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ARTICLE

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Esterification and ketalization of levulinic acid with desilicated zeolite β and pseudo-homogeneous model for reaction kinetics

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Abstract

To maximize the production of esters (E), keto (K) and keto-ester (KE) by esterification and ketalization of levulinic acid (LA) has been reacted using diols such as 1,2-propane diol (PDOL),1,2-ethane diol (EDOL), and 1,2,3-propane triol or glycerol (TRIOL) with desilicated Hβ. This work aims to assess the conversion and selectivity for the production of esters using conventional and microwave-irradiated (MWI) reactors. Catalysts characterizations were performed using NH_3-temperature programme desorption, Brunauer, Emmett and Teller surface area (BET), Barrett, Joyner, and Halenda (BJH), scanning electron microscope, transmission electron microscope, and dynamic light scattering. Operating parameters such as reaction temperature (170–180°C), reaction time (20–80 min), feed composition (LA:PDOL/EDOL/TRIOL, 1:8/10/12), and microwave energy (300–500 watt) have been systematically investigated. Note that 99–100% conversion was achieved with the product selectivity of E (40%), K (30%), and KE (30%) with1,2-EDOL; E (56%), K (2%), and KE (17%) with 1,2-PDOL; E (69%), K(0%), and KE (22%) with TRIOL using D-Hβ as a solid catalyst in an MWI reactor. Reaction paths and kinetics were studied using pseudo-homogeneous (PH) model.

KEYWORDS

esterification, ketalization, levulinic acid, microwave irradiation, pseudo-homogeneous (PH) model

1 | INTRODUCTION

For energy and material production, fossil-based resources currently used are not infinite and will be exhausted in due time, and hence the worldwide scientific community has driven to find reasonably valid, environmental-friendly, sustainable alternatives to current petroleum-based industry. This on-going depletion together with the unfavorable growth of greenhouse effects creates the situation of global warming.[1] In the past few decades, biodiesel has emerged as a promising renewable energy source produced by different routes using biomaterials. Biomass conversion into useful chemicals, materials and fuels emerged as a promising alternative toward replacing the current production of most of specialty products from petroleum feed stocks and other nonrenewable sources. Interestingly, not only end products but also side products and isomers of different esters and carboxylic acid keto-esters (KEs) from biomass valorization have a significant potential for future research and further conversion into useful derivatives.[1] In these processes, due to advantages of heterogeneous catalysis, the work has been highlighted to produce biofuels' additives. In view of this, for the environmental benefits and economic aspects, more research is needed to be carried out to strengthen this new field.[2]

Esterification reaction has been reported at ambient temperatures using various heterogeneous acid catalysts such as zeolite Hβ, Hγ, H-mordenite, and HZSM parent and with metal oxides of zinc, ruthenium, titanium, etc., with an increase in yields and reaction rates to achieve desired

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Nomenclature: C_{A0}, initial concentration of LA; C_{B0}, initial concentration of diols; k_0, frequency factor; M, ratio of C_{B0} to C_{A0}; r_A, rate of reaction; X_A, conversion of LA selectivity.[3] Zeolites have been also used to achieve good yield of glucose acetalized products with alcohols of different chain lengths with the change of Si/Al ratio of zeolites and shape selectivity varies the amount of oligomers formed.[3]

Levulinic acid (LA) or 4-oxopentanoic acid is a main renewable, most promising alternative compound and can be derived from lignocellulose by acid-catalyzed reactions of cellulose-containing biomass.[4] At DuPont Co., researchers are actively pursued to make utilization of LA in syntheses of solvents and surfactants such as pyrolidones, monomer as α-methylene Y-valerolactone, and fuel additives such as LA esters.[5] Also as per global LA consumption of around 2600 tons/year, it is going to be increased in the coming years, especially due to the research enhancement in the biofine process, which will lower the LA costs to 0.09–0.22 \$/kg,[4] and hence it can be used as a raw material to produce different esters and KEs. Amarasekara et al.[6] reported LA oligomerization with glycerol using solid acidic catalysts such as Sb_2O_3, p-toluenesulfonic acid, and 1-(1-propylsulfonic)-3-methylimidazolium chloride for the production of keto (K), glycerol-ketal (KE), and glycerol-ester (E). Freitas et al.[7] also performed the ketalization between ethyl levulinate (Elevu) and ethylene glycol (EG) and 1,2-dodecanediol using acid catalysts such as *p*-toluensolfonic acid, Amberlyst 70, zeolite H-ZSM-5, and niobium phosphate. Mullen et al.[8] mentioned that low to moderate to strong protic acidity of catalyst can improve the synthesis of cyclic ketals. It shows better selectivity of ketal (>95%) and conversion (>95%) with ethyl levulinate.

1,2,3-Propane triol or glycerol (TRIOL) is available as abundant by-product from soap- and biodiesel-making industries. It is a renewable resource with a three-carbon TRIOL having many applications in food, pharmaceutical, and personnel care product industries. The new area of interest is also the utilization of such feed stock by converting glycerol to value-added products. It is used as a model compound for the exploration of its conversion to H_2 and CO_2, and transformation to other alcohols, such as 1,2-propanediol (1,2-PDOL) and 1,3-propanediol (1,3-PDOL), which can be utilized as solvents for the organic synthesis.[9] These diols and glycerol have been utilized for the production of esters and KEs for the present work.

To apply green energy concept, the thermal energy source choice is the use of microwave (MW)-assisted chemistry for the organic synthesis. Effects like much shorter reaction times, improved selectivity of the most desired product, enhanced product yields, cleaner reaction with easier workup, and reduction in waste are mostly observed with MW activation in organic reactions.[10] Despite of abundant literatures on aspects cited above, very few publications dealt with zeolite-catalyzed conventional as well as microwave-irradiated (MWI) esterifications of bio-derived carboxylic acids.

Based on above studies, the reaction of LA with diols, such as 1,2-PDOL ,1,2-ethane diol (EDOL), and TRIOL, using a solid heterogeneous catalyst Hβ and desilicated Hβ (D-Hβ) was studied to produce value-added chemicals or polymers and biofuel additives using conventional and MW-irradiated reactors. The main objective of this study is to valorize LA and diols using optimum amount and enhancement of the selectivity of intermediates, such as E (ester), K (ketal), and also the final product, that is, KE, and to reduce the amount of oligomerized or polycondensate products.

2 | EXPERIMENTAL

2.1 | Catalyst preparation

2.1.1 | Desilication

Pretreatment of Hβ (Si/Al ratio = 25) catalyst was carried out using 0.2 M alkali (NaOH) solution (30 mL/g) at 340 K under continuous stirring for 45 min. The samples were washed with distilled water followed by ammonium exchange in 10 wt% NH_4NO_3 solution (15 mL/g) under reflux for 4 h. The procedure was repeated twice, and the sample was washed and dried overnight at 100°C. Finally, the dry sample was calcinated by flowing air (50 mL/min) at 550°C at a rate of 10°C/min for 10 h in a conventional drier.

2.2 | Materials and methods

LA, 1,2-PDOL, EDOL, TRIOL, and Hβ with a quoted purity of 0.99 (each) were obtained from Merck (Mumbai, India). Other analytical solvents such as diethylether, alcohol, sodium bicarbonate for neutralization and separation in case of the conventional process, and diethylether for a gas chromatography mass spectrophotometer (GCMS) were also procured from Merck. Product analysis was carried out using a gas chromatograph mass spectrometer (7890A GC and MS of ACCUTOF GCV (JMS-T100GCV) system) with oven temperature of 131.9–250°C, at a flow rate of 1 mL/min of helium gas with ion source temperature of 250°C. GC ramp program used is 110–1 M-8-200-5 M-10-280 HP5.

2.3 | Experimental procedure

Esterification and ketalization reactions were performed in a continuous fixed bed reactor (using H_2 as a carrier gas at the flow rate of 10 mL/min) having length (*L*) and diameter (*D*) as $L \times D = 1 \times 2.5$ (cm × cm). Catalyst particle size and properties are shown in Table 1, and MWI reactions were carried out in a thermostated batch reactor equipped with a magnetic stirrer with a closed reflux. For each run, LA and polyols (PDOL, EDOL, and TRIOL) were mixed at different operating conditions, and a product mixture was withdrawn at different intervals of time and analyzed by GCMS.

TABLE 1 Catalyst characteristics

Sr. no.	Characterization	Hβ	D-Hβ
1	NH_3 TPD (acidity measurement) (mmol/g)	1.67	3.16
2	BET surface area (m^2/g)	510	470
3	BJH adsorption cumulative surface area of pores (between 17.000 Å and 3000.000 Å diameter) (m^2/g)	112	113
4	Pore volume (cm^3/g) by BET	0.38	0.35
5	BJH adsorption cumulative volume of pores(cm^3/g)	0.26	0.24
6	Average adsorption pore width by BET(Å)	29	30
7	BJH adsorption average pore diameter (4V/A) (Å)	93	86
8	Average particle size (nm) by dynamic light scattering (DLS)	524	412

2.4 | Microwave heating principle

Electromagnetic waves employed in MW heating represent radiation energy for molecular interactions of ions and aligned to field rotation of the dipoles, which are the main cause of energy generation by nonionizing radiation without any molecular structural defects. Molecular dipoles align with respect to the applied field of different frequencies of MWs. In this field, molecules start to align–realign to generate friction by oscillations. Due to this friction, heat is generated between molecules. This is also due to the dielectric loss factor of the molecules. In some cases, if dipole is not realigned to its field rotation due to high or low frequencies, then energy is slowly produced and hence there is no change in molecules because no or negligible heat is generated.[11–13]

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

Solid Hβ was characterized using NH_3-temperature programme desorption measurement (AutoChem 2910 instrument; Micromeritics, Norcross, GA), Brunauer, Emmett and Teller surface area (BET)/Barrett, Joyner, and Halenda (BJH) (ASAP 2010; Micromeritics), scanning electron microscope (SEM) (JEOL model JSM-6390LV), and transmission electron microscope (TEM) measurements (JEOL/JEM 2100).

From the literature, it was found that moderate acidity of catalyst favors the formation of ketoester or ester.[14,15] From Table 1, it is observed that due to desilication of zeolite Hβ, acidity of D-Hβ increases from 1.67 to 3.16 mmol/g of parent Hβ, so zeolites Hβ and D-Hβ were chosen for the reaction. The BET surface area is a pore area including external surface area. For mesoporous, BJH gives more appropriate values specific to the actual pore diameter of zeolite. With the rise in temperature, the obvious change of specific surface area tends to take place in smaller micropores rather than in larger pores. And by BJH, observed specific surface area decreases and the average pore diameter of the porous particle increases with the rise of the geothermal nature of coal.[16] Zeolite gives the same observation with BET and BJH (Figure 1A–D). As shown in Table 1, the pore sizes of Hβ and D- Hβ using BET are found to be 29 and 30 Å, whereas the pore sizes of Hβ and D- Hβ using the BJH method are found to be 93 and 86 Å, respectively. While calculating pore sizes of Hβ and D- Hβ, intercrystalline void volume is also included, which results in a higher average diameter.

SEM images (Figure 2A and B) confirm the particle size (200–500 nm) obtained from the dynamic light scattering. TEM analysis of the samples revealed the presence of much smaller catalyst crystals of up to 10–30 nm size with very thin particle size distribution for both Hβ and D-Hβ (shown in Figure 2C and D), which is responsible for improved catalytic activity.

3.2 | Heterogeneous acid-catalyzed synthesis of esters and keto-compounds of LA

3.2.1 | Conventional method

The esterification of LA with *n*-butanol occurs even in the absence of catalyst, because LA is able to act autocatalytically.[17,18] Such reactions take 48–50 h to complete, and with excess alcohol these reactions take place without any catalyst,[17] but good yield can be obtained with a solid acid catalyst. Reaction parameters were measured with respect to the best performance of the LA conversion both in conventional and MW reactors. It is also observed that with homogeneous catalyst (H_2SO_4), the product selectivity is good, but it affects separation and purificationas it requires neutralization before quantification of the product.

In the present work, in a tubular reactor reaction parameters were kept constant at the atmospheric pressure to optimize the reaction temperature and the reaction time in a range of 1–7 h (at an interval of 0.5 h). Products were collected at regular intervals, and final samples were analyzed by GCMS. The GCMS was always calibrated before injecting the samples by the carrier solvents. The retention time and GC ramping program as mentioned earlier (110-1 M-8-200-5 M-10-280 HP5) were used based on the boiling point of the solvent and desired products.

A feed ratio of the mixture (1:8/10/12) for LA:ROH and catalyst (D-Hβ) amount (0.25–1.0 g) were used. Optimized molar feed ratio and catalyst amount (in terms of maximum percentage of conversion and selectivity) were found to be1:8 (LA:ROH) and 1 g, respectively. It was observed that the reduction in the feed ratio (1:6) leads to formation of more amount of ketal than ketoester or ester. It is reported that the

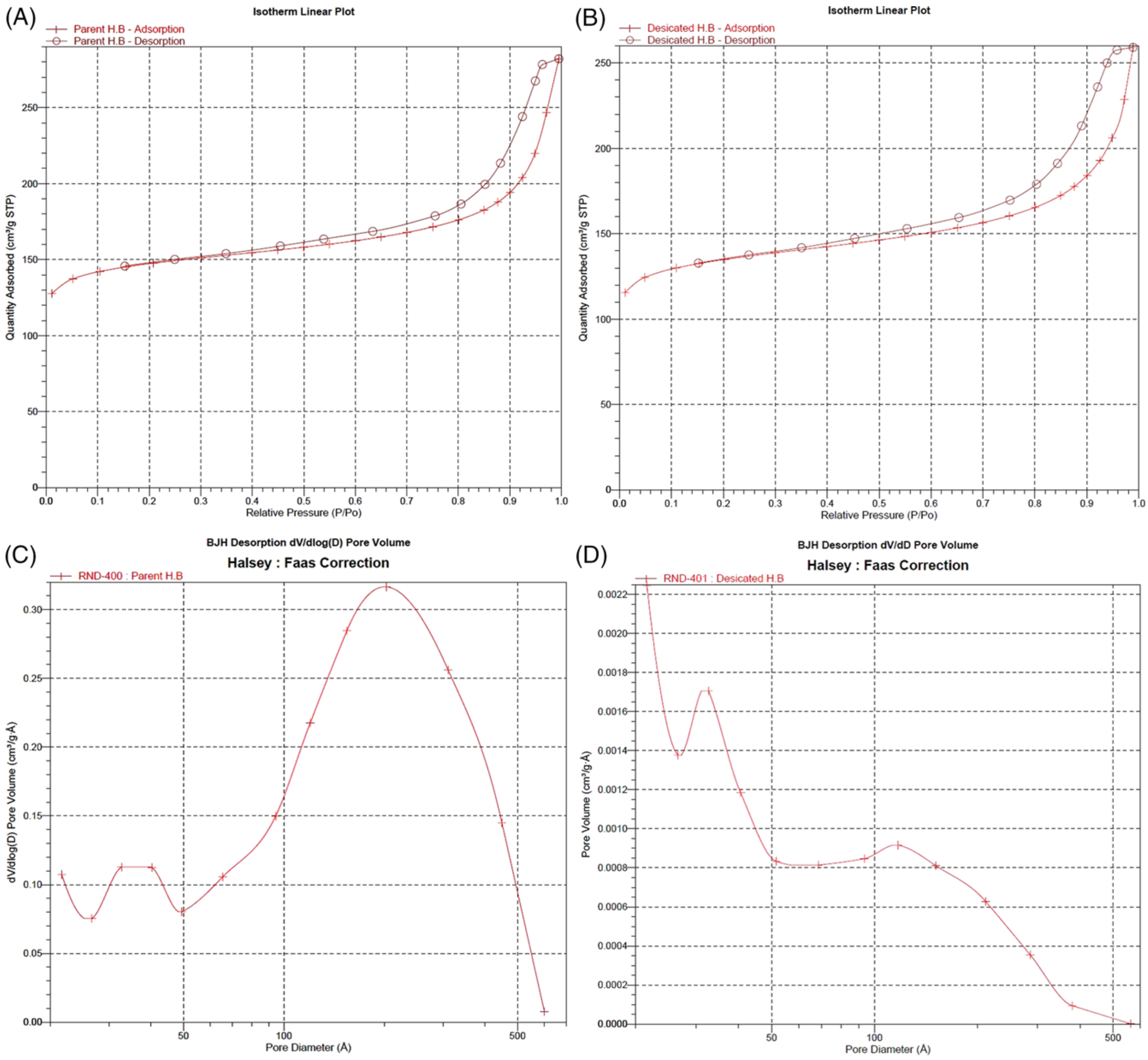


FIGURE 1 BET isotherms (A) Hβ and (B) D-Hβ and BJH (Barret, Joyner and Halenda) desorption pore volume versus pore diameter for (C) Hβ and (D) D-Hβ [Color figure can be viewed at wileyonlinelibrary.com]

ketalization employs 6 molar equivalents of diol per equivalent of ketone and 0.0077 molar equivalents of catalyst per equivalent of ketone. Yield of the ketal is 72% after 66 h of reaction.[15]

Figure 3A shows conversion and selectivity of E, K, and KE with the feed ratio of 1:8 (LA:PDOL) at elevated temperature using 1 g D-Hβ as a catalyst. At 180°C reaction temperature (near to the boiling point of 1,2-PDOL, 188°C), esterification of LA with PDOL occurs effectively but at high temperatures (above 190°C) conversion and selectivity of the respective ester decrease. With 1,2-EDOL (boiling point 197°C), optimum reaction temperature was found to be 190°C. To compare conversion and selectivity with diols, a maximum temperature of 190°C was maintained though boiling point of triol was higher (290°C). With 1,2-EDOL, product selectivity was found to be as follows: E (42%), K (26%), and KE (31%). Due to competitive and reversible nature of the reaction with 1,2-EDOL, it shows an s-shaped graph at 170180°C. As chain length of the alcohol increases in 1,2-PDOL, ketoester formation predominates. 1,2-PDOL produces mainly E. Further as the reaction progresses, the E reacts with excess 1,2-PDOL, available in the reaction mixture produces KE but still ester is the major product with selectivity of E (71%), K (8 %), and KE (20%). For TRIOL, product selectivity increases for KE but with better selectivity of E (20%), K (8%), and KE (14%). With an increase in a molar feed ratio (1:12), selectivity toward K, E, and KE decreases and undesired side products are formed due to polycondensation in the reaction mixture. In line with the present work, researchers have highlighted a maximum conversion rate of

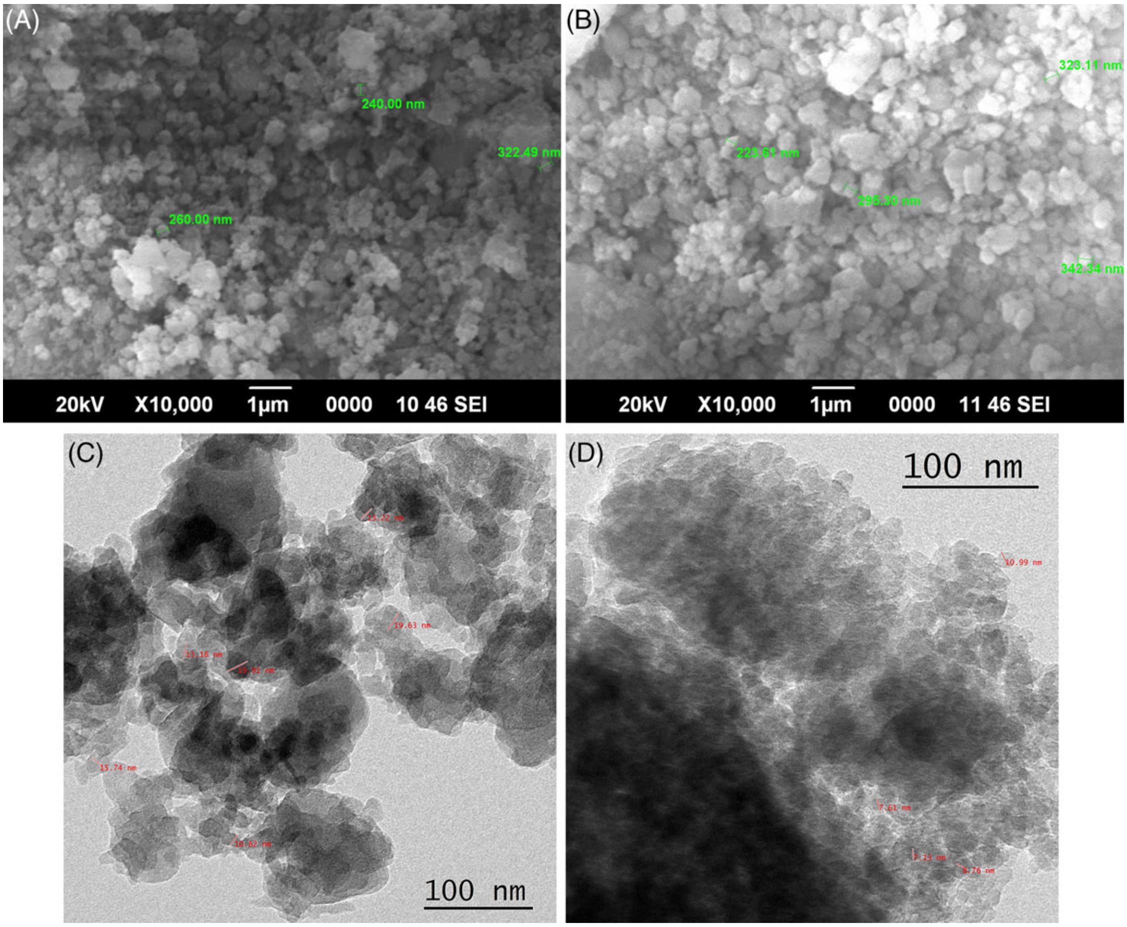


FIGURE 2 SEM images: (A) Hβ and (B) D-Hβ and TEM images: (C) Hβ and (D) D-Hβ [Color figure can be viewed at wileyonlinelibrary.com]

93% and 100% for 1,2 and 1,3 hydroxyls ketals, respectively, by heating an equimolar mixture of LA and glycerol at the temperature range of 23–210°C in nitrogenous atmosphere for 1 h, and then at 210°C in a vacuum for 9 h using a solid Sb_2O_3 catalyst. Catalysts *p*-toluenesulfonic acid and 1-(1-propylsulfonic)-3-methylimidazolium chloride have also been utilized for the production of oligomers with relatively lower molecular weights.[6] Niobium phosphate-catalyzed ketalization of ethyl levulinate with EG afforded 98% selectivity to ketal with the change in the feed ratio from 1 to 2.5 for ELevu/EG and with1,2-dodecanediol with the same feed ratio having catalyst loading of 1 wt% for 24 h at 130°C has yielded almost 100% selectivity to ketal compounds.[7].

From Figure 3A–C, it was observed that selectivity of ester was high (71%) with 1,2-PDOL, moderate (42%) with 1, 2-EDOL, and less (20%) with TRIOL. As diol also has the tendency to undergo transesterification with the carboxylate moiety of the ketoester, it forms monohydric ester having a residual hydroxyl moiety by an acyclic ketalization reaction, and so with diol, the ester formation is good compared to triol. Also with triol, cyclic ketal ester forms as a KE molecule in which the cyclic ketal ester has a mono-hydroxy moaiety.[8]

3.2.2 | MW-irradiated method

At a favorable reaction temperature, that is, 180°C for 1,2-PDOL, and 190°C for 1,2-EDOL and TRIOL, esterification of LA with different alcohols was carried out using D-Hβ (1 g) as a catalyst and the reaction time of 1.5 h with an optimum molar feed ratio (1:8) using the MWI method (300–500 W). As esterification is an equilibrium-limited reaction, excess of alcohols is used to shift the reaction toward formation of the desired product (Scheme 1). Products were collected at regular intervals and analyzed after extraction of reaction mass. At 300 W , 100% conversion could be achieved. Hence, 300 W MW power was used for further experiment (Figure 4A–C). Higher selectivity of the products such as E (50–71%), K (8–30%), and KE (14–30%) was obtained with the use of different alcohols within a short reaction time. Gyula et al.[19] reported MW-assisted ketalization of 4-chlorobenzophenone into the corresponding 1, 3-dioxolan-2-yl derivative. The mixture of ketone, EG, and toluene was irradiated at 500 W in a Milestone MicroSYNTH® MW reactor. Note that 100% conversion and good yields of 98% are achieved in 3 h of reaction time. Pourjavadi et al.[20] also synthesized a series of new acetals and ketals based on spiro-1,3-dioxane-5-norbornene

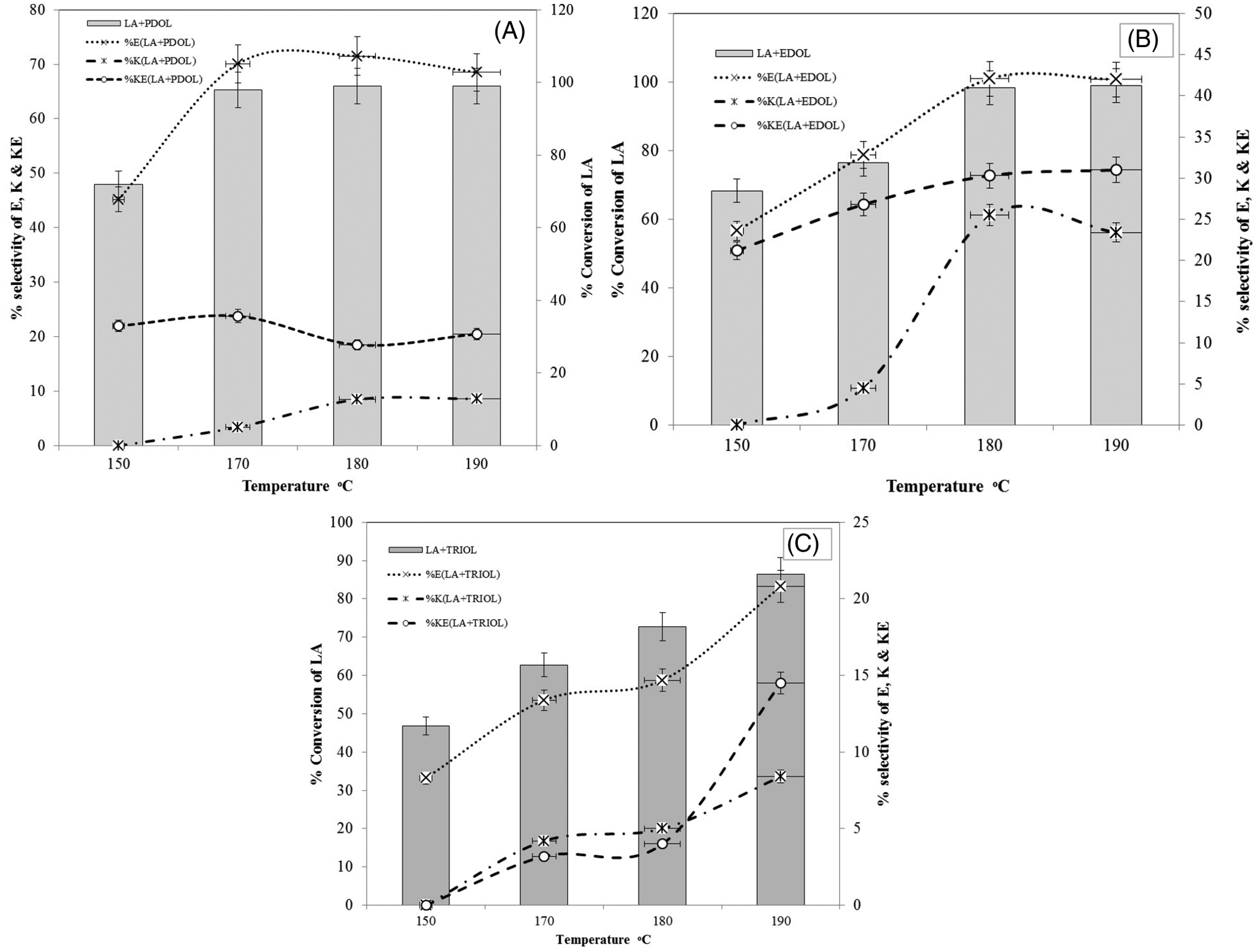


FIGURE 3 Conventional esterification/ketalization of (A) LA + PDOL, (B) LA + EDOL, and (C) LA + TRIOL at 150–190°C in tubular-fixed bed reactor using D-Hβ (1 g) at 1 atm with 0.1 mL/min feed flow rate

by the MWI reaction to achieve high yield (80–90%) of different products.

With different solvents, the alkyl groups attached by the replacement of hydroxyl moiety give different chain lengths of E, K, and KE (Scheme 1). Product distribution shows that smaller size molecules are formed along with higher molecular weight or long-chain products[21] and percentage distributions of E and KE are also different. In porous catalysts, due to diffusion of reactants and products, active sites of catalyst are blocked and sometimes further reaction is restricted to form long-chain products. The present study analyzes the penetration limitations of the reactants and variation in molecular size of products due to variation in particle size (30–320 nm) and surface area (113–470 m^2/g) of D-Hβ catalyst.

The competitive nature of the reaction mechanism is analyzed with the pseudo-homogeneous (PH) model:

$$\mathrm{LA\,(A) + 1,2-EDOL\,(B) \rightarrow E + 1,2-EDOL \rightarrow KE} \quad (1)$$

$$\mathrm{LA\,(A) + 1,2-EDOL\,(B) \rightarrow K + 1,2-EDOL \rightarrow KE} \quad (2)$$

$$-r_A = kC_AC_B$$

$$-r_A = k\left(C_{A0} - C_{A0}X_A\right)\left(C_{B0} - C_{A0}X_A\right)$$

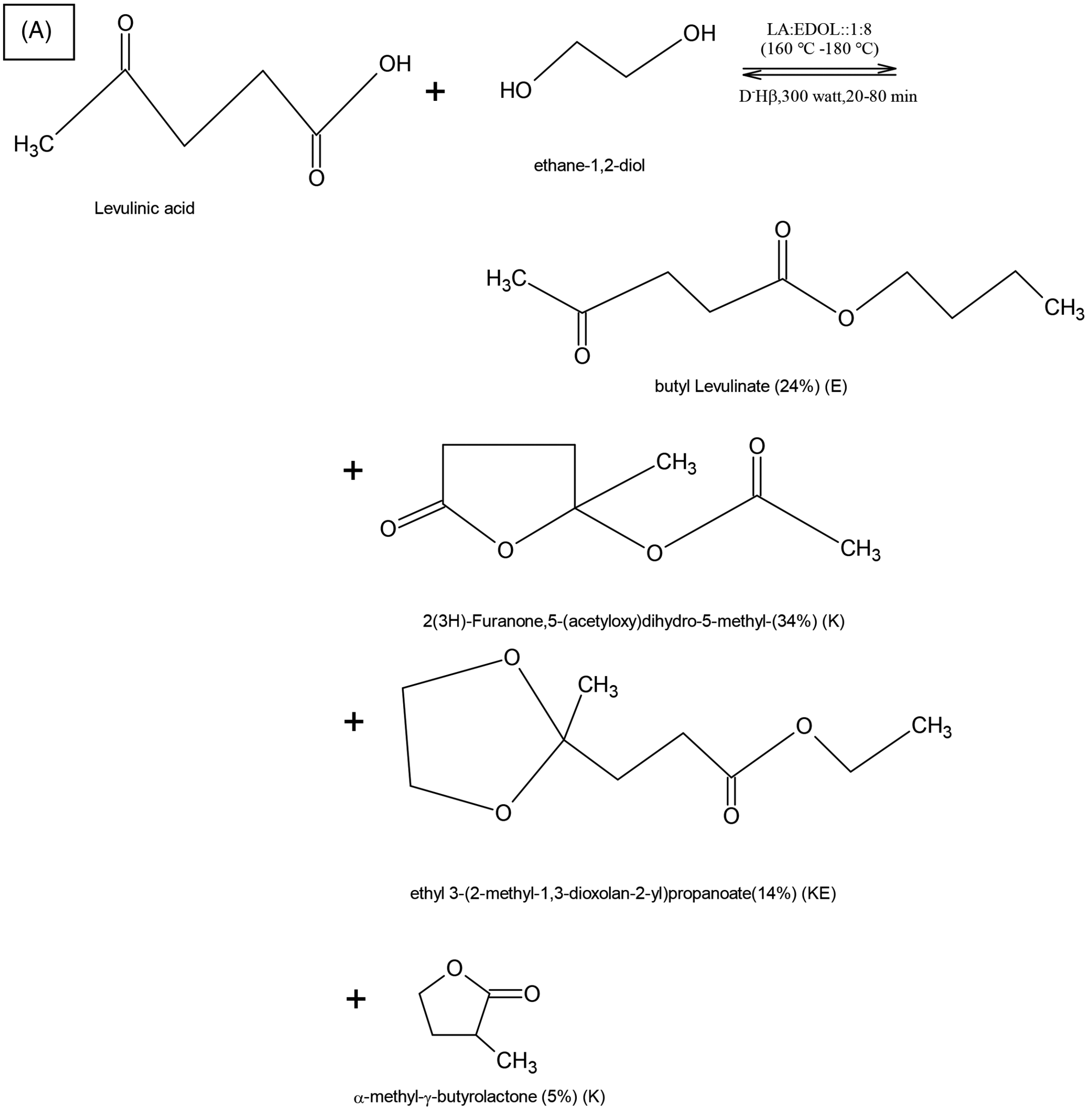
When $M = C_{B0}/C_{A0}$ be the initial molar ratio of the reactants,

$$-r_A = C_{A0}dX_A/dt = k\,C_{A0}{}^2\left(1 - X_A\right)\left(M - X_A\right)$$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}kt\int_0^t dt \qquad (3)$$

After breakdown into partial fractions, integration and rearrangement result in

$$\ln\frac{1 - X_B}{1 - X_A} = \ln\frac{M - X_A}{M(1 - X_A)} = C_{A0}(M - 1)kt$$
$$= (C_{B0} - C_{A0})kt,\, M \neq 1 \qquad (4)$$



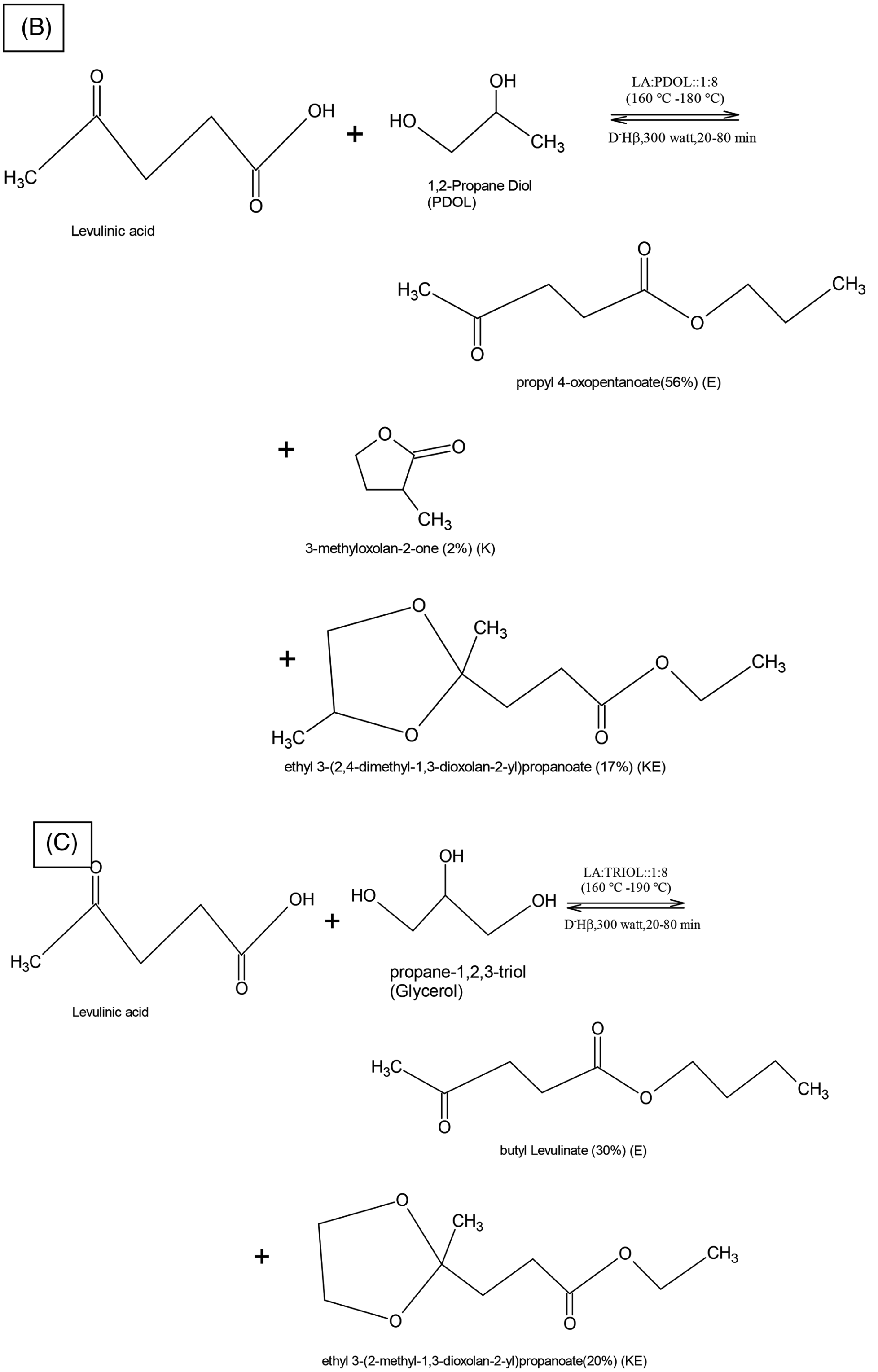
SCHEME 1 MWA esterification of LA using (A) EDOL, (B) PDOL, (C) TRIOL with D-H*β*

If C_{B0} is much larger than C_{A0}, C_B remains approximately constant at all times. Thus, the order higher than 1 becomes a pseudo–first-order reaction.[22]

$$\ln \frac{1}{1 - X_A} = kt \tag{5}$$

In the presence of excess alcohols, esterification follows the pseudo–first-order reaction and hence the plot of $-\ln(1 - X_A)$ versus time (not shown) is used to determine the reaction rate constants. It has been found that 1,2-PDOL and TRIOL follow the linear regression kinetics ($R^2 > 0.94$), whereas 1,2-EDOL follows some other path of reaction leading to formation of more K as products. Table 2 shows rate constants and activation energies calculated from the Arrhenius plot (Figure 5).

With higher speed and smaller particle sizes of catalyst (<100 nm), the internal and external mass transfer rates are not the main controlling step of reaction. It is reported that, for esterification of LA with *n*-butanol, there is no external or internal mass transfer resistance at an agitation speed of above 200 rpm and at an average catalyst particle size of below 82.5 nm.[18] In line with this, all experiments carried out at an agitation speed of 400 rpm and with pore width of D-H*β* catalyst in nanometers (Table 1) have no external/internal diffusional resistance. Activation energy values are also important to determine whether the reaction rate is limited by mass transfer/diffusion or by the kinetic regime with proper utilization of catalyst. It has been reported that if the activation energy exceeds 15 kJ mol^{-1}, then it



SCHEME 1 Continued

lies in the kinetic regime.[18] Activation energy of LA with *n*-butanol is reported as 24 kJ mol^{-1} [18], while in this work, LA + 1,2-PDOL, LA + 1,2-EDOL, and LA + triol give 109, 53, and 72 kJ mol^{-1}, respectively. Based on this evaluation, it can be concluded that all reactions highlighted above are performed in kinetic regime only and not controlled by mass transfer. High values of activation energies might be achieved within short time due to high impact of thermal effects of MW heating. Out of three alcohols, 1,2-EDOL shows lowest activation energy as compared to larger molecular weight alcohols, and thus exhibits a higher rate of reaction.

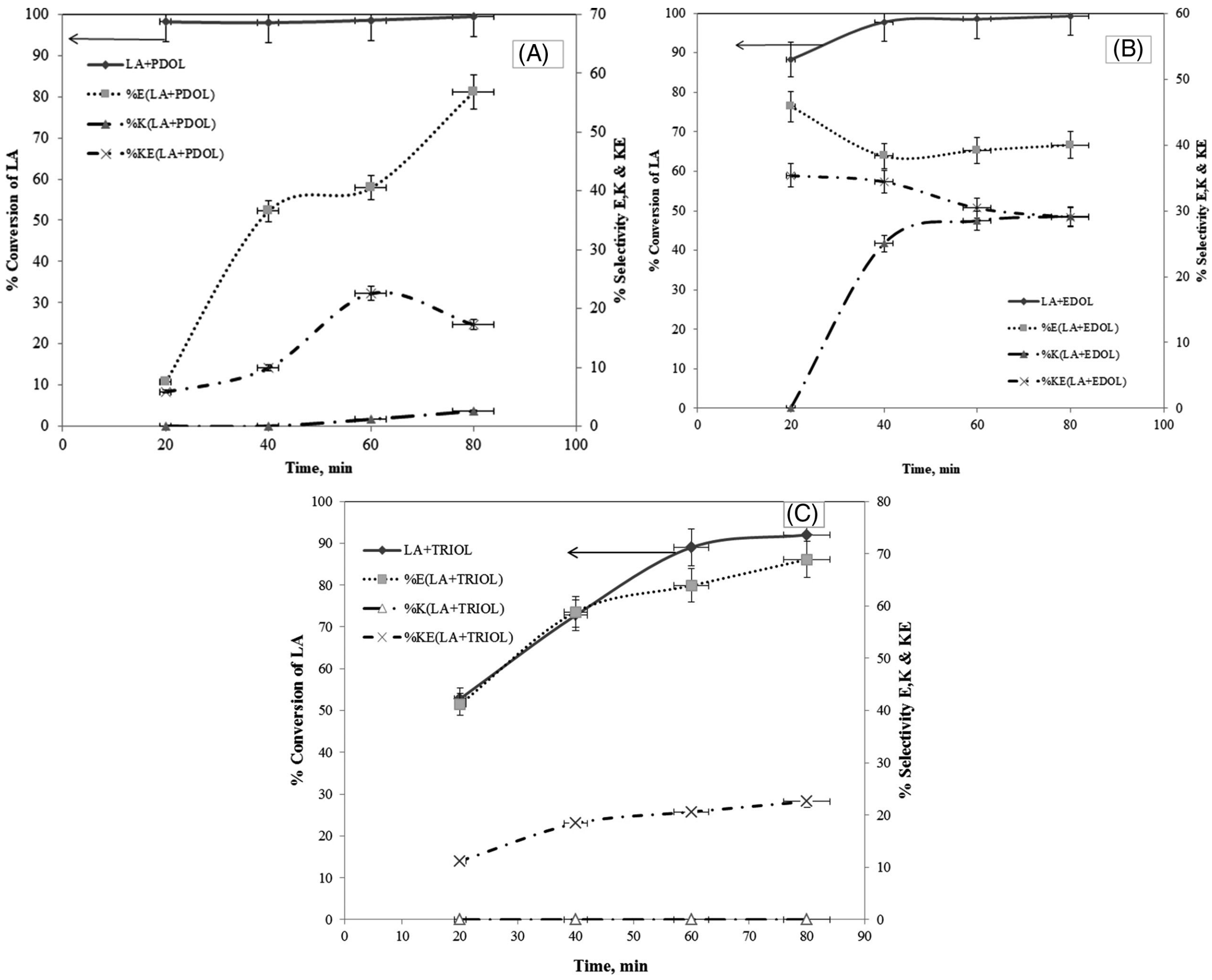


FIGURE 4 MW-assisted esterification/ketalization of (A) LA + PDOL, (B) LA + EDOL, and (C) LA + TRIOL at 180°C in a microwave batch reactor using D-Hβ (1 g) at 300 W, with feed ratio of LA:polyol (1:8)

TABLE 2 Rate constants, frequency factors, and activation energy for LA+ (alcohols) under MWI

	Rate constant, *k* (mol/min)		
Temperature (°C)	LA + 1,2-PDOL	LA + 1,2-EDOL	LA + TRIOL
170	0.0051	0.0331	0.0137
180	0.0172	0.0381	0.0181
190	0.0181	0.0621	0.0319
Activation energy, E (kJ mol^{-1})	109	53	72
Frequency factor, k_0 (min^{-1})	1.3546×10^{11}	6.2130×10^{4}	3.8903×10^{6}

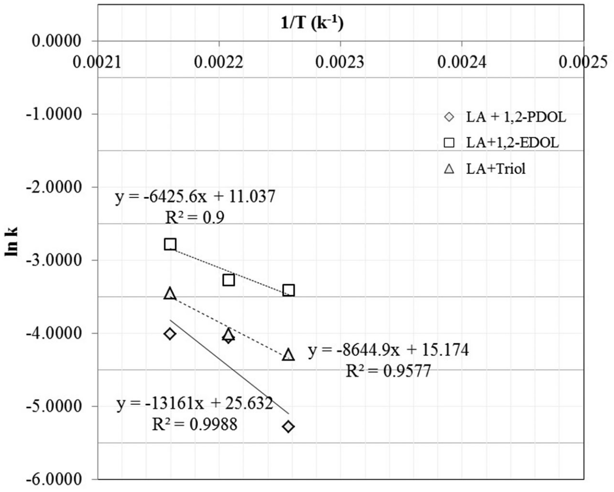


FIGURE 5 Arrhenius plot for LA esterification

4 | CONCLUSIONS

Esterification/ketalization of LA with different alcohols (1,2-ethanediol, 1,2-propanediol, and glycerol) is established using conventional and MWI methods. Liquid phase reaction was performed at optimized condition (180°C for 1,2-PDOL, and 190°C for 1, 2-EDOL and TRIOL, molar feed ratio, LA:ROH = 1:8, 1 g D-Hβ catalyst) in a continuous fixed bed tubular reactor and in a MW batch reactor. The effects of different parameters such as reaction time, MW power, and molar feed composition are systematically investigated to achieve promising results in terms of conversion and selectivity.

The reaction mechanism shown here states that the equilibrium nature of the esterification and competitive with ketalization increases the complexity of the reaction. Using excess amount of alcohol, higher conversion of LA (99–100%) is achieved with D-Hβ catalyst using the MWI method. Higher selectivity of the products such as E (50–71%), K (8–30%), and KE (14–30%) was obtained using different alcohols within a short reaction time. It also proves that the higher acidity and mesoporosity generated in D-Hβ have great effect on the reaction mechanism for the production of ester, whereas the chain length of diols and TRIOL also has impact on the rate of the reaction and product distributions.

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