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Selective conversion of cassava mash to glucose using solid acid catalysts by sequential solid state mixed-milling reaction and thermo-hydrolysis

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ABSTRACT

Solid acid catalysts have been recently studied in starch thermo-hydrolysis owing to their high catalytic activity, recyclability, ease to separate and environmental advantages. However, the solid state reaction of effective catalyst and starch molecules requires specific interaction between active sites in catalyst and α,1-4 glycosidic bonds in starch. Therefore, in this study catalyst mixed-milling was conducted prior to thermal hydrolysis to enhance glucose production efficiency. The results showed that catalyst mixed-milling process (24 h) followed by thermo-hydrolysis at 140 °C for 6 h using HA-L-SO_3H gave highest starch conversion of 93.72% corresponding to 37.45% glucose yield and 83% selectivity. From the kinetic study, the rate constant of cassava mash-to-oligomers conversion (k_1) using catalyst mixed-milling was 1.77 times higher than ball-milling without adding catalyst. This indicated that mixed-milling solid state reaction with effective catalyst significantly provided complete cassava mash conversion and enhanced selectivity as well as rate of starch depolymerization reaction.

1. Introduction

Cassava is one of the most plentiful carbohydrate resources suitable for biofuel production in Asia Pacific region, especially in Thailand. Apart from its high availability, it is cheap and has well established supply chain and logistic management for industrialization [1]. Typical mature cassava roots are composed of two main parts, peel and parenchyma. Peel consists mostly of lignocellulose while parenchyma contains high amount of starch component and small amount of cellulose known as fibers. Both parts of cassava usually consist of glucose repeating units connected through α-1,4 and β-1,4 glycosidic linkages for starch and cellulose, respectively. Thus, cassava roots are considered to be inexhaustible raw material for sustainable production of chemicals and fuels via sugar platform [2]. To produce ethanol from cassava root, liquefaction and saccharification were used prior to fermentation process. Overall process efficiency of ethanol production from cassava could be enhanced by several approaches e.g. shorten the process duration, reduce energy utilization, chemical costs, and reduce wastewater treatment cost, etc. Although mineral acids and enzyme are most commonly used catalysts for the hydrolysis reaction of polysaccharides but mineral acid catalytic reaction possess a series of problems such as reactor corrosion, wastewater treatment, and poor recyclability. Enzyme catalytic reaction although achieves high selectivity but low process reliability as the cost of enzyme depends solely on companies having genetic engineering know-how [3]. Apart from that, low process efficiency was obtained as long reaction time for more than two days is needed for starch liquefaction and saccharification [4]. To solve the mentioned situations, a recent development of starch hydrolysis catalyzed by heterogeneous catalysts has been widely investigated. Lately, carbonaceous solid acid catalysts have been studied in starch hydrolysis process owing to their high catalytic activities, recyclability, ease to separate and economic impact [5,6]. For the development of heterogeneous catalyst for starch hydrolysis, Kumar and coworkers reported the conversion of starch to glucose using activated carbon-supported heteropoly acid (HSiW/C) at 150 °C for 4 h. The use of HSiW/C was found effective to hydrolyze starch with 94 wt % glucose conversion [7]. Namchot and

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colleagues also found that lignin catalyst synthesized by sulfonation in fuming sulfuric acid for hydrolysis of cassava starch achieved 96.5% total reducing sugar (TRS) yield at 140 °C for only 3 h [5]. In addition, Hermiati and colleagues used microwave irradiation for 5 min at high temperature (200–220 °C) in the presence of activated carbon to obtain 73.91% glucose yield from tapioca flour [8]. Therefore, heterogeneous acidic catalysts play an important role on catalytic starch hydrolysis.

However, the solid-state reaction between heterogeneous catalyst containing high amount of sulfonic acid groups in the chemical structure and starch molecules requires specific interaction between active sites in catalyst and either α,1-4 or α,1-6 glycosidic bonds in amylose and amylopectin. To increase the contact efficiency in solid-state reaction, milling process may be necessary. Yabushita and coworkers [9] reported the results of the effective mechanical treatment namely mixed-milling process by using cellulose and catalyst (K26) milled together with alumina balls. Besides, mixed-milling process also gave a good result of glucose yield higher than individual-milled cellulose. As the mixed-milling pretreatment and subsequent dilute hydrochloric acid hydrolysis, 98.0% cellulose conversion was achieved at 180 °C for 20 min.

From the literature survey as mentioned above, synthesis of solid acid catalysts by sulfonation technique using sulfuric acid was well known for starch hydrolysis. A little was done on catalyst synthesis using hydrochloric acid impregnation in which chlorine atoms may form ionic bonds with carbon in starch or carbon within catalyst structure and facilitate to enhanced reactivity of the synthesized catalyst [7]. Therefore, this research aimed to study the effect of different methods namely hydrochloric acid dipping, carbonization and sulfonation, and various precursors for synthesis of carbon support namely microcrystalline cellulose and lignin. Synthesized catalysts were then used to hydrolyze cassava mash from which the hydrolysate can be subsequently utilized as raw material for biofuels and building block chemicals production via sugar platform.

In addition, it has been reported that beating of biomass or mechanical pretreatment significantly increased bioconversion both anaerobic digestion and enzymatic hydrolysis [10–12]. Milling is another mechanical pretreatment method to reduce particle size and leads to an increased specific surface area accessible for microorganism or enzyme. It is postulated that milling results in reduction of reaction time and increase product yields from the reaction. The energy requirement is a limitation of this kind of pretreatment [13,14]. However, milling is a promising process to facilitate the solid-state reaction between solid acid catalyst and solid substrate. Therefore, in this study mechanical treatment was used to enhance the possible contact between substrate and effective synthesized catalyst that led to an increased catalytic conversion [10]. The effect of different mechanical treatment methods namely ball-milling without catalyst and mixed-milling of substrate and catalyst were investigated in pre-hydrolysis step of cassava mash prior to thermo-hydrolysis step in glucose production for biorefinery process. Kinetic models from experimental studies were proposed to predict and to compare the effect of mechanical treatment methods on glucose and oligomers production rate from different mixing methods.

2. Material and methods

Sweet-type fresh cassava roots (*Manihot esculenta* Crantz, Five minutes variety) were harvested at 18 months from a field in Nakorn Ratchasima Province, Thailand. Fresh roots were chopped, ground to small pieces, and sun-dried for 2–3 days. Prior to use, substrate was milled, sieved to a desired particle size (+50/-200 mesh), oven-dried to the moisture content less than 6 wt% and stored in a desiccator.

The study of the effect of synthesized solid acid catalysts on cassava root hydrolysis started from the screening study of active catalyst on cassava mash thermo-hydrolysis in a 50-mL hydrothermal reactor. Subsequently, milling process was introduced as an initial pretreatment step prior to thermo-hydrolysis of cassava mash. The synthesized solid acid catalyst was added in the milling process to enhance the reactivity of catalyst through solid state reaction so call mixed-milling while the control called ball milling was used when cassava mash was milled without adding solid acid catalyst. The schematic diagram of the sequential solid state mixed-milling reaction and thermo-hydrolysis of cassava root was shown in Fig. 1.

2.1. Chemical reagents

Chemicals used in the study included microcrystalline cellulose powder (20 μm in particle size, Merck), lignin (Alkali lignin, low sulfonate content, Sigma-Aldrich), standard D (+)-Glucose monohydrate (Sigma-Aldrich), D (+)-Xylose (Merck), maltose monohydrate (Merck), maltotriose (98% purity, Alfa-Aesar) and dextrin hydrate (Daejung). Concentrated sulfuric acid (98% H_2SO_4) was purchased from RCI Labscan Co., Ltd. Hydrochloric acid (36% HCl) was purchased from Ajax Finechem. Standard formic acid (98-100%) and acetic acid (Gracial, 100%) were purchased from Merck. Cassava root and cassava starch were contributed from Corn products (Thailand) Co., Ltd.

2.2. Compositional analysis of substrates

Composition of cassava root such as starch, protein, fiber and ash contents were determined. The chemical composition fiber of substrates were analyzed by Goering and Van (1970) [15] from which Neutral Detergent Fiber (NDF), Acid Detergent Fiber (ADF) and Acid Detergent Lignin (ADL) were analyzed. The contents of cellulose, hemicelluloses and lignin (%wt) were calculated by using eqs. (1)–(3), respectively.

$$\text{Hemicellulose} = \%\text{NDF} - \%\text{ADF} \tag{1}$$

$$\text{Cellulose} = \%\text{ADF} - \%\text{ADL} \tag{2}$$

$$\text{Lignin} = \%\text{ADL} - \%\text{Ash} \tag{3}$$

The starch content in cassava mash was determined by AOAC standard method (1990) using dilute hydrochloric acid digestion followed by colorimetric analysis. The quantity of residual starch content in pulp taken for fiber analysis was obtained by subtracting the fiber content from the total insoluble carbohydrate [16]. To measure protein content in cassava root and starch, the reaction of extracted solution from starch analysis with Bradford reagent was carried out. Amount of protein content was calculated from the absorbant at 595 nm when bovine serum albumin was standard [17].

2.3. Synthesis of catalysts

Four types of carbonaceous solid acid catalysts were synthesized using carbonization (C) and sulfonation ($-SO_3H$) techniques. Effect of hydrochloric acid (HA) dipping on hydrolysis yields and glucose selectivity of cassava mash hydrolysis reaction was studied. The name of synthesized catalysts were coded as shown in Table 1.

For the synthesis of catalysts type I ($HA-XC-SO_3H$), the catalysts were synthesized starting when cellulose (C) or lignin (L) was