organic solvents and chemicals were purchased from major chemical suppliers i.e. Sigma-Aldrich, Merck, and Fluka.

B. Solid Acid Catalyst Preparation

The solid acid catalyst was prepared by mixing 10 g of activated carbon with 100 ml of concentrated acid (H_3PO_4) in a 4-neck round bottom flask. The reaction was heated to 230-250 °C under flow of nitrogen. A 1-L flask containing 300 g of activated carbon was connected to the reaction flask to adsorb acid vapor. Apparatus setup for catalyst preparation instrument (1: round bottom 4-neck flask, 2: nitrogen inlet, 3: thermometer, 4: connection tube, 5: vacuum pump, 6: flask-contained the activated carbon) as shown in Fig. 1. The nitrogen inlet flow was switched off when the reaction reached the desired temperature and the sample was further heated until the acid solution was completely evaporated. The obtained solid was repeatedly washed with boiling water until no pH change was observed in the filtrate, which was used as solid acid catalyst as described in Suganuma et al. 2010 [6].

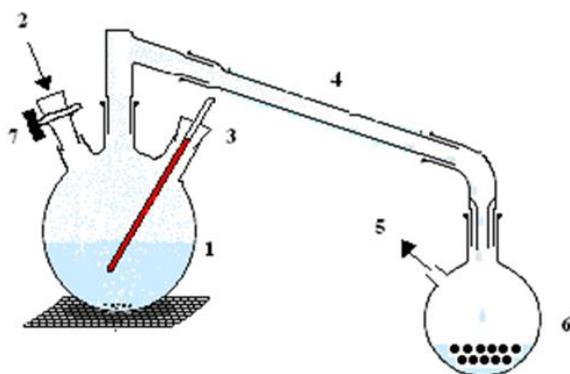


Fig. 1. Apparatus setup for catalyst preparation instrument (1: round bottom 4-neck flask, 2: nitrogen inlet, 3: thermometer, 4: connection tube, 5: vacuum pump, 6: flask- contained the activated carbon).

C. Product Analysis and Material Characterization

The liquid product analysis, after the hydrolysis reaction, the supernatant solution of overall product under this experiment is analyzed to find the type and total of sugars. Fermentable sugar profiles were analysed on a high performance liquid chromatography (SPD-M10A DAD, Shimadzu) equipped with a refractive index detector using an Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA) operating at 65 °C with 5mM H_2SO_4 as the mobile phase at a flow rate of 0.5 ml/min. The soluble product yield is reported as wt.% based on the amount of the starting biomass on a dried weight basis.

D. Fractionation Process

Eucalyptus wood chips were investigated to isolate (i.e. cellulose, hemicelluloses, and lignin) with single-phase mixture of methanol, water and a water-immiscible organic solvent (e.g., methyl isobutyl ketone (MIBK)) [7]. For the organosolv fractionation is carried out using a system consisting of stainless steel tube (1/2 inch O.D. and 13 cm. length), each capable of holding approximately 1 g of eucalyptus wood chips and 6 ml of single-phase mixture in the presence with and without the homogeneous (0.008 M of H_2SO_4 or 0.05 g of heterogeneous acid promoters (solid-state

Activated carbon- H_3PO_4) [8] as shown in Fig. 2. Then nitrogen is contained into reactor to load for purging and increasing the pressure of 20 bars in batch reactor before placing the reactor in furnace while the pressure inside of reactor is measured by gauge of nitrogen tank. Then the temperature controller is used to heat up and control the furnace; however, the thermocouple is placed into reactor as shown in Fig. 2 to measure reaction temperature in system. The reaction temperature and time are operated under 180 °C and 60 minutes respectively). After that, the reaction time is reached; the reaction was immediately stopped by quenching in water bath. After that, the cellulose fraction (This fraction is kept for subsequent hydrolysis reaction) is produced as an undissolved solid, which is washed with water, either directly or after rinsing the solids with methanol as a preliminary removal of the solvent mixture. The liquor is combined with rinsate and stored for separating of the lignin and hemicelluloses. Clean eucalyptus wood chips are obtained by a wash/dry step until pH 7 for keeping for subsequent hydrolysis reaction. A second separation is then performed on the soluble material to isolate the lignin from the hemicellulose. The amount of water is adjusted so that there is phase separation. The mixture is stirred and the layers allowed separating over 15-20 minutes. The organic solvent (black liquid) is dried at 105 °C and the aqueous phase includes hemicelluloses and any dissolved sugar.

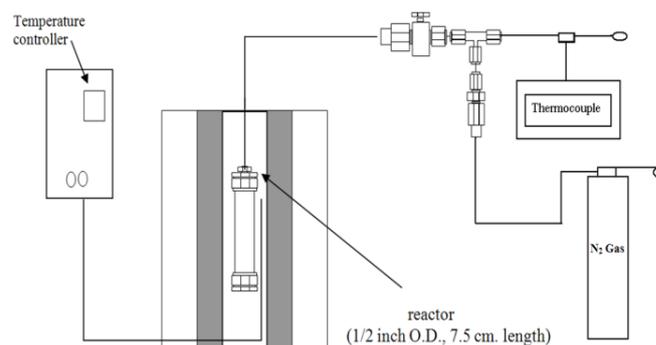


Fig. 2. The experimental setup apparatus for fractionation and hydrolysis process.

E. Hydrolysis Eucalyptus

The hydrolysis reaction will be carried out in batch reactor, which is made stainless steel tube (1/2 inch O.D. and 7.5 cm. length). For this experiment, is setup apparatus as shown in Fig. 2. When the experiment is started follow this; 1 g of eucalyptus wood chip is mixed with 6 cm^3 of water or dilute acid (0.008 M of H_2SO_4) with and without the presence of 0.05 g solid acid catalyst respectively. Then nitrogen is flowed into reactor to load for purging and increasing the pressure until 20 bar [8] in batch reactor before placing the reactor in furnace while the pressure inside of reactor is measured by gauge of nitrogen tank. Then the temperature controller is used to heat up and control the furnace; however, the thermocouple is placed into reactor as shown in Fig. 2 to measure reaction temperature in system. The reaction temperature is 200 °C while the reaction time is varied between 5-60 minutes). After that, the reaction time is reached; the reaction was immediately stopped by quenching in water bath. In case of hydrolysis reaction by solid acid catalyst, it will be separated between solid and liquid by

centrifuge about 5-10 minutes.

F. Procedure for Integration of Fractionation and Subsequent Hydrolysis Reaction with Solid Acid Catalyst in HCW

After the fractionation process is achieved, then is separated follow as cellulose, hemicelluloses and lignin. The solid phase (cellulose phase) will be bought to test in hydrolysis reaction in HCW. From the reaction, the products will be analyzed to determine the yield.

III. RESULT AND DISCUSSION

Eucalyptus (with the percentages of cellulose, hemicelluloses and lignin of 45:21:30) was used as the lignocellulosic biomass in the present work. For this work, the experimental results are divided into 2 main sections: (1) hydrolysis of eucalyptus chip (without fractionation), and (2) hydrolysis of fractionated eucalyptus. It is noted that two types of catalysts i.e. solid-state AC-H₃PO₄ and liquid-state H₂SO₄ catalysts were applied in the study. The main products from the hydrolysis of eucalyptus are sugars (i.e. glucose, and xylose); whereas by-product (i.e. organic acid, furfural and HMF) can also be formed via the further dehydration of sugars particularly at high reaction temperatures and longer time [9]. For this work, the total sugar yield produced was analyzed by HPLC method.

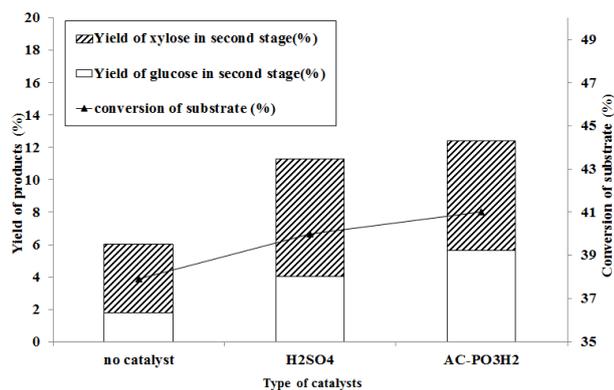


Fig. 3. The activity of solid acid catalysts compare to commercial catalyst via hydrolysis reaction.

A. Hydrolysis of Eucalyptus Chip (without Fractionation)

The hydrolysis of eucalyptus chip with and without the presence of catalyst was studied by using the certain hydrolysis condition i.e. eucalyptus wood chip of 1 g, water amount of 6 ml, reaction temperature at 200 °C, reaction time of 5 minutes, pressure at 20 bar, in the presence of 0.05 g of solid catalyst or presence of 0.008 M of H₂SO₄ according to the report from the literature. As shown in Fig. 3, it was observed that in the presence of AC-H₃PO₄ (activated carbon phosphonation), the yields of sugars are higher than the reaction without catalyst and the reaction catalyzed by H₂SO₄. For the homogeneous catalyst (H₂SO₄), although the highest conversion of eucalyptus can be obtained, the yield of sugars formation was significantly lower than the reaction presence of solid acid catalysts. This could be due to the too strong acid condition by applying H₂SO₄ as catalyst, from which the sugar can be further converted to other unwanted by-products i.e. organic acids. These results are good agreement with the report from Sasaki *et al.*, 2008 [9] and Karimi *et al.*, 2006

[10]. Hence, this highlights the benefit of presence of AC-H₃PO₄ for promoting the hydrolysis of eucalyptus under HCW system.

As the next step, the effect of reaction time was studied by various time from 5 to 60 min, which other operating conditions were kept constant (i.e. using 1 g eucalyptus wood chips in the presence of 0.05 g AC-H₃PO₄ (activated carbon phosphonation) and without catalyst of 6 ml DI water at the reaction pressure of 20 bar, and reaction temperature of 200 °C. The effect of reaction time on the yields of liquid product and eucalyptus conversion are shown in Fig. 4.

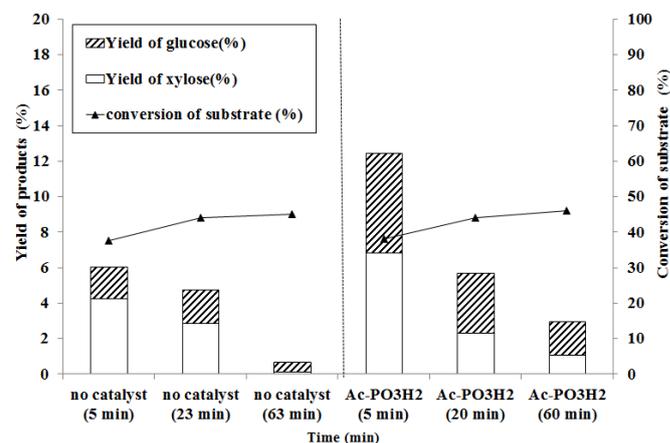


Fig. 4. Effect of reaction time on the product yield and eucalyptus conversion via hydrolysis reaction.

It was observed that the yield of sugars (with and without solid catalyst) decreased rapidly with increasing the reaction time until at 60 min (at longer reaction time). Theoretically, at longer reaction time, the formation of by-product (i.e. organic acid, HMF and furfural) could be formed due to the occurring of dehydration reaction [10]. As shown in Fig. 4, the hydrolysis reactions additional the solid catalyst can be achieve the highest sugar yield (xylose yield of 6.8%, and glucose yield of 5.6%). For the conversion of eucalyptus with and without solid catalyst are almost same. It is possible that the lignocelluloses biomass can be hydrolyzed (without catalyst) in to two main products (monosaccharide and oligosaccharide). Therefore, in case of hydrolysis reaction with solid catalyst (AC-H₃PO₄) promoted to hydrolyze oligosaccharide into monosaccharide. Hence, this experiment was summarized from all studies that the optimized condition for lignocellulosic biomass hydrolysis in the presence solid acid catalyst is at 200 °C for 5 min, from which the highest sugar yield (xylose yield of 6.8%, and glucose yield of 5.6%) can be achieved.

B. Hydrolysis of Fractionated Eucalyptus Chip

In this section, the hydrolysis of fractionated eucalyptus was performed under several conditions (i.e. reaction temperature, and reaction time) in the presence of AC-H₃PO₄. Firstly, the testing was performed over three groups of samples including (i) hydrolysis of non-fractionated eucalyptus without catalyst and in the presences of H₂SO₄ and AC-H₃PO₄, (ii) hydrolysis of fractionated eucalyptus without catalyst and in the presences of H₂SO₄ and AC-H₃PO₄; and (iii) integration of fractionation (with H₂SO₄ or AC-H₃PO₄) and hydrolysis reaction (without catalyst). As shown in Fig. 5, it was observed that first group of sample can achieve the mixture of glucose and xylose in the liquid

product, from which higher xylose yield than glucose yield was observed. For the second group of sample, the integration of fractionation and hydrolysis of eucalyptus in the presences of H_2SO_4 and $AC-H_3PO_4$ promoted the higher sugar yield with higher glucose proportion in the product. By integrating the fractionation with hydrolysis, high proportion of xylose yield can be achieved from the fractionation step (as called first stage in Fig. 5). Then, from the hydrolysis process (as called second stage in Fig. 5), the glucose yield of 10% (35 % of substrate) and xylose yield of 3.88% (19% of substrate) can be achieved. For this study, it highlights the great benefit of fractionation prior to the hydrolysis in terms of higher sugar yield achievement and the capability to separate glucose and xylose in the final product. In case of third group, it can be seen that integration of fractionation (with H_2SO_4 or $AC-H_3PO_4$) and hydrolysis reaction (without catalyst) can be obtained lower sugar yield in second stage than second group (with H_2SO_4 or $AC-H_3PO_4$). Therefore, it is clear that the presences of solid catalyst ($AC-H_3PO_4$) or liquid catalyst (H_2SO_4) are required for both fractionation and hydrolysis processes.

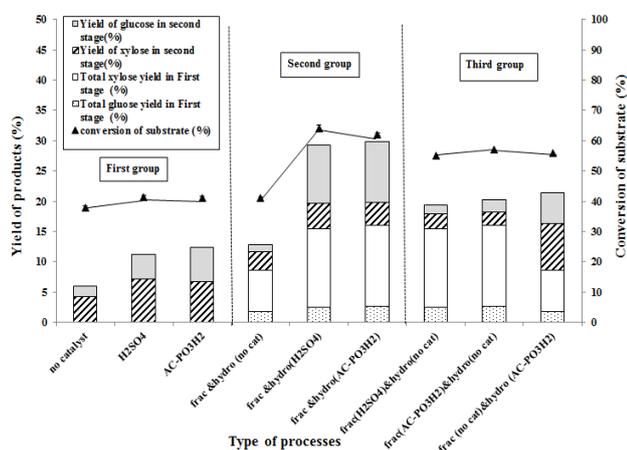


Fig. 5. Compare the hydrolysis reaction (with and without fractionation) under various conditions on the product yield and eucalyptus conversion.

IV. CONCLUSION

This research is to enhance the procedures for lignocellulose fractionation and conversion to sugar via the hydrolysis for further transform to several value-added products. The main focus of this work is to study the fractionation of lignocellulose by organosolv (with or without solid acid promoters) approaches, from which expects to achieve separate products with high purity. Another approach of this work is to prepare the super solid acid catalyst for using in hydrolysis reaction under HCW condition with an aim to obtain maximum yield of sugar

production. From these studies, the suitable conditions for integration of fractionation and subsequent hydrolysis will be determined for further developing to commercial scale in the future.

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