Research Article

Yuli Bai, Yi Liu, Fudong Bai, Qimei Sun, Lanpeng Li, Tong Zhang*

Conversion of furfuryl alcohol to ethyl levulinate in the presence of mesoporous aluminosilicate catalyst

Abstract: The one-pot acid-catalyzed the conversion of furfuryl alcohol (FA) to ethyl levulinate (EL) was investigated in the presence of mesoporous aluminosilicate (TUD-1) with a high surface area (up to 579 m$^2$ g$^{-1}$) and well-interconnected mesospheres synthesized via a solvothermal process and characterized using scanning electron microscope, transmission electron microscope, X-ray diffraction, $^{27}$Al-NMR, and $N_2$ sorption isotherm. The resulting solid acid catalyst was tested for the alcoholysis of FA with ethanol, affording 87.8% EL yield under the optimal reaction conditions of 120°C and 4 h. Moreover, the catalyst showed a good reusability with less loss of activity after a simple solvent washing and calcination procedure.

Keywords: mesoporous aluminosilicate, ethyl levulinate, furfuryl alcohol, solid acid catalyst

1 Introduction

The conversion of renewable biomass resources into non-petroleum derived fuels and chemicals is becoming increasingly attractive as a way to avoid intensification of global warming and to diversify energy sources [1–6]. Among the biomass carbohydrate-derived chemicals, alkyl levulinites have received particular attention due to their oxygenate fuel additive characteristics [7–9]. Ethyl levulinate (EL), especially, can not only be used up to 5 wt% as the diesel miscible biofuel but also has found various potential applications in flavoring and fragrance industry [10–14]. In general, EL is obtained by acid catalyzed esterification of levulonic acid with alcohol [15]. However, levulinic acid is a high cost raw material for this purpose. A number of techniques have been developed for the production of EL from a wide range of sources such as cellulose, saccharides, and furfuryl alcohol (FA). FA, one of the most important furan derivatives, is used as a model compound of biomass-derivatives and contains carbon–oxygen bonds both within and outside the furan ring and produced industrially via hydrogenation of furfural derived from the hydrolysis and dehydration of xylan contained in the lignocellosic biomass [16–19]. It has been proved that EL can be effectively obtained through ethanolysis of FA over acidic catalysts [20,21].

Earlier researchers used strong and corrosive homogeneous acids such as HCl and $H_2SO_4$ as effective catalysts for the alkyl levulinites production [22–24]. Currently, a series of efficient solid acid including acidic ion-exchange resins, sulfated oxides, supported heteropolyacids, and zeolites has been successfully developed and utilized [25–34]. Acidic ion-exchange resins are organic-solid acids, less corrosive, easier/safer to handle than liquid acids, whereas the regeneration and reuse of organic-solid acid catalysts in these systems may be seriously compromised by their limited thermal and chemical stabilities [35–40]. The sulfated oxides and supported heteropolyacid catalysts may sustain coke burn off, but the leaching problem of acid sites during the reaction restricts the application of the two kinds of catalysts. Of the studied catalysts, zeolites or zeotype materials are quite promising and have been widely used in the conversion of biomass to biofuels or high value-added chemicals due to their tunable acidity and three-dimensional porosity structure [41,42]. However, the transformation of relatively bulky substrates as FA may be hindered in a microporous structure for large size and volume; hence, the use of mesoporous aluminosilicate (TUD-1) may be preferable for this reaction. Neves et al. [23] have reported the studies for the aluminosilicates and the sulfonic acid resin Amberlyst™-15 on the basis of EL yields, the undesirable formation, and catalyst stability.
Herein, based on the previous research, TUD-1 was explored as a solid acid catalyst for the alcoholysis of FA to form EL with the optimum reaction conditions, different treatment processes for recycling efficiency, and the activity of the catalyst using different alcohols as the starting material.

2 Materials and methods

2.1 Materials

Tetraethoxysilane (98%), aluminium isopropoxide (98.5%), ethanol (99.5%), isopropanol (99.9%), tetraethylammonium hydroxide (25 wt% in water), triethanolamine (99.0%), methanol (99.9%), 1-propanol (99.0%), 1-butanol (99.8%), and FA (98%) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China), and used as received. All the deionized water used in the experiments was prepared in the laboratory.

2.2 Synthesis of TUD-1

Aluminium isopropoxide (1.4 g) was first dissolved in a mixture of isopropanol (10 g) and water (23 mL). Under vigorous stirring, tetraethoxysilane (35 g), triethanolamine (25 g), and tetraethylammonium hydroxide (31 g) were successively added. The sol obtained was stirred at room temperature for 24 h and dried at 98°C for 12 h, followed by the hydrothermal treatment in a Teflon-lined stainless steel autoclave at 180°C for 8 h. The solid products were separated from the system by filtration and washed with water for three times. Finally, the solid products were dried at 100°C for 12 h and calcined at 600°C in air for 6 h.

2.3 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected on a D/MAX-2500 diffractometer (Rigaku Corporation, Japan) with Cu target (40 kV, 100 mA). Observation of the morphology of the samples was conducted using a JEM 7500 F (JEOL Ltd, Japan) field-emission scanning electron microscope and a JEM 2100 (JEOL Ltd, Japan) transmission electron microscope (TEM), respectively. 27Al-NMR spectroscopy was measured using a AVANCE III HD 500 nuclear magnetic resonance spectrometer from Burker (Germany). Nitrogen sorption isotherms were measured using an ASAP 2420 (Micromeritics, USA) analyzer at −196°C. The acid properties were measured by Nexus-Thermo Nicolet FTIR (Thermo Nicolet Corporation, USA) instrument using pyridine as the basic probe molecule.

2.4 Catalytic performance and quantification of the products

To evaluate the catalytic performance of TUD-1, the conversion of FA into EL was carried out using these catalysts. The batch catalytic reactions were carried out in a 50 mL Hastelloy high pressure reactor under N2 atmosphere. A certain amount of TUD-1, FA, and ethanol were added to the reactor. Then, the reaction mixture was allowed to proceed under stirring and at 80–140°C for a certain time. Samples were taken from the reactor, filtered, and analyzed in the aqueous phase by Agilent GC 7890A gas chromatograph (Agilent Technologies Inc., USA). For recycling experiments, the used catalyst was separated using centrifugation followed by thoroughly washing with ethanol, drying, and calcination at 600°C for 2 h before reuse [43]. The recovered catalyst was weighed, and a reaction was run using amounts of solvent and reactant proportional to the recovered catalyst amount to maintain the same substrate/catalyst ratio and substrate concentration.

The quantification of the concentrations of the reagents and products was based on the external standard calibration method. After separating the solid catalyst, the liquid phase of the reaction mixture was analyzed by GC with a HP-INNOWax polyethylene glyco column (The carrier gas was helium at a constant flow rate of 3.0 mL min$^{-1}$; the primary oven temperature was programmed from 120 to 220°C at a heating rate of 15°C min$^{-1}$). The FA conversion ($C_{FA}$) and the yield of EL ($Y_{EL}$) product were calculated according to equations (1) and (2). The $C_e$, $C_T$, and $C_{EL}$ were initial concentration of FA, concentration of FA at time $T$, and concentration of EL at time $T$.

$$C_{FA} = (C_i - C_T)/C_i \times 100\%$$

$$Y_{EL} = C_{EL}/C_i \times 100\%$$
morphology of the catalyst (Figure 1a), which confirmed the worm-like mesopore structure of the material. Figure 1b shows the SEM image of TUD-1. It can be observed that the TUD-1 is composed of large amounts of nanoparticles and exhibits an irregular shape [43].

The powder XRD pattern of TUD-1 shows a very broad peak centered around 23° (Figure 2a), indicating the amorphous nature of the mesoporous structure material [44–46]. In addition, crystalline alumina or other phases cannot be detected in the pattern. The nature of Al was investigated using \(^{27}\)Al-NMR spectroscopy (Figure 2b). The spectrum exhibits a strong resonance at \(\delta = 53.2\) ppm, which can be attributed to tetrahedrally coordinated aluminium species. A high-field signal at \(\delta = 0\) ppm is attributed to hexacoordinate aluminium species [43].

The textural properties of TUD-1 materials were studied by nitrogen gas porosimetry measurement. From the result shown in Figure 3, the pattern clearly displayed a typical type IV isotherm with a type H2 hysteresis loop, and the capillary condensation steps occur at the relative pressure \(P/P_0 = 0.6–0.7\), which indicates that the tested samples possess mesoporosity with a disordered mesoporous material with an interconnected pore network [45,47–51]. Additional data, derived from the isotherm, illustrate that TUD-1 has a large BET specific surface area of 579 m\(^2\) g\(^{-1}\), a total pore volume of 1.03 cm\(^3\) g\(^{-1}\) and an average pore diameter of 6.5 nm. Infrared spectroscopy of adsorbed pyridine were observed to distinguish the Brønsted (around 1,545 cm\(^{-1}\)) and Lewis acid sites (around 1,450 cm\(^{-1}\)) of the catalysts in Figure 4. The amount of acid sites (L + B) of TUD-1 was 0.15 mmol g\(^{-1}\) which was quantified at 150°C.

### 3.2 Catalytic tests

TUD-1 was used as a solid acid catalyst to prepare EL from FA. The effects of catalyst dosage, solvent amount, reaction time and reaction temperature on the conversion of FA to EL, and the reusability of solid acid catalyst were tested.
Initially, the catalyst dosage and solvent amount factors were investigated as shown in Table 1. From Entry 1–4, it can be found that when the catalyst dosage was increased from 0.5 to 1.2 g, the EL yield was changed from 76.1 to 88.3%. Notably, the EL yield of 88.3% was little higher than that of using the similar catalyst and reacting for 24 h reported elsewhere \cite{23}. The EL yields were almost the same for the catalyst dosages of 1.0 and 1.2 g and complete FA conversions were obtained for all the cases. This may be because beyond a certain dosage, the number of catalyst sites was greater than that actually required by reactant molecules. Therefore, further investigation was conducted at 1.0 g catalyst dosage.

Moreover, the amount of ethanol used in EL synthesis is also important. As FA easily polymerizes to form oligomeric products under the condition of acids at high temperature, the alcoholysis of FA is always carried out in a large excess of alcohols to minimize this undesired reaction. As shown in Table 1, the maximum EL yield was obtained from 20 mL of ethanol.

### 3.2.2 Effect of reaction temperature and reaction time

The effect of temperature on EL yield was studied in the range of 80–140°C (Figure 5a). It can be seen that the EL yield was enhanced significantly from 13.1 to 87.8% as the reaction temperature was gradually elevated from 80 to 120°C, suggesting a kinetically controlled reaction. However, further increasing the reaction temperature to 140°C led to a slight decrease in EL yield, which may be attributed to the increase of some oligomeric by-products at a higher temperature.

To study the kinetic aspects of reaction, the alcoholysis experiments were performed within reaction time ranging from 1 to 6 h. Figure 5b showed the yield of EL within 2 h increased greatly from 0 to 77.3% and remained high value of 86–88% in the latter 4 hours. The results demonstrated that the optimal reaction time for the alcoholysis of FA was 4 h.

### 3.3 Catalyst reusability studies

In contrast to traditional homogeneous catalysts such as liquid acid catalysts, heterogeneous catalysts show advantages in the separation and reusability. The reusability of TUD-1 catalyst was tested by conducting seven
consecutive 4 h batches of the FA reaction including the fresh one. In the first four runs, the catalyst was recovered by centrifugation after the completion of the reaction, washed by ethanol, and dried in an oven to reuse in the next run of the reaction. In the latter three runs, calcination was added after the catalyst drying procedure. As evident from Figure 6, the alcoholysis efficiency decreased slightly in the first four runs. The EL yield decreased from 87.8% of fresh catalyst to 77.0% of reused catalyst for the third time. The results may be partly due to catalyst surface passivation by organic by-products such as oligomeric products or humins from the FA polymerization. Organic by-products become increasingly difficult to remove by simple solvent washing. As the introduction of calcination procedure to the catalyst treatment process, the regenerated catalyst could nicely regain its activity, similar to that of the fresh catalyst, indicating its good stability and reusability.

To investigate the versatility of TUD-1 catalyst, we have replaced the ethanol with different alcohols such as methanol, propanol, and butanol to get various levulinate esters. It was observed that for all these alcohols, the yields of levulinate ester were high, whereas as we go from methanol to butanol, the carbon chain length increases, simultaneously the yield of ester and conversion of FA decreases due to the reduction of reaction activity caused by the steric factor (Figure 7). For butanol, we have got 65% ester product with 86% conversion under optimized reaction conditions.

4 Conclusion

A novel kind of TUD-1 was successfully synthesized and turned out to be an active catalyst for the reaction of FA with ethanol to obtain EL. A high EL yield of 87.8% under the optimal conditions (N2 atmosphere, 1.0 g catalyst, 120°C, 300 rpm, and 4 h) was obtained. In addition, the solid acid catalyst shows a good recyclability and could be reused for seven consecutive runs without obvious activity loss. As FA can be produced from renewable
resources, this method is environmentally benign and economical for the conversion of biomass-based derivate into fine chemicals. More applications of this solid acid catalyst in sustainable chemistry should be researched in the future.

Acknowledgements: This study was supported by Key Laboratory of Sinopec and Dalian Research Institute of Petroleum and Petrochemicals. Thanks for the help in catalyst characterization.

Funding information: This research was funded by special Key Laboratory of Sinopec, grant number KL19009.

Author contributions: Yuli Bai – conceptualization; Tong Zhang – conceptualization; Yi Liu – data curation; Fudong Bai – formal analysis; Qimei Sun – investigation; and Lanpeng Li – resources.

Conflict of interest: The authors declare no conflict of interest.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: All data, models, and code generated used during the study appear in the submitted article.

References

[1] Bozell J, Petersen G. Technology development for the production of biobased products from bioenergy carbohydrates-the US Department of Energy’s “Top 10” revisited. Green Chem. 2010;12(4):539–54.
[2] Corma A, Iborra S, Velty A. Chemical routes for the transformation of biomass into chemicals. Chem R. 2007;107(6):2411–502.
[3] Chheda JN, Román-Leshkov Y, Dumesic JA. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides. Green Chem. 2007;9(4):342–50.
[4] Oh YH, Eom IY, Joo JC, Yu JH, Song BK, Lee SH, et al. Recent advances in development of biomass pretreatment technologies used in bioenergy for the production of bio-based fuels, chemicals and polymers. Korean J Chem Eng. 2015;32(10):1945–59.
[5] Khemthong P, Yimsukan C, Narkkun T, Srifa A, Witoon T, Pongchaiphol S, et al. Advances in catalytic production of value-added biochemicals and biofuels via furfural platform derived lignocellulosic biomass. Biomass Bioenergy. 2021;148:106033.
[6] Bertrut PF. Biomass valorization for fuel and chemicals production – a review. Int J Chem React Eng. 2008;6(1):1–49.
[7] Climent MJ, Corma A, Iborra S. Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Cheminform. 2014;16(2):516–47.
[8] Démolis A, Essayem N, Rababoul F. Synthesis and applications of alkyl levulinites. ACS Sus Chem Eng. 2014;2(6):1338–52.
[9] Zhang Z, Dong K, Zhao ZK. Efficient conversion of furfuryl alcohol into alkyl levulinites catalyzed by an organic-inorganic hybrid solid acid catalyst. Chem Sus Chem. 2011;4(1):112–8.
[10] Pierre G. Conversion of biomass to selected chemical products. Chem Soc Rev. 2012;41:1538–58.
[11] Budarin VL, Clark JH, Henschen J, Farmer TJ, Macquarrie DJ, Mascal M, et al. Processed lignin as byproduct of the generation of 5-(chloromethyl)furfural from biomass: a promising new mesoporous material. Chem Sus Chem. 2015;8(24):4172–9.
[12] Christensen E, Williams A, Paul S, Burton S, McCormick RL. Properties and performance of levulinate esters as diesel blend components. Energy Fuels. 2011;25(11):5422–8.
[13] Mei C, Dumesic JA. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ-valerolactone over metal oxide catalysts. Chem Commun. 2011;47(44):12233–5.
[14] Serrano-Ruiz JC, Dong W, Dumesic JA. Catalytic upgrading of levulinic acid to 5-nonanone. Green Chem. 2010;12(4):574–7.
[15] Serrano-Ruiz JC, Dumesic JA. Catalytic routes for the conversion of biomass into liquid hydrocarbon transportation fuels. Energy Environ Sci. 2011;4(1):83–99.
[16] Moreau C, Durand R, Peyron D, Duhamel J, Rivalier P. Selective preparation of furfural from xylose over microporous solid acid catalysts. Ind Crop Product. 1998;7(2):95–9.
[17] Bond JQ, Alonso DM, Wang D, West RM, Dumesic JA. Integrated catalytic conversion of γ-valerolactone to liquid alkenes for transportation fuels. Science. 2010;327(5969):1110–4.
[18] Horváth IT, Mehdi H, Fábos V, Boda L, Miksa LT. γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals. Green Chem. 2008;10(2):338–42.
[19] Dam H, Kieboom A, Bekkum HV. The conversion of fructose and glucose in acidic media: formation of hydroxymethylfurfural. Starch—Strke. 1986;38(3):95–101.
[20] Gobara HM, Aboutaleb WA, Hashem KM, Hassan SA, Henein SA. A novel route for synthesis of alpha-Fe2O3-CeO2 nanocomposites for ethanol conversion. J Mater Sci. 2017;52:550–68.
[21] González Maldonado GM, Assary RS, Dumesic JA, Curtiss LA. Acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in liquid ethanol. Energy Environ Sci. 2012;5(10):8990–7.
[22] An S, Song D, Lu B, Yang X, Guo HY. Morphology tailoring of sulfonyl acid functionalized organosilica nanohybrids for the synthesis of biomass-derived alkyl levulinates. Chem Eur J. 2015;21(30):10786–98.
[23] Neves P, Lima S, Pillinger M, Rocha SM, Rocha J, Valente AA. Conversion of furfuryl alcohol to ethyl levulinate using porous aluminosilicate acid catalysts. Catal Today. 2013;218:76–84.
[24] Lake MA, Burton SW, Fuller WC, Sasser R, Lindstrom ME, Wheless JT, et al. Production of levulinic acid and levulinate esters from biomass; 2010. US20100312006.
[25] Islam MM, Bhunia S, Molla RA, Bhaumik A, Islam SM. Organic solid acid catalyst for efficient conversion of furfuryl alcohol to biofuels. Chem Sel. 2016;1(19):6079–85.

[26] Fernandes DR, Rocha AS, Mai EF, Mota CJA, Teixeira da Silva V. Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts. Appl Catal A. 2012;425–426:199–204.

[27] Lange JP, van de Graaf WD, Haan RJ. Conversion of furfuryl alcohol into ethyl levulinate using solid acid catalysts. Chem Sus Chem. 2009;2(5):437–41.

[28] Akiyama G, Matsuda R, Sato H, Takata M, Kitagawa S. Cellulose hydrolysis by a new porous coordination polymer decorated with sulfonic acid functional groups. Adv Mater. 2011;23(29):3294–7.

[29] Yamada T, Otsubo K, Makiura R, Kitagawa H. Designers coordination polymers: dimensional crossover architectures and proton conduction. Chem Soc Rev. 2013;42(16):6655–69.

[30] Colin SC, Paul AC. The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. Chem Rev. 2003;103(3):663–702.

[31] Tu J, Ding M, Zhang Q, Zhang Y, Wang C, Wang T, et al. Design of carbon-encapsulated Fe3O4 nanocatalyst with enhanced performance for Fischer–Tropsch synthesis. ChemCatChem. 2015;7(15):2323–7.

[32] Dutta A, Patra AK, Uyama H, Bhaumik A. Template-free synthesis of a porous organic-inorganic hybrid tin(IV) phosphonate and its high catalytic activity for esterification of free fatty acids. ACS Appl Mater Interfaces. 2013;5(20):9913–7.

[33] Su Y, Wang Y, Li X, Li X, Wang R. Imidazolium-based porous organic polymers: anion exchange-driven rapid capture and luminescent probe of Cr2O72−. ACS Appl Mater Interfaces. 2016;8(29):18904–11.

[34] Zhao G, Sun Y, Zeng X, Lin L. Efficient conversion of furfuryl alcohol into ethyl levulinate in an extremely low sulfuric acid catalyst system. J Bioprocess Eng Biorefinery. 2013;3(2):182–7.

[35] Zuo Y, Zhang Y, Fu Y. Catalytic conversion of cellulose into levulinic acid by a sulfonated chloromethyl polystyrene solid acid catalyst. ChemCatChem. 2014;6(3):753–7.

[36] Tiwari MS, Dicks JS, Keogh J, Ranade VV, Manyar HG. Direct conversion of furfuryl alcohol to butyl levulinate using tin exchanged tungstophosphoric acid catalysts. Mole Catal. 2020;488:110974.

[37] Bhat NS, Mal SS, Dutta S. Recent advances in the preparation of levulinic esters from biomass-derived furanic and levulinic chemical platforms using heteropoly acid (HPA) catalysts. Mole Catal. 2021;S05:111484.

[38] Neves P, Russo PA, Fernandes A, Antunes MM, Farinha J, Pillinger M, et al. A mesoporous zirconia-based mixed oxides as versatile acid catalysts for producing bio-additives from furfuryl alcohol and glycerol. Appl Catal A. 2014;487:148–57.

[39] Zhao G, Liu M, Xia X, Li L, Xu B. Conversion of furfuryl alcohol into ethyl levulinate over glucose-derived carbon-based solid acid in ethanol. Molecules. 2019;24(10):1881.

[40] Simons C, Hanefeld U, Arends NE, Sheldon RA, Maschmeyer T. Noncovalent anchoring of asymmetric hydrogenation catalysts on a new mesoporous aluminosilicate: application and solvent effects. Chemistry. 2010;10(22):5829–35.

[41] Zhou J, Hua Z, Shi J, He Q, Guo L, Ruan M. Synthesis of a hierarchical micro/mesoporous structure by steam-assisted post-crystallization. Chem Eur J. 2009;15(47):12949–54.

[42] Anand R, Maheswari R, Hanefeld U. Catalytic properties of the novel mesoporous aluminosilicate ALITUD-1. J Catal. 2006;242(1):82–91.

[43] Ramli N, Amin N. Fe/HY zeolite as an effective catalyst for levulinic acid production from glucose: characterization and catalytic performance. Appl Catal B Environ. 2015;163:487–98.

[44] Xu Y, Zheng X, Yu H, Hu X. Hydrothermal liquefaction of Chlorella pyrenoidosa for bio-oil production over Ce/HZSM-5. Bioresour Tech. 2014;156:1–5.

[45] Jansen JC, Shan Z, Maschmeyer T, Marchese L, Zhou W, Pull N. A new templating method for three-dimensional mesopore networks. Chem Commun. 2001;8:713–4.

[46] Telalov S, Hanefeld U. Noncovalent immobilization of chiral cyclopropanation catalysts on mesoporous TUD-1: comparison of liquid-phase and gas-phase ion-exchange. Appl Catal A. 2010;372(2):217–23.

[47] Bliin JL, Léonard A, Su BL. Well-ordered spherical mesoporous materials CMI-1 synthesized via an assembly of deacetoxyethylene cetyl ether and TMOS. Chem Mater. 2001;13(10):3542–53.

[48] Russell SD, Douglas SB, Todd JL. A new adsorption model for analyzing gassolid equilibria in porous materials. J Phys Chem B. 1996;100(5):1718–24.

[49] Webster CE, Drago RS, Zerner MC. Molecular dimensions for adsorbents. JACS. 1998;120(22):5509–16.

[50] Lima S, Antunes MM, Fernandes A, Pillinger M, Ribeiro MF, Valente AA. Catalytic cyclodehydration of xylose to furfural in the presence of zeolite H-Beta and a micro/mesoporous Beta/TUD-1 composite material. Appl Catal A. 2010;388(1–2):141–8.

[51] Antunes MM, Lima S, Fernandes A, Pillinger M, Ribeiro MF, Valente AA. Aqueous phase dehydration of xylose to furfural in the presence of MCM-22 and ITQ-2 solid acid catalysts. Appl Catal A. 2012;417–418:243–52.

[52] Peng L, Li H, Xi L, Chen K, Chen H. Facile and efficient conversion of furfuryl alcohol into n-butyl levulinate catalyzed by extremely low acid concentration. Bioresour. 2014;9(3):3825–34.