

Esterification of Levulinic Acid to *n*-Butyl Levulinate Over Various Acidic Zeolites

Kalpana C. Maheria · Janusz Kozinski ·
Ajay Dalai

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Abstract Levulinic acid (LA) has been recognized as a versatile building block for the synthesis of various organic chemicals as it contains ketone and carboxylic functional groups. Levulinate esters are important chemical feedstocks having potential applications either in flavouring and fragrance industries or biodiesel as blending component. The present work focuses on the synthesis of *n*-butyl levulinate by esterification of LA with *n*-butanol using various small and large pore zeolites. The preferential order to yield *n*-butyl levulinate was found to be: H-BEA > H-Y > H-ZSM-5 > H-MOR. Further, a study for optimizing the reaction conditions such as acid to *n*-butanol molar ratio, reaction time and catalyst concentration has been described. Under optimized reaction conditions, zeolite H-BEA has been found as most efficient catalyst with 82.2 % LA conversion and 100 % selectivity of *n*-butyl levulinate.

Keywords Solid acid catalyst · Zeolite · Esterification · Levulinic acid · *n*-Butyl levulinate

1 Introduction

In the present scenario, there is growing interest in research towards utilization of lignocellulosic biomass to produce chemicals, fuels, and energy due to increasing environmental concerns and global energy consumption [1, 2]. In order to meet future energy demands, replacement of fossil fuel based technologies with sustainable and renewable carbon-neutral technologies that utilize lignocellulosic biomass feedstocks becomes essential. Levulinic acid (LA) (4-oxypentanoic acid) is a platform organic chemical and one of the top 12 building blocks, that can be derived from biomass and used for the production of biofuels [3]. Extensive literature is available on useful properties and potential industrial applications of LA and its derivatives [4–6]. Owing to presence of a ketone and a carboxylic acid group in LA, the numerous useful chemicals can be derived from LA such as levulinate esters, γ -valerolactone, acrylic acid, 1,4-pentanediol, β -acetylacrylic acid, α -angelica lactone, 2-methyl THF, δ -amino levulinic acid, etc. [5, 7–10]. For instance, 2-methyl-tetrahydrofuran and various levulinic esters may be used as gasoline and biodiesel additives, respectively. δ -Aminolevulinate is a known herbicide and the bisphenol derivatives may be used as interesting substitutes for bisphenol A [11]. Ethyl levulinate, product of esterification reaction of LA with ethanol, can be used as an oxygenate additive in fuels [12]. One of the levulinate esters, *n*-butyl levulinate has important use as an intermediate in organic process industries for different purposes such as plasticizing agent, solvents and odorous substances [13].

Levulinate esters can be obtained by esterification reaction in the presence of suitable acid catalyst, such as sulphuric, polyphosphoric or *p*-toluenesulfonic acid in homogeneous medium [14–16]. However, it is well known that the use of these homogeneous catalysts have serious drawbacks associated with environmental problems such as handling,

K. C. Maheria
Applied Chemistry Department, Sardar Vallabhbhai National
Institute of Technology, Surat 395 007, Gujarat, India

K. C. Maheria · A. Dalai (✉)
Department of Chemical and Biological Engineering, University
of Saskatchewan, Saskatoon, SK S7N 5A9, Canada
e-mail: ajay.dalai@usask.ca

J. Kozinski
Faculty of Science and Engineering, York University, Toronto,
ON, Canada

containment, disposal and regeneration due to their corrosive and toxic nature. The use of heterogeneous catalysts in organic synthesis has grabbed significant levels since they provide green alternatives to homogeneous catalysts [17, 18]. Number of other heterogeneous catalyst have been also reported for this reaction such as heteropoly acids (HPAs) and supported HPA [19]. It is worthy to note that, heteropolyacids (HPAs) have been widely used in numerous acid-catalyzed esterification reactions due to their strong Bronsted acidity. However, some of the major problems associated with HPAs in the bulk form are their low surface areas (1–10 m²/g) and separation problem from reaction mixture [20, 21]. Recently, Dharne and Bokade [19] have reported the esterification of LA with *n*-butanol to produce corresponding ester, *n*-butyl levulinate using solid acid catalyst, dodecatungstophosphoric acid (DTPA) supported on acid treated clay. They have observed 97 % LA conversion for two cycles. However, thereafter, noticed drastic decrease in LA conversion due to increasing leaching of DTPA from the support [19].

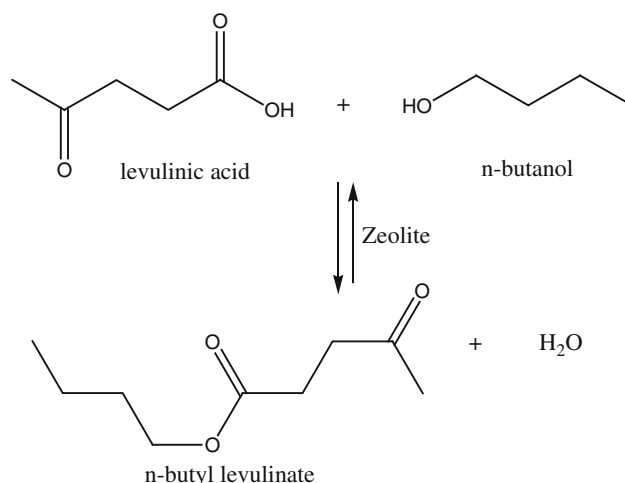
Zeolites are crystalline, highly ordered, microporous aluminosilicates with intracrystalline channels and cages of molecular dimensions [22]. Zeolites find wide applications in production of petrochemicals, often replacing environmentally unfriendly catalysts. The hydrogen form of zeolites (prepared by ion-exchange) are powerful solid-state acids, and used to catalyzed host of organic reactions, such as isomerization, alkylation, and cracking. Excellent reviews have been devoted to a large number of zeolite-catalyzed organic reactions [23, 24]. For carrying out various kinds of organic transformations, zeolite catalysts of different acid strengths and textural properties are required.

Moreover, zeolite beta is widely being studied in liquid phase organic transformations and some of the processes are being commercialized [25]. The large pore beta (BEA) zeolite is structurally disordered and its framework structure was described as a three-dimensional intersecting channel system. It is well known that, amongst the various zeolite, the unique acid properties, mainly related to local defects, the optimal pore dimensions and higher surface area make zeolite beta a very promising catalyst in acid catalyzed shape selective organic conversions [26, 27]. To the best of author's knowledge there are no reports available for the esterification of LA using various acidic zeolites. The present work includes the synthesis of *n*-butyl levulinate by esterification reaction of LA with *n*-butanol using various acidic zeolites (Scheme 1).

2 Experimental

2.1 Catalyst Preparation and Characterization

The zeolites H-Beta [BEA; SiO₂/Al₂O₃ = 25], H-Mordenite [H-MOR; SiO₂/Al₂O₃ = 20], H-Y (SiO₂/Al₂O₃ = 5.1),



Scheme 1 Zeolite catalyzed esterification of levulinic acid

HZSM-5 (SiO₂/Al₂O₃ = 30) zeolites were obtained from Sud-Chemie India Pvt Ltd., Vadodara, Gujarat, INDIA. The phase purity and crystallinity of the zeolites were analyzed by XRD (D8 Advanced Bruker AXS, Germany) with Cu K α radiation using nickel filter and Bruker Smart 6000 CCD detector. Surface area measurement (BET method) was carried out on Micromeritics Gemini at -196 °C using nitrogen adsorption isotherms. Acidity of zeolites were determined on Micromeritics Chemisorb 2720, by a temperature programmed desorption (TPD) of ammonia. Ammonia was adsorbed at 120 °C and then desorption was carried out up to 700 °C at heating rate of 10 °C/min. Levulinic acid (98 %) and *n*-butanol (99 %) were obtained from Alfa Aesar, Ward Hill, MA, USA. All the reagents used were of analytical grade and used without further purification. The solvents were distilled before use.

2.2 Typical Procedure for the Esterification of LA with *n*-Butanol

All zeolites were activated, by heating at higher temperature of 550 – 550 °C for 3–4 h, before loading into the reactor. Esterification reaction has been carried out in order to optimize various reaction conditions such as reaction time, catalyst concentration, molar ratio etc. All the reactions were carried out in a round bottom flask attached to a condenser and equipped with a magnetic stirrer under heating in an oil bath. Typically, a 50 ml round-bottom flask was charged with LA and *n*-butanol, both weighed sequentially, followed by the addition of the desired amount of preactivated catalyst. The reagent amounts were calculated according to the desired molar ratio for each reaction. Then, the system was heated up to 120 °C, the reaction was carried out, for 4–12 h while stirring at 400 rpm and finally the products were collected after removing the catalyst. After completion of the

reaction, the spent catalysts were collected by filtration and then washed with ethanol. Crude product was recovered by evaporating the solvent under reduced pressure. This product was purified by recrystallization with ethanol to afford pure *n*-butyl levulinate. The yield of the product formed was determined by titrating the combined liquid with 0.1 M KOH-EtOH solution. The yield of the esters were calculated using the formula: % Yield = [(A–B)/A] × M × 100; Where, A acid value of the sample before reaction, B = acid value of sample withdrawn after reaction and M mole ratio of acid:alcohol [28]. The yield of *n*-butyl levulinate formed were also determined using GC (Agilent–7890 A) (Capillary column, HP-5, 30 m length × 0.32 mm diameter × 0.25 micron film) with Helium as a carrier gas and programmed temperature range of 40–300 °C. The product was characterized by GC–MS (PerkinElmer, Clarus 600, Column-DB-5, Mass detector), FT-IR and ¹H NMR spectra.

In order to investigate reusability, catalyst was separated from the reaction mixture by filtration, washed with ethanol, dried overnight at 60 °C and reactivated by heating in a stream of air at 400–500 °C for 4 h. This procedure was followed for each recycle study of the catalyst.

The desire product, *n*-butyl levulinate was characterized by comparison of their physical data with those of known compound [29] and the spectral data by physical and spectral analysis (GC–MS, FT-IR and ¹H NMR). The spectral data of *n*-butyl levulinate are as given below.

FTIR (KBr) ν_{\max} = 3407, 2960, 1721, 1465, 1358, 1161, 1072 cm^{-1} ; ¹H NMR (DMSO, 400 MHz): δ 0.74–0.76 (t, J = 7.2 Hz, 3H), 2.3–2.58 (m, 1H), 3.38–3.42 (t, J = 7.2 Hz, 3H), 1.16–1.38 (m, 6H) ppm; GC/MS: 172(M+).

3 Results and Discussion

3.1 Effect of Geometry and Surface Acidity

Zeolites with different topologies as solid acid catalysts were used to elucidate the role of the zeolite channel system on their activity and selectivity on the synthesis of *n*-butyl levulinate (Table 1). All experiments were performed in duplication. The results are reproducible and have ± 2 % error.

Different zeolites such as 12-member-ring (MR) tridirectional zeolites (H-Y and H-BEA), a 12-MR monodirectional zeolite (H-MOR) and 10-MR bidirectional zeolite (ZSM-5) were screened to obtain *n*-butyl levulinate via esterification reaction of LA with *n*-butanol with process parameters of 120 °C, molar ratio (LA:alcohol) of 1:7 and catalyst loading of 10 % (w/w) with respect to LA. Each reaction was conducted for a reaction time of 4 h. Usually, the yield of the ester can be increased by additional use of either alcohol or acid. As the LA is an expensive reagent, it was used as limiting reactant in this study. Table 2 shows the effect of various structural features such as, geometry (pore structure and dimension), acidity and Si/Al ratio of zeolites on the synthesis of *n*-butyl levulinate. H-BEA with three-dimensional 12-membered ring (large pore) showed the highest yield (Table 2) as compared to other zeolites indicating higher acid strength of the acid centre. In all cases *n*-butyl levulinate selectivity was found 100 %.

In the present case, the preferential order to yield *n*-butyl levulinate was found to be: H-BEA > H-Y > H-ZSM-5 > H-MOR. The observed low activity of medium pore zeolite, ZSM-5, is probably ascribed to the diffusional limitation of the pores towards bulkier reactant molecules and geometrical constraints for the formation of intermediates inside the pores, whereas, MOR exhibits largest number of acid sites compared to other zeolites (Table 1) but it seems that the unidirectional channels system causes either inherent diffusional limitations or pore blocking owing to strong adsorption of the reactant or products. It is worthy to mention that strong Bronsted acidity of catalyst is most favorable for the esterification of LA [19]. But, in the present case, zeolites ZSM-5 and MOR with higher strong acidity are found to be less reactive as compared to zeolite BEA. It may be ascribed to lower surface area of zeolite ZSM-5 and MOR compared to the BEA zeolite. The absence of strong acidity in zeolite HY makes it less reactive compared to BEA zeolite. Moreover, it is noteworthy that, with increasing framework Si/Al ratio, the catalyst becomes more hydrophobic, the concentration of acid sites decreases and strength of remaining sites increases [30]. According to the results and conclusions presented above, we could expect that the less polar zeolite should favour desorption of adsorbed polar product. Hence,

Table 1 Physiochemical properties of various zeolites

Catalysts	SiO ₂ /Al ₂ O ₃	Pore structure (nm)	SBET (m ² /g)	Ammonia uptake (mmol/g)		
				Weak	Strong	Total
H-BEA	25	0.76 × 0.64 0.55 × 0.55	710	0.89	0.70	1.60
H-MOR	20	0.65 × 0.70	412	2.02	2.39	4.41
H-Y	5.1	0.74 × 0.74	480	2.30	–	2.30
H-ZSM-5	30	0.53 × 0.56	320	1.95	1.40	3.35

Table 2 Esterification reaction of Levulinic acid and *n*-butanol using different zeolites

Catalysts	SiO ₂ /Al ₂ O ₃	Yield (%) ^a
H-BEA	25	82.2
H-MOR	20	29.5
H-Y	5.1	32.2
H-ZSM-5	30	30.6

(Reaction conditions: LA/*n*-butanol/Catalyst (H-BEA):1/7/10 wt%, reaction temperature: 120 °C, reaction time: 4 h)

^a Isolated yield

it is concluded that low to moderate acidity along with higher surface area and higher Si/Al ratio of zeolite BEA are prime factors for higher catalytic activity towards the synthesis of *n*-butyl levulinate.

The catalytic activity of H-BEA zeolite for the esterification of LA to obtain *n*-butyl levulinate was investigated and results are discussed in subsequent sections.

3.2 Effect of Acid:Alcohol Molar Ratio

The efficacy of the H-BEA zeolite for this reaction was further explored by increasing the *n*-butanol concentration (6–8 mol) in the feed. The effect of molar ratio of LA to *n*-butanol on the esterification of LA at a fixed catalyst amount (10 %), temperature (120 °C) and reaction time (4 h). 76.9, 82.2 and 79.3 % LA conversion observed for acid:alcohol ratio 1:6, 1:7 and 1:8 respectively. Thus a molar ratio 1:7 of LA to *n*-butanol was observed to be the optimum molar ratio. For all feed ratios, the *n*-butyl levulinate selectivity was found to be 100 %. The decrease in the conversion for the molar ratio 1:8, may be attributed to the fact that, increase in alcohol concentration hinders the reaction by blocking the active sites on the catalyst surface or the prevention of nucleophilic attack by shielding protonated alcohol due to its own excess, as mentioned by Parida et al. [31]. The decrease in conversion rate also may be due to the formation of a greater amount of water moving the equilibrium in the direction of the inverse reaction [32]. Further, the water may strongly adsorb on active sites of the catalyst which results in the deactivation of the catalyst.

3.3 Effect of Catalyst Concentration

The effect of catalyst concentration on the conversion of LA with molar ratio of acid:alcohol at 1:7, reaction time 4 h and reaction temperature, 120 °C, is depicted in Fig. 1. From Fig. 1, it is observed that, the conversion is increased with increase in the catalyst amount from 7 to 12 wt% (with respect to LA concentration), thereafter, it starts

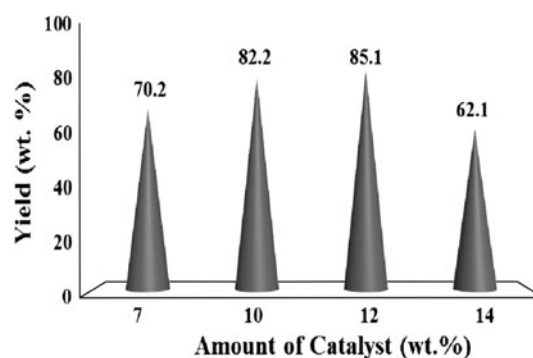


Fig. 1 Effect of catalyst concentration on synthesis of *n*-butyl levulinate (Reaction conditions: LA/*n*-butanol: 1/7, time: 4 h, reaction temperature: 120 °C; stirring speed: 400 rpm)

decreasing. Increase in catalyst amount up to 12 wt % seems to have marginal effect. The product yield beyond this concentration decreased which may be due to formation of water molecules which may deactivate the catalytic sites [33]. Thus, the optimum conversion of LA to *n*-butyl levulinate takes place at 10 wt% catalyst concentration.

3.4 Effect of Reaction Time

The effect of reaction time on the conversion of LA with molar ratio of acid:alcohol at 1:7, catalyst concentration, 10 %, reaction temperature, 120 °C, is depicted in Fig. 2. Results from Fig. 2 reveal that, with increase in reaction time from 2.5 to 10 h, there has been significant increase in the conversion of LA from 19.3 to 82.2 %. The conversion was found to be slightly decreased beyond 4 h. This may be due to formation of water molecules, leading to hydrolysis, a reversible process to occur. The addition of water to the ester link will cause breaking apart of the ester into their parent carboxylic acid and alcohol. The optimum conversion of LA to *n*-butyl levulinate takes place at 4 h reaction time. In all cases, the *n*-butyl levulinate selectivity was found to be 100 %.

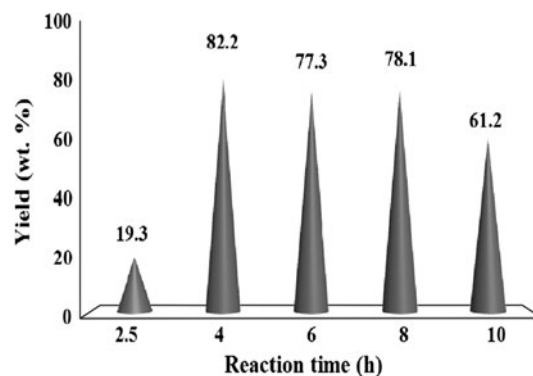


Fig. 2 Effect of reaction time on synthesis of *n*-butyl levulinate (Reaction conditions: LA/*n*-butanol/Catalyst (H-BEA): 1/7/10 wt%, reaction temperature: 120 °C; Stirring speed: 400 rpm)

3.5 Catalyst Reusability

In order to regenerate a Zeolite BEA after 4 h reaction, the catalyst was separated by filtration, washed with ethanol several times followed by drying overnight at 60 °C and reactivated by heating in a stream of air at 400–500 °C for 4 h and then was used for the esterification reaction with a fresh reaction mixture. The XRD patterns of zeolite before and after the reaction revealed that the zeolite retained its crystallinity throughout. Thus, the catalyst can be reused. Further, the catalysts were recycled for five runs without significant loss of activity (Figs. 3 and 4). Obtained % yield for runs 1 to 5 is 82.2, 80.9, 79.9, 78.4 and 78.4 % respectively.

3.6 Merits of the Present Method

Literature survey clearly reveals that, till date, very few reports are available on the reaction of LA with *n*-butanol to synthesize *n*-butyl levulinate. Yadav and Borkar [33]

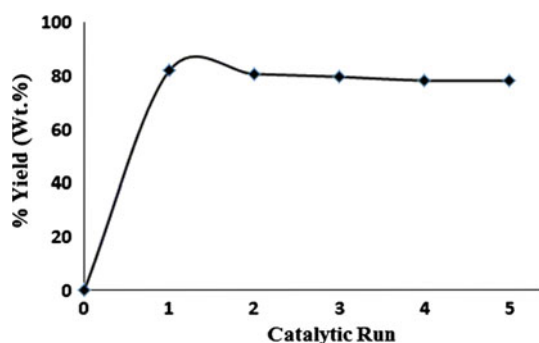


Fig. 3 Effect of reaction time on synthesis of *n*-butyl levulinate (Reaction conditions: LA/*n*-butanol/Catalyst (H-BEA): 1/7/10 wt%, reaction temperature: 120 °C; stirring speed: 400 rpm)

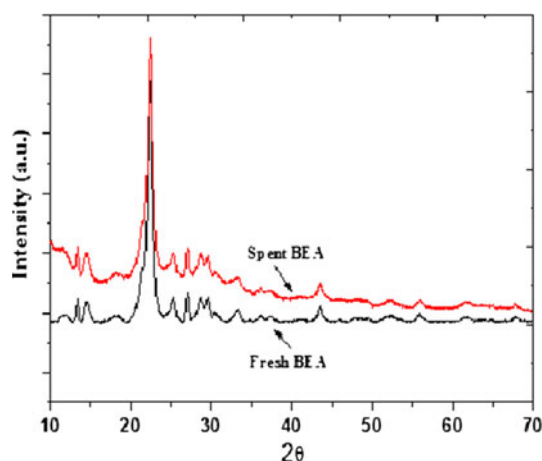


Fig. 4 XRD patterns of H-Beta before use (Fresh BEA) and after five runs (Spent BEA)

have reported immobilized lipase catalyzed synthesis of *n*-butyl levulinate by esterification of LA. Amongst the studied lipases, Novozym 435 (*Candida antarctica* lipase), was found to be the most active catalyst (with 89 % yield) and can be reused thrice. However, after each run, solvent washing and in turn solvent evaporation was found essential for the lipase regeneration. Also, the activity was found to be reduced after each reuse [34]. Dharme and Bokade [19] have reported *n*-butyl levulinate synthesis from LA and *n*-butanol using 20 % (w/w) DTPA/K10 catalyst. They observed 97 % LA conversion and indicated that, the catalyst could be used without any post treatment for two recycles, thereafter, drastic decrease in LA conversion was observed due to increase in leaching of DTPA from K10 support. In this context, the present method of using zeolites for the synthesis of *n*-butyl levulinate offers greener methodology with potential advantages with respect to easy separation, regeneration and reusability.

4 Conclusions

The environmentally benign method has been investigated for the conversion of biomass-based derivatives into fine chemicals. The overall 82.2 % less yield of *n*-butyl levulinate reveals that there is still scope of further development of zeolite catalyst with regards to restricted pore size of zeolite which limits the application of zeolite towards the synthesis of *n*-butyl levulinate. Enhancing the surface area of zeolite BEA may serve the purpose of enhancing catalytic activity thereby increasing % yield of *n*-butyl levulinate. The research work in this direction is currently under progress.

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