

Direct preparation of butyl levulinate by a single solvolysis process of cellulose

Yukako Hishikawa · Mami Yamaguchi ·
Satoshi Kubo · Tatsuhiko Yamada

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Introduction

The Great East Japan Earthquake and the subsequent nuclear accident have triggered debates on the energy system of Japan. Renewable energies such as solar power, wind power and biomass are anticipated to be reliable domestic energy sources. Among these renewable energies, liquid fuels such as bioethanol and biodiesel produced from biomass are expected to be major alternative transportation fuels. There has been considerable research conducted on the conversion of cellulose into bioethanol [1–3], but none on converting cellulose directly into biodiesel. Biodiesel mainly consists of fatty acid esters derived from oilseed plants such as oil palm and vegetables [4–6]. For the purpose of producing cellulosic biodiesel, cellulose needs to be converted into organic acids that can be transformed into liquid ester compounds. In the organic acids, levulinic acid can be produced from cellulose, and has the potential to be converted to liquid ester compounds of levulinates

(levulinic acid esters). This study focuses on the single stage production of levulinic acid esters using cellulosic biomass as the starting material. Some levulinic acid mono-alcohol esters derived from cellulosic biomass could be used as bio-based liquid fuels since those esters have physical properties that resemble those of diesel fuel. Therefore, we named those levulinic acid esters “bio-levulinates”. Butyl levulinate was selected as the first trial for the production of bio-levulinate, considering its potential properties and practicality to function as a diesel fuel or fuel additives.

Levulinic acid has been produced through acid-catalyzed hydrolysis of sugars, including polysaccharides such as cellulose. Hydrolysis comprises the major chemical processes in which depolymerization of cellulose into glucose, transformation of formed glucose into 5-hydroxymethylfurfural (HMF) and cleavage of HMF by splitting off formic acid lead to formation of levulinic acid [7]. It should be noted that condensation reaction of HMF would prevent the production of levulinic acid, which suggests that each reaction step needs to be precisely controlled to obtain high yields of levulinic acid. Following this concept, Fitzpatrick [8] invented a processing technique pursuing a high yield of levulinic acid by combining two types of reactors sequentially, which enables strict control of hydrolysis.

Concerning levulinic acid esters, the authors' previous report [9, 10] revealed that the acid-catalyzed solvolysis of cellulose using alcohols as reaction media leads to formation of levulinic acid esters through a similar reaction mechanism as occurring during acid-catalyzed hydrolysis. Since the solvolysis condition could be controlled by selecting reaction media, the process of levulinic acid esters production could be more precisely controlled. In this paper, we demonstrated a high yield of butyl levulinate

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Y. Hishikawa · S. Kubo · T. Yamada (✉)
Forestry and Forest Products Research Institute (FFPRI),
1 Matsunosato, Tsukuba 305-8687, Japan
e-mail: yamadat@affrc.go.jp

M. Yamaguchi
Paper Technology Center, Ehime Institute of Industrial
Technology, 127 Mendori-cho, Shikokuchuo 799-0113, Japan

using 1-butanol (1-BuOH) by the single step process of acid-catalyzed solvolysis of cellulose under atmospheric pressure.

Materials and methods

Materials

Cellulose powder (100–200 mesh, ADVANTEC) was dried in an oven at 105 °C and kept in a desiccator at room temperature before use. All other chemicals used were extra pure grade reagents in accordance with the Japanese Industrial Standard and used without further purification.

Acid-catalyzed solvolysis of cellulose

The acid-catalyzed solvolysis of cellulose was performed in a glass flask equipped with a magnetic stirrer and a reflux condenser using a thermo block heater (Personal Organic Synthesizer, EYELA). Cellulose powder weighing 0.28 g was added to 28 g of the mixture of 1-BuOH (boiling point: 117 °C) and 97 % sulfuric acid (H_2SO_4) in the glass flask. The charge ratio of 1-BuOH and H_2SO_4 was 80/20 or 70/30 (w/w). Following stirring for 1 h at room temperature, the glass flask was put into the block heater preheated to 130 °C with stirring. After a predetermined duration, the glass flask was then immersed in cold water to quench the reaction.

Measurement of residue content

The content in the glass flask was separated with a G4 glass filter to obtain a residue and filtrate. The residue was rinsed well, first with 1-BuOH and then distilled water, followed by drying in a desiccator at room temperature under reduced pressure. The completely dried residue was then weighed using an electric balance.

Butyl levulinate analysis

The toluene/1-BuOH internal standard solution (1 ml) was added to the filtrate contained in a 50-ml volume measuring flask, whereupon the solution in the measuring flask was diluted to the mark with 1-BuOH. A portion (2.5 ml) of the solution in the measuring flask was placed in a 50-ml volume sample bottle, to which 20 ml of distilled water was added. The contents of the bottle were stirred vigorously using a vortex mixer (VORTEX-GENIE2, Scientific Industries, Inc.) and allowed to stand for 30 min. Normal hexane (10 ml) was added, whereupon the contents were again stirred vigorously using the vortex mixer and allowed to stand for 1 h. The hexane layer in the bottle was then

transformed to a test tube with a cap, to which anhydrous sodium sulfate was added to dry the hexane layer overnight at room temperature. The butyl levulinate in the hexane layer was analyzed by gas chromatography using a GC-2010 unit (SHIMADZU). Quantification was performed by external calibration curves based on peak areas of pure standards. The production rate of butyl levulinate was obtained by dividing the amount of butyl levulinate produced by the amount of butyl levulinate theoretically produced, as estimated from the original amount of cellulose powder (0.28 g).

Results and discussion

Figure 1 shows the decreasing insoluble residue content with increasing solvolysis time. As the reaction proceeded, the residue content decreased to reach less than 1 % in 18 h in a reaction media of 80/20 (1-BuOH/ H_2SO_4 , w/w) and in 5 h for a media of 70/30 (w/w). This data suggested that the conversion of cellulose into soluble compound proceeded steadily without producing condensed insoluble residue. Figure 2 shows the production rate of butyl levulinate as a function of the reaction time. The produced butyl levulinate was monitored by gas chromatography and the production rate was obtained using the theoretical yield of butyl levulinate calculated from the starting amount of cellulose as stated before. The yield of butyl levulinate using the reaction media of 80/20 (w/w) increased gradually and reached over 60 % of the theoretical yield. Concerning the reaction media of 70/30 (w/w), the yield of butyl levulinate increased over 60 % in 5 h and then decreased gradually.

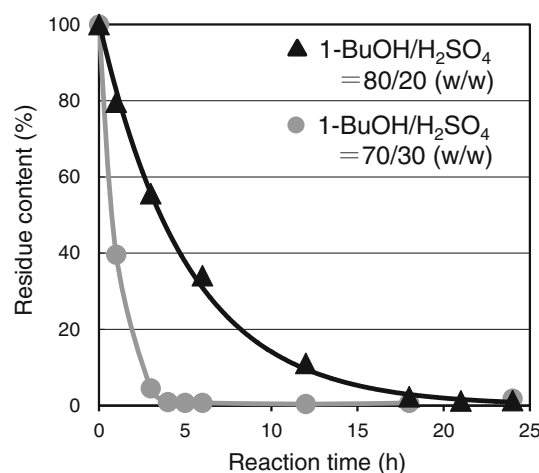


Fig. 1 The residue content (%) as a function of the reaction time [*triangle* the reaction media of 80/20 (1-BuOH/ H_2SO_4 , w/w); *circle* the reaction media of 70/30 (1-BuOH/ H_2SO_4 , w/w)]

The single reaction process we used consisted of solely refluxing the reaction media under atmospheric pressure. Nevertheless, our single-step process enabled a production rate of 60 %, which is relatively high when compared to the yield of levulinic acid (about 40 %) in the acid-catalyzed hydrolysis of mono sugars such as glucose using the single process [11]. From the result of the high yield of butyl levulinate in the single-step solvolysis, it seems that solvolysis is advantageous to control the process of the levulinate formation from cellulose. The first step of the levulinate formation from cellulose is depolymerization of cellulose chains to form glucosides (Fig. 3). The following two factors affect the first step of the reaction: one is the accessibility of the reaction media to cellulose chains and the other is the acidity of the reaction media.

The higher degree of accessibility of the reaction media to cellulose enhanced the swelling of the crystalline regions of cellulose and the depolymerization of cellulose chains. However, since the accessibility of 1-BuOH to cellulose

was not very high, the speed of the degradation was slow as shown in this paper (Fig. 1). On the other hand, we previously reported that when using glycols such as ethylene glycol (EG) and polyethylene glycol (PEG) as reaction media, the rate of cellulose degradation was not so slow [9, 10]. In these glycol series, the reaction using average molecular weight of 400 (PEG400) showed to be the fastest reaction [12] due to the higher accessibility of PEG to cellulose. The higher accessibility might be influenced by the hydrogen bond between the ether oxygen of PEG and the hydroxyl group at the C6 position of glucose ring of cellulose [13, 14]. Concerning acidity, the reaction will depend on the dielectric constant value of the reaction media used for the acid–base reaction in non-aqueous solutions. Generally, the higher dielectric constant value of the media gives the higher acidity and allows materials to be dissolved more efficiently. Our previous report revealed that ethylene carbonate (EC) dramatically improved the rate of acid-catalyzed solvolysis of cellulose due to its high dielectric constant value [15]. The reaction on PEG and EC systems showed that they were effective reaction media for the depolymerization of cellulose chain, however, the yield of levulinate was low (less than 15 %) [9, 15].

On the other hand, in the solvolysis system using 1-BuOH shown in this paper, the yield of the levulinates was high (exceeding 60 %). As shown in Fig. 3, the second step of the mechanism involves the decomposition of glucoside to produce HMF derivative as an intermediate. The produced HMF derivatives were liable for condensation to insoluble residue in the reaction media. To avoid this condensation, HMF derivatives should be provided slowly to the reaction media. At the same time, the reaction media should provide optimum condition to convert HMF derivatives to levulinates. Result from the solvolysis using 1-BuOH suggested that the lower cellulose accessibility of 1-BuOH resulted in slower supply of glucosides and HMF derivatives to the reaction media. The reaction media of

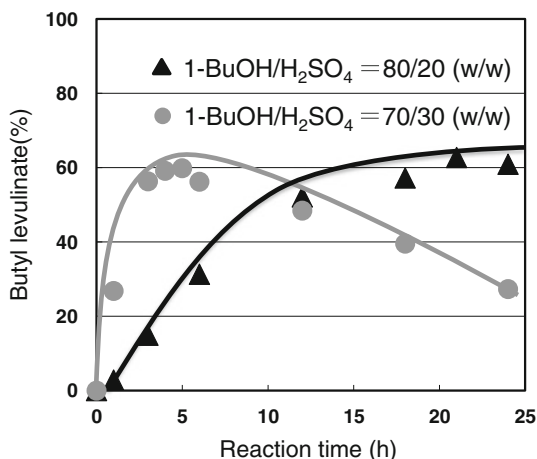
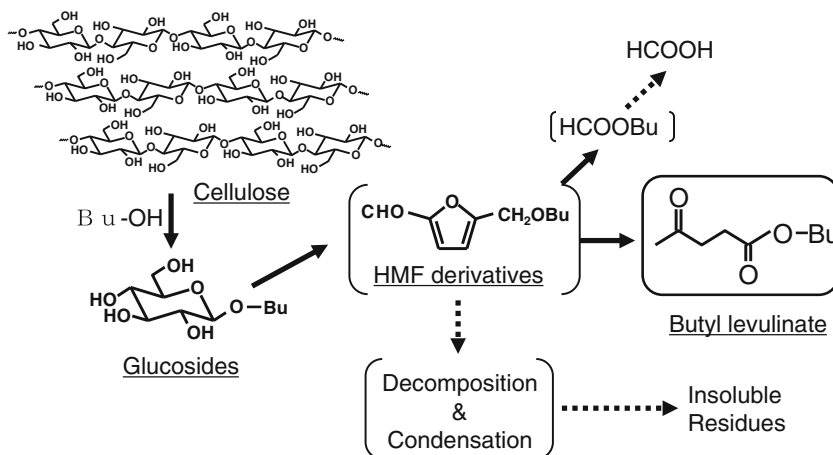


Fig. 2 The production rate of butyl levulinate as a function of the reaction time [triangle the reaction media of 80/20 (1-BuOH/H₂SO₄, w/w); circle the reaction media of 70/30 (1-BuOH/H₂SO₄, w/w)]

Fig. 3 A reaction mechanism of cellulose degradation to lead levulinates in the acid-catalyzed solvolysis process



strongly acidified 1-BuOH converted the HMF derivatives to butyl levulinate smoothly. Consequently, a high yield of butyl levulinate exceeding 60 % was obtained in the single reaction process under atmospheric pressure. Garves [16] reported an acid-catalyzed degradation of cellulose with alcohols such as methanol, ethanol and propanol, applied at a temperature of 180–200 °C under the pressurized condition in an autoclave, gave a yield of levulinate about 10–45 %. On the other hand, the results in this paper showed that a much higher yield of levulinate (exceeding 60 %) could be achieved using a more simple reaction process of just refluxing in 1-BuOH under atmospheric pressure. The results in this paper suggested that our simple solvolysis process using alcoholic reaction media that have a high boiling point and a low accessibility to cellulose has high potential for conversion of cellulose into bio-levulinate.

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