Direct Production of Alkyl Levulinates from Cellulosic Biomass by a Single-Step Acidic Solvolysis System at Ambient Atmospheric Pressure

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A simple method was invented to achieve a high yield of cellulosic biomass-derived alkyl levulinates, which have the potential to be alternative fuel additives. Alkyl levulinates, such as butyl-, pentyl-, and hexyl levulinates, were produced using single-step acid-catalyzed solvolysis of cellulosic biomass without the use of elevated pressure. Reactions were performed by refluxing alcohols such as 1-butanol, 1-pentanol, and 1-hexanol at their boiling points of 117, 138, and 157 °C, respectively, with sulfuric acid at ambient pressure. After 1 hour of the reaction, the cellulosic biomass was converted into an alcohol-soluble compound, and a high yield of alkyl levulinates was achieved. Although the process involved simple treatment under atmospheric pressure, the alkyl levulinate yield was quite high: 60 to 80% based on the hexose content of the cellulosic biomass. The factors influencing the reaction, such as the accessibility to cellulose and acidity of the reaction media, could be controlled appropriately in this solvolysis system.

Keywords: Alkyl levulinate; Solvolysis; Cellulosic biodiesel; Papermaking sludge

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INTRODUCTION

Biomass-derived liquid fuels, such as bioethanol and biodiesel, are expected to become major alternative transportation fuels. The use of cellulose, the most abundant organic compound on earth, has been examined in many trials of cellulosic bioethanol production (Chandrakant and Bisaria 1998). For the production of biodiesel, typical commercial biodiesel has been mainly comprised of fatty acid esters derived from oilseed plants, such as oil palm and vegetables (Demirbas 2005; 2007; 2009). In the case of cellulosic biodiesel and its related chemicals production, some cellulose degradation techniques have been applied, such as pyrolysis (Bridgwater 2012) and gasification with Fischer-Tropsch synthesis (Kumar *et al*. 2009). One idea for synthesizing cellulosic biodiesel would be to convert cellulose into organic acids that could then be transformed into liquid ester compounds. In cellulose-derived organic acids, levulinic acid would be a candidate to produce cellulosic biodiesel (Windom *et al.* 2011). Levulinic acid can be produced from sugars, such as cellulose-derived glucose, and it can potentially be converted into liquid ester compounds of levulinates (levulinic acid esters). Some levulinic acid mono alcohol esters (alkyl levulinate) could be used as biodiesel, since they have suitable physical properties to serve as diesel fuels. These cellulosic-derived alkyl levulinates were named "Bio-levulinate" (Hishikawa *et al*. 2013).

Ethyl levulinate has been the main focus of this study as a potential additive for diesel and other fuels. Windom *et al.* (2011) reported the potential of using ethyl levulinate as a diesel fuel oxygenate additive. Joshi *et al.* (2011) reported the enhanced cold-flow properties of diesel fuel by adding ethyl levulinate. To produce ethyl levulinate, Chang *et al.* (2012) reported the production of ethyl levulinate from wheat straw in ethanol reaction media with an acid catalyst and using a pressurized reactor.

Levulinic acid has been produced through acid-catalyzed hydrolysis of hexoses, including polysaccharides such as cellulose. This hydrolysis comprises the major chemical processes of the depolymerization of cellulose into glucose, transformation of the formed glucose into 5-hydroxylmethylfurfural (HMF), and cleavage of HMF by splitting off formic acid, which leads to the formation of levulinic acid. It should be noted that the 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. Accordingly, Fitzpatrick (1997) invented a processing technique to obtain a high yield of levulinic acid by combining two types of reactors sequentially, which enables strict hydrolysis control.

Concerning levulinic acid esters, previous reports by the authors (Yamada *et al.* 1999, 2001) revealed that the acid-catalyzed solvolysis of cellulose using alcohols as reaction media led to the formation of levulinic acid esters through a similar reaction mechanism as that of acid-catalyzed hydrolysis. Since the solvolysis condition could be controlled by selecting reaction media, levulinic acid ester production could be controlled more precisely than hydrolysis. Recently, we reported a unique system to provide a high yield of butyl levulinate *via* the single-step acid-catalyzed solvolysis of cellulose with a laboratory glass flask and without using any pressurized reactor (Hishikawa *et al.* 2013).

The present paper describes a solvolysis system for high-yield production of pentyl levulinate and hexyl levulinate, as well as butyl levulinate, from cellulosic biomass. Alkyl levulinates such as butyl- , pentyl-, and hexyl levulinates are promising candidates as diesel fuel and fuel additives. Cellulose powder, hardwood kraft pulp, softwood kraft pulp, and various kind of papermaking sludge were used as the starting materials to obtain cellulosic biomass.

EXPERIMENTAL

Materials

Cellulosic biomass such as cellulose powder (ADVANTEC Cellulose Powder A, ADVANTEC INC.), kraft pulps, and papermaking sludge were dried in an oven at 105 °C for 24 h and kept in a desiccator at room temperature before use. Softwood kraft pulp (NBKP), hardwood kraft pulp (LBKP), and 7 kinds of papermaking sludge (A-G) were provided by several papermaking companies in the industrial zone of Shikokuchuo Ehime, Japan. The chemical composition of the cellulosic biomass was determined by the alditol-acetates sugar analysis method (Blakeney *et al*. 1983). The ash content of the papermaking sludge was measured following the TAPPI standard method (TAPPI T 211). Elemental analysis of the inorganic compounds in the papermaking sludge was determined with energy-dispersive X-ray fluorescence spectrometers (Shimadzu EDX-800). All other chemicals used were extra-pure grade reagents in accordance with the Japanese Industrial Standard.

Acid-catalyzed Solvolysis System

The acid-catalyzed solvolysis of cellulosic biomass was performed in a 200 mL-volume glass flask equipped with a magnetic stirrer and reflux condenser. Cellulosic biomass, such as dried papermaking sludge weighing 0.28 g, was added to a 28 g of the reaction media of alcohols, such as 1-butanol, 1-pentanol, and 1-hexanol (boiling points: 117, 138, and 157 °C, respectively) with a 97% sulfuric acid in the glass flask. The percentage of sulfuric acid relative to the reaction media was 20 or 30 weight %. After stirring for 1 h at room temperature, the glass flask was placed into the oil bath preheated to about 10 °C above the boiling point of each reaction medium while stirring. After the preset reaction time (1 to 6 h), the glass flask was immersed in cold water to quench the reaction.

Measurement of the Residue Content

The content in the glass flask was separated with a fine glass filter (pore size: 160~250 μm) to obtain a residue and filtrate. The residue was rinsed well, first with the reaction media of alcohols and then distilled water and subsequently dried in a desiccator at room temperature under reduced pressure. The completely dried residue was then weighed to determine the residue content based on the weight of the starting cellulosic biomass.

Alkyl Levulinate Analysis

The alcohol-soluble filtrate was transferred to a 50 mL-volume measuring flask with 1 mL of the internal standard solution, whereupon the solution in the measuring flask was diluted to the mark with the reaction media of alcohols. The internal standards were 20 mg/mL of toluene/1-butanol solution, 10 mg/mL of biphenyl/1-pentanol solution, and 10 mg/mL of biphenyl/1-hexanol solution to analyze the butyl-, pentyl-, and hexyl levulinates, respectively. 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 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 one hour. The hexane layer in the bottle was then transferred to a test tube with a cap, to which anhydrous sodium sulfate was added to dry the hexane layer overnight at room temperature. The alkyl levulinates in the hexane layer were analyzed by gas chromatography using a GC-2010 unit (Shimadzu) with a non-polar capillary column (InertCap 1, GL Sciences, Inc.). Quantification was performed by the calibration lines based on peak areas of pure standards. The production rate of alkyl levulinates was obtained by dividing the amount of alkyl levulinate produced by the amount of alkyl levulinate that could theoretically be produced, as calculated from the original amount of hexose in the cellulosic biomass.

RESULTS AND DISCUSSION

Chemical Composition of the Starting Materials

Table 1 shows the sugar composition of cellulose powder (CELP), softwood kraft pulp (NBKP), hardwood kraft pulp (LBKP), and 7 kinds of papermaking sludge (A-G). The greater total hexose content in NBKP was attributable to the lower amount of xylose in softwood. Various sugar content totals were determined in the papermaking sludge. The ash content data of the papermaking sludge (A: 68, B: 6, C: 14, D: 60, E: 18, F: 17, and G: 9%) suggested that most of the papermaking sludge (Table 1) was composed of inorganic substances. Elemental analysis showed that papermaking sludges A and D had significant calcium content (Ca in A: 72 and D: 62%), while the other sludge had a high silicon content (Si in B: 73, C: 64, E, 65, F: 53, and G: 50%).

Table 1. Sugar Composition* of Cellulose Powder (CELP), Soft Wood Kraft Pulp (NBKP), Hard Wood Kraft Pulp (LBKP), and Seven Kinds of Papermaking Sludge (A-G)

	Glucan	Mannan	Galactan	Arabinan	Xylan	Other	Total hexose content**
CELP	98.6	0.0	0.0	0.0	0.0	1.4	98.6
NBKP	84.0	5.9	0.8	0.9	8.2	0.2	90.7
LBKP	78.4	0.6	0.0	0.1	19.2	1.7	79.1
Sludge A	11.6	0.9	0.0	0.2	1.5	85.7	12.6
Sludge B	63.7	3.5	0.1	0.3	8.9	23.5	67.3
Sludge C	50.3	1.2	0.1	0.2	11.1	37.1	51.6
Sludge D	17.5	0.3	0.0	0.1	3.0	79.1	17.8
Sludge E	51.4	1.9	0.5	0.2	10.9	35.0	53.8
Sludge F	49.0	1.6	0.2	0.3	8.9	40.0	50.8
Sludge G	48.4	0.5	0.0	0.2	14.9	36.1	48.9

* Weight percentage calculated from the data of mono sugar analysis by the alditol-acetate method.

**Total amount of glucan, mannan and galactan.

Levulinate Production from Cellulose

Figure 1 shows the levulinate yields based on theoretical production from cellulose powder and for butanol-, pentanol-, and hexanol solvolysis. Butyl-, pentyl-, and hexyl-levulinate were produced with reaction media of butanol, pentanol, and hexanol, respectively.

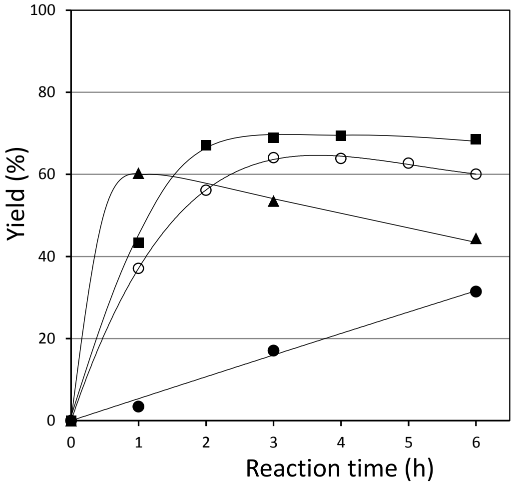

Fig. 1. Yield of levulinates production based on the theoretical production from cellulose powder on butanol solvolysis (circle), pentanol solvolysis (square), hexanol solvolysis (triangle) on the 20 % of sulfuric acid content (closed circles), and on the 30% of sulfuric acid content(open circles).

Since this simple solvolysis system features a reaction just by refluxing the reaction media under atmospheric pressure, the reaction temperature is set at the boiling point of the reaction media for 1-butanol, 1-pentanol and 1-hexanol (117, 138 and 157 °C, respectively). The production speed for butyl levulinate at a 20% rate of sulfuric acid was very slow due to its lower reaction temperature, hence a system of 30% sulfuric acid was applied. Interestingly, every solvolysis system showed considerable levulinate production, exceeding 60% of the theoretical yield. The optimal conditions were as follows: Butanol solvolysis- 3 h reaction with 30% sulfuric acid, pentanol solvolysis- 3 h reaction with 20% sulfuric acid, and hexanol solvolysis- 1 h reaction with 20% sulfuric acid. Under the optimal conditions above, the residue contents of solvolysis for the cellulose powder reached almost zero (Table 2).

Table 2. Residue Percentage of Cellulose Powder (CELP), Soft Wood Kraft Pulp (NBKP), Hard Wood Kraft Pulp (LBKP), and Seven Kinds of Papermaking Sludge (A-G) at the Optimum Reaction Conditions for High Yield Levulinates Production

	CELP	NBKP	LBKP	Paper making sludge						
				A	B	C	D	E	F	G
Butanol solvolysis*	0.1	0.1	0.1	83.9	4.7	29.4	88.3	36.1	40.7	26.7
Pentanol solvolysis**	0	0.9	0.2	104.3	6.4	28.5	88.4	38.0	43.0	28.1
Hexanol solvolysis***	0.3	0	0	103.2	10.8	32.2	85.2	36.8	45.4	29.1

* 3 hour of reaction with 30% of sulfuric acid. ** 3 hour of reaction with 20% of sulfuric acid.
*** 1 hour of reaction with 20% of sulfuric acid

Alkyl Levulinates from Cellulosic Biomass

Figure 2 shows the yield of butyl levulinate based on theoretical production levels and the butanol solvolysis of CELP, NBKP, LBKP, and 7 kinds of papermaking sludge (A-G) under the optimum butanol solvolysis condition that was determined for the solvolysis of cellulose powder (3 h reaction and 30% sulfuric acid). The produced butyl levulinate was monitored by gas chromatography, and the yield was obtained using the theoretical yield of butyl levulinate calculated from the starting amount of hexose. The data showed a relatively high yield of butyl levulinate, about 60 to 80%. The residue contents of the papermaking sludge from butanol solvolysis (Table 2) correlated with the amounts of other materials in Table 1, most of which were inorganic compounds.

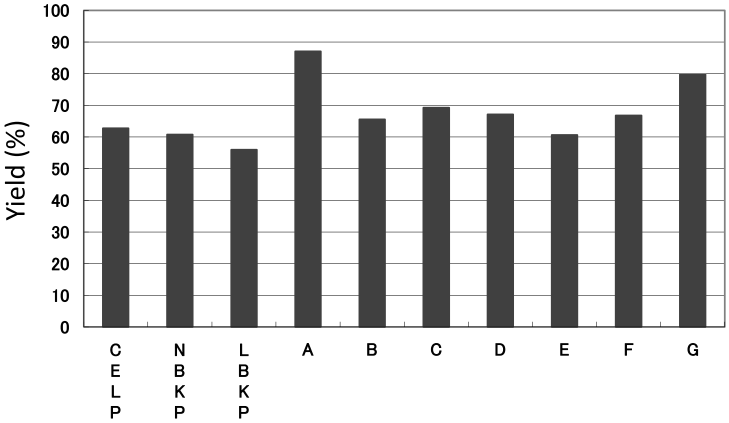

Fig. 2. Yield of butyl levulinate based on the theoretical production on the butanol solvolysis of cellulose powder (CELP), soft wood Kraft pulp (NBKP), hard wood Kraft pulp (LBKP), and 7 kinds of papermaking sludge (A-G)

Figure 3 shows the pentyl levulinate yield based on theoretical production and the pentanol solvolysis of CELP, NBKP, LBKP, and 7 kinds of papermaking sludge (A-G) under the optimum pentanol solvolysis condition that was determined for the solvolysis of cellulose powder (3 h reaction with 20% sulfuric acid). The data showed a relatively high yield of pentyl levulinate production at about 70 to 90%.

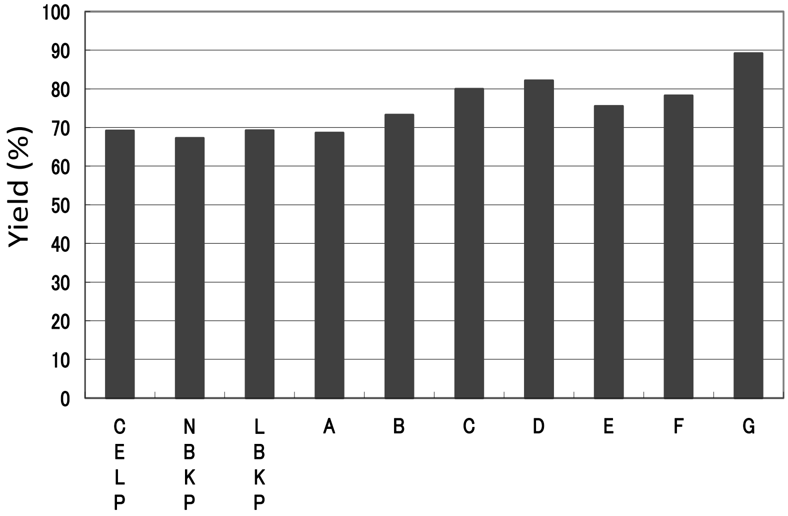

Fig. 3. Yield of pentyl levulinate based on the theoretical production on the pentanol solvolysis of cellulose powder (CELP), soft wood Kraft pulp (NBKP), hard wood kraft pulp (LBKP), and 7 kinds of papermaking sludge (A-G)

Figure 4 shows the yield of hexyl levulinate based on theoretical production and the hexanol solvolysis of CELP, NBKP, LBKP, and 7 kinds of papermaking sludge (A-G), under the optimum hexanol solvolysis condition that was determined for the solvolysis of cellulose powder (1 h reaction with 20% sulfuric acid). The data showed a high yield of hexyl levulinate production at 60 to 80%.

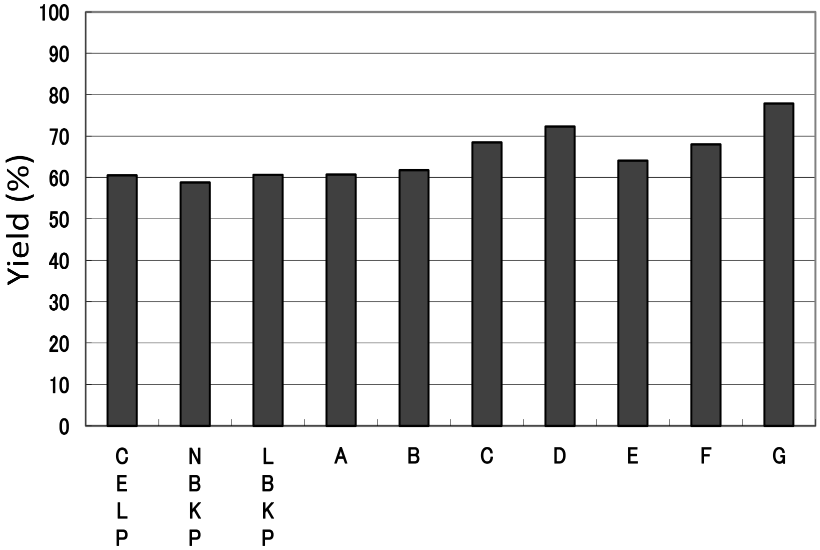

Fig. 4. Yield of hexyl levulinate based on the theoretical production on the hexanol solvolysis of cellulose powder (CELP), soft wood kraft pulp (NBKP), hard wood kraft pulp (LBKP), and 7 kinds of papermaking sludge (A-G)

Alkyl Levulinates and Their Potential

The single reaction process used in this work consisted solely of refluxing the reaction media at atmospheric pressure. Nevertheless, the single-step process enabled a yield exceeding 60%, which is relatively high compared to the yield of levulinic acid (about 40%) in the acid-catalyzed hydrolysis of monosugars, such as glucose, subjected to a similar single-step hydrolysis (Takahashi 1944). Based on the high yield of alkyl levulinate in this single-step solvolysis system, solvolysis seemed to facilitate control of the levulinate formation process from cellulose.

Figure 5 shows the alkyl levulinate production mechanism from cellulosic biomass, which is influenced by the following two factors: the accessibility of the reaction media to cellulose chains and the acidity of the reaction media.

The first step of the reaction is the depolymerization of cellulose chains to form glucosides and subsequent formation of HMF derivatives. The greater accessibility of the reaction media to cellulose enhances the swelling of the crystalline regions of cellulose and accelerates the depolymerization of cellulose chains to produce intermediates. However, higher accessibility will lead to a higher concentration of reactive intermediates in the media, which might accelerate the side reactions and thus lower the levulinate yields. In our previous report of acid-catalyzed solvolysis of cellulose using glycol-type reaction media, *e.g.*, ethylene glycol, polyethylene glycol, and ethylene carbonate which have high accessibility to cellulose, the degradation speed of cellulose was quite fast, but the levulinate yield was relatively low (under 15%) (Yamada 1999; 2001; 2007). On the other hand, in the solvolysis system of this paper, the yield of levulinates was high (exceeding 60%). Since the accessibility of butanol, pentanol, and hexanol to cellulose was relatively low, the speed of the degradation was slow, with the reactive intermediates slowly exposed to the reaction media.

As shown in Fig. 5, the second step of the mechanism involves the decomposition of glucoside to produce HMF derivatives as an intermediate. The produced HMF derivatives were liable to condense into insoluble residues in the reaction media. To avoid this, HMF derivatives should be exposed slowly to the reaction media. At the same time, the reaction media should provide an optimum acidified condition to convert HMF derivatives to levulinates. Solvolysis with less accessible reaction media to cellulose slowed the supply of glucosides and HMF derivatives to the reaction media, whereupon the reaction media of strongly acidified alcohols converted the intermediates to alkyl levulinate smoothly.

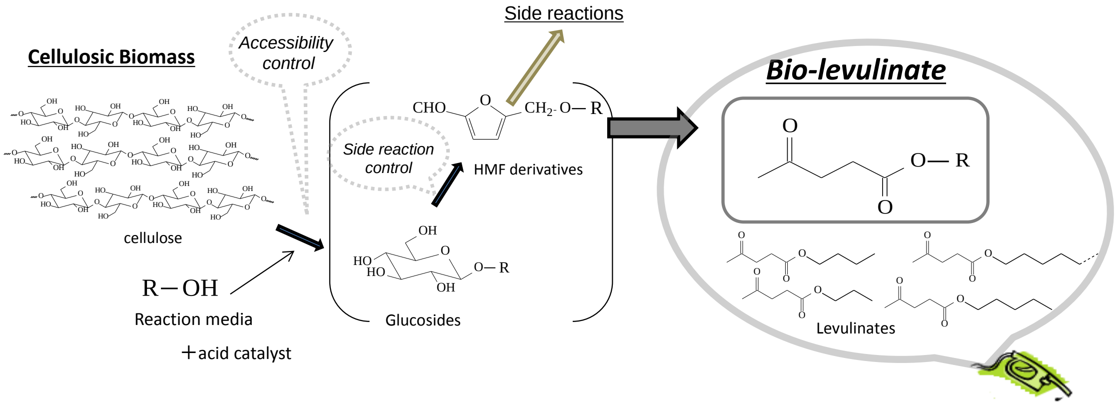

Fig. 5. A pathway to produce alkyl levulinates from cellulosic biomass

Garves (1988) reported on the acid-catalyzed degradation of cellulose with alcohols *e.g.*, methanol, ethanol, and propanol, applied at a temperature of 180 to 200 °C under a pressurized condition in an autoclave and giving a levulinate yield of about 10 to 45%. Conversely, the results in this paper showed that a far higher levulinate yield (exceeding 60%) was achievable using a simpler reaction process of refluxing in higher boiling-point alcohols *e.g.*, butanol, pentanol, and hexanol under atmospheric pressure. The results in this paper suggested that a simple solvolysis process, using alcoholic reaction media with a high boiling point and low accessibility to cellulose, has significant potential for converting cellulosics into useful alkyl levulinates.

CONCLUSIONS

1. A high production yield of alkyl levulinates was achieved *via* a simple acid-catalyzed solvolysis process and without using any pressurized reactors. Cellulosic waste, *e.g.*, papermaking sludge, was used as the starting material for levulinate production.
2. Yields of around 60 to 80% of butyl-, pentyl-, and hexyl levulinates were produced from the solvolysis reaction with butanol, pentanol, and hexanol, respectively, by reflux at their boiling point under atmospheric pressure. The results suggested that the solvolysis reaction was suited to controlling the process of levulinate formation from cellulosic biomass.

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REFERENCES CITED

Blakeney, A. B., Harris, P. J., Henry, R. J., and Stone, B.A. (1983). "A simple and rapid preparation of alditol acetates for monosaccharide analysis," *Carbohydrate Research* 113(2), 291-299. DOI: 10.1016/0008-6215(83)88244-5.

Bridgwater, A. V. (2012). "Review of fast pyrolysis of biomass and product upgrading," *Biomass & Bioenergy* 38, 68-94. DOI: 10.1016/j.biombioe.2011.01.048

Chandrakant, P., and Bisaria, V. S. (1998). "Simultaneous bioconversion of cellulose and hemicellulose to ethanol," *Critical Reviews in Biotechnology* 18(4), 295-331. DOI: 10.1080/0738-859891224185

Chang, C., Xu, G., and Jiang, X. (2012). "Production of ethyl levulinate by direct conversion of wheat straw in ethanol media," *Bioresource Technology* 121, 93-99. DOI: 10.1016/j.biortech.2012.06.105

Demirbas, A. (2005). "Biodiesel production from vegetable oils *via* catalytic and non-catalytic supercritical methanol transesterification methods," *Progress in Energy and Combustion Sci*. 31(5-6), 466-487. DOI: 10.1016/j.pecs.2005.09.001

Demirbas, A. (2007). "Importance of biodiesel as transportation fuel," *Energy Policy* 35(9), 4661-4670. DOI: 10.1016/j.enpol.2007.04.003

Demirbas, A. (2009). "Progress and recent trends in biodiesel fuels," *Energy Conversion and Management* 50(1), 14-34. DOI: 10.1016/j.enconman.2008.09.001

Fitzpatrick, S. W. (1997). "Production of levulinic acid from carbohydrate containing materials," U.S Patent 5608105

Garves, K. (1988). "Acid-catalyzed degradation of cellulose in alcohols," *J. Wood Chem. Tech.* 8(1), 121-134. DOI: 10.1080/02773818808070674

Hishikawa, Y., Yamaguchi, M., Kubo, S., and Yamada, T. (2013). "Direct preparation of butyl levulinate by a single solvolysis process of cellulose," *J. Wood Sci.* 59(2), 179-182. DOI: 10.1007/s10086-013-1324-8

Joshi, H., Moser, B. R., Toler, J., Smith, W. F., and Walker, T. (2011). "Ethyl levulinate: A potential bio-based diluent for biodiesel which improves cold flow properties," *Biomass and Bioenergy* 35(7), 3262-3266. DOI: 10.1016/j.biombioe.2011.04.020

Kumar, A., Jones, D. D., and Hanna, M. A. (2009). "Thermochemical biomass gasification: A review of the current status of the technology," *Energies* 2(3), 556-581. DOI: 10.3390/en20300556

Takahashi, T. (1944). "Degradation of carbohydrate by strong mineral acid (in Japanese)" *Nogeikagaku* 20,553-556.

TAPPI T211 (2002), "Ash in wood, pulp, paper, and paperboard: Combustion at 525 °C," TAPPI Press, Atlanta, Georgia.

Windom, B. C., Lovestead, T. M., Mascal, M., Nikitin, E. B., and Bruno T. J. (2011). "Advanced distillation curve analysis on ethyl levulinate as a diesel fuel oxygenate and a hybrid biodiesel fuel," *Energy & Fuels* 25(4), 1878-1890. DOI: 10.1021/ef200239x

Yamada, T., and Ono, H. (1999) "Rapid liquefaction of lignocellulosic waste by using ethylene carbonate," *Bioresource Technology* 70, 61-67. DOI: 10.1016/S0960-8524(99)00008-5

Yamada, T., and Ono, H. (2001). "Characterization of the products resulting from ethylene glycol liquefaction of cellulose," *J. Wood Sci.* 47 (6), 458-464. DOI: 10.1007/BF00767898

Yamada, T., Aratani, M., Kubo, S., and Ono, H. (2007). "Chemical analysis of the product in acid catalyzed solvolysis of cellulose using polyethylene glycol and ethylene carbonate" *J. Wood Sci.* 53(6), 487-493. DOI: 10.1007/s10086-007-0886-8

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