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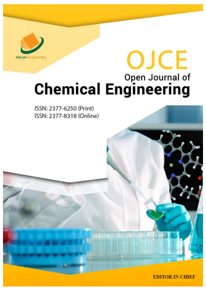

SYNTHESIS OF ETHYL LEVULINATE BY ESTERIFICATION OF RENEWABLE LEVULINIC ACID OVER DODECATUNGSTOPHOSPHORIC ACID SUPPORTED ON ACIDIC CLAY CATALYST

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ABSTRACT

Ethyl levulinate (EL) an oxygenate for diesel miscible bio-fuel or bio-diesel is a clean additive reduces global warming, lesser sulfur content, increase lubricity etc. Ethyl levulinate has been prepared by esterification of biomass derived levulinic acid (LA) with ethanol as an alkylating agent. Dodecatungstophosphoric acid (DTPA) was supported on acidic clay (K10). The increase in conversion of levulinic acid was observed with increase of DTPA loading due to increase in total acidity. 20% (w/w) Dodecatungstophosphoric acid (DTPA) supported on acidic clay (K10) was found to be the optimum solid acid catalyst for the esterification reaction with 79% LA conversion. The present work also extended on optimization of process parameters such as DTPA loading on K10, catalyst loading, molar ratio of ethanol to LA, catalyst reusability and stability. Kinetic modeling is based on pseudo-homogeneous (P-H) model. The reaction follows second order kinetics with activation energy of 33.32 KJ/mol.

KEYWORDS

levulinic acid; esterification; ethyl levulinate; dodecatungstophosphoric acid; K10

1. INTRODUCTION

Levulinic acid (LA), derived from the acid hydrolysis of cellulose contains two functional groups, a carboxylic acid and a ketone. Based on a study, it is one of the top-twelve building blocks, which can be used for the synthesis of several chemicals such as 1,4-pentanediol, acrylic acid levulinate esters for applications such as fuel additives, polymer and resin precursors [1,2].

Study showed Ethyl levulinate up to 5 wt % can be used as an oxygenate additive in the diesel miscible biofuel (DMB), preventing global warming by decreasing atmospheric CO2 generated from the consumption of fossil fuels [3-8]. The addition of ethyl levulinate to the diesel leads to clean burning fuel with lesser sulphur content, stability in flash point, increase in lubricity and improvement in viscosity. Ethyl levulinate has been used in numerous industries as a solvent, plasticizer and as a fragrance and flavor-inducing agent. Ethyl levulinate (EL) has been reported as a chemical feedstock, which has various potential industrial applications.

Ethyl levulinate (EL) obtained from esterification of LA with ethanol is an attractive green process. Esterification reaction has reported in liquid-phase using inorganic liquid acids such as sulphuric, polyphosphoric or p-toluenesulfonic acid in homogeneous medium. The inorganic liquid acids used in this reaction could cause environmental problems in disposal, containment, handling, and cannot be regenerated due to their toxic and corrosive nature.

To overcome these problems, it is extremely important and necessary to develop new and environmentally benign heterogeneous catalysts with high activity for the production of levulinate esters.

The heterogeneous catalysts reported in the literature for esterification reactions include sulfonated carbons, modified zirconias, mesoporous sulfonic acid, heteropoly acid-based catalysts, MCM, different zeolites (HUSY, HBEA, HMOR, HZSM-5, HMCM-22), zeolites-Y and sulfated oxides (SnO2, ZrO2, Nb2O5, TiO2), sulfonic resin, amberlyst-15, ion exchange resin etc [9-17]. However, the systematic study of esterification of Levulinic acid (LA) with ethanol using solid acid as catalyst is not yet adequate.

According to a research, Heteropoly acids (HPAs) have been widely used in various acid-catalysed reactions because of their strong Bronsted acidity [18-20]. Dodecatungstophosphoric acid (DTPA) is the most stable among all reported HPAs. A scholar said DTPA possesses the highest Bronsted acidity hence it is commonly used for acid catalysis [21-23]. DTPA is less volatile, more acidic, less corrosive, high thermal stability up to 300-350 0C, possesses higher activity and flexibility [24].

The main disadvantages of such HPAs as catalysts lie in their relatively low surface area (1–10 m2/g) and in separation problems from reaction mixture. HPAs on suitable supports are expected to overcome these problems. Based on a study, a number of porous supports with high surface areas such as silica, ZrO2, activated carbon, SBA- 15 and zeolites have been used for supporting HPAs [25-28].

Acid modified clay minerals could be used as an efficient support because they exhibit higher surface area, pore volume, pore diameter and higher surface acidity, which results in its improved adsorption and catalytic properties [29,30]. In particular, the acid treated montmorillonite clay (K10) catalyst has received considerable attention in different organic syntheses as a catalyst or as a support because of their environmental compatibility, low cost and operational simplicity.

The present study deals with the application of dodecatungstophosphoric acid (DTPA) supported on acid treated montmorillonite clay (K10) as an eco-friendly solid catalyst for the

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synthesis of ethyl levulinate (fuel additive) by esterification of biomass derived levulinic acid. The optimization of process parameters and kinetic study based on P-H model is also presented.

2. EXPERIMENTAL

2.1 Chemicals and reagents

Dodecatungstophosphoric acid [$H3PO4\cdot 12WO3\cdot xH2O$] (DTPA) and clay (Montmorillonite, K10) were obtained from M/s S. d. Fine Chem. Ltd., Mumbai (India). Levulinic acid (99%) and ethanol (99%) were obtained from M/s E. Merck, Mumbai (India). All the reagents are of analytical grade and used without further purification.

2.2 Catalyst preparation

DTPA on montmorillonite K10 support was prepared by incipient wetness technique. Typically, for 20 g scale catalyst preparation, the following procedure was adopted: 20 g of support, viz., K10, was taken. A 2.0 g amount of DTPA was weighted, which corresponds to 10% (w/w) DTPA loading with respect to K10 weight. The measured DTPA was dissolved in methanol, which formed a homogeneous solution. The methanolic DTPA solution was added slowly on the measured quantity of K10 with constant stirring using a glass rod. Initially, the support (K10) was in a powdered form, but, upon subsequent addition of methanolic DTPA solution, it formed a paste or wet cake. The cake was dried on a water bath. The sample was further dried in an oven, in order to achieve complete removal of methanol and the dried catalyst was stored in a sealed bottle. Prior to use, the catalyst sample was dried in an oven. A similar procedure was used to prepare other compositions of the catalysts up to 30% (w/w) DTPA/K10.

2.3 Catalyst characterization

The crystallinity and the phase purity of synthesized samples were analyzed by powder X-ray diffraction (XRD) patterns using an X-ray diffractometer (Rigaku Miniflex, Tokyo, Japan) using Cu-Kα radiation. XRD was performed by scanning the catalyst sample within the 2θ range of 10-800 (Fig. 2, Fig. 3, and Fig. 4).

Specific surface area of catalyst was obtained from nitrogen adsorption-desorption isotherms measured in a SA 3100 analyzer (Beckman Coulter, CA, USA). The adsorption was carried out at 77 K overnight under a residual presence of nitrogen. The surface area of all the prepared samples was calculated by using Brunaer-Emmett-Teller (BET) method (Table 1).

Table 1: Nitrogen adsorption by BET method.

Sr. No.	Catalyst	BET Surface Area (m^2/g)
1	Plain K10	223
2	5% (w/w) DTPA/K10	217
3	10% (w/w) DTPA/K10	195
4	15% (w/w) DTPA/K10	156
5	20% (w/w) DTPA/K10	135
6	30% (w/w) DTPA/K10	104
7	20% (w/w) DTPA/K10 (four times used)	110

Temperature programmed ammonia desorption (TPAD) was performed by using a Micromeritics AutoChem 2910 (Norcross, GA, USA). Thermal analyses have been carried out of bulk DTPA, K10 and 20% (w/w) DTPA/K10 samples (Fig. 5). Fourier Transform of Infrared (FTIR) has been carried out of bulk DTPA, K10 and 20% (w/w) DTPA/K10 samples (Fig. 6).

2.4 Reaction procedure

The esterification reaction of levulinic acid with ethanol was carried out in a stirred batch reflux system (Fig. 1). A 50 ml glass round bottom flask was charged with levulinic acid and the ethanol, both weighted sequentially, followed by the addition of the catalyst. The reagent amounts were calculated according to the desired molar ratio for each reaction (ethanol: LA). Then, the system was heated up to 78 0C, the reaction was carried out for 4 h and finally the product was collected after removing the catalyst. The product was analyzed by gas chromatography.

By comparing three weight loss rate curves, two obvious weight loss peaks can be found at the heating rates of 20 K/min and 30 K/min respectively, while no obvious weight loss peak can be found at the heating rate of 10 K/min, exhibiting a much higher weight loss rate than the former two curves. The reason is that when the temperature reaches 200℃, the drying time for lower heating rate is longer than that for higher heating rate. Moreover, the evaporation rate of volatiles is lower at lower heating rate, resulting in poor ignition and combustion performances. However, at high heating rate, it took less time to go up to the same drying temperature, and volatiles are separated before complete drying of moisture. There might be a period when water evaporation coexists with volatiles vaporization in the temperature range of 200-250℃. Meanwhile, at high heating rate, volatiles of sludge are built up to a high concentration in a short time, leading to improved ignition and combustion performance of sludge. As the concentration and temperature of volatiles both increase to a certain level, severe combustion reaction occurs, and the flammable stage begins. When fixed carbon is burnt at the later combustion stage of volatiles, another weight loss peak at lower combustion rate is observed, forming the non-inflammable stage.

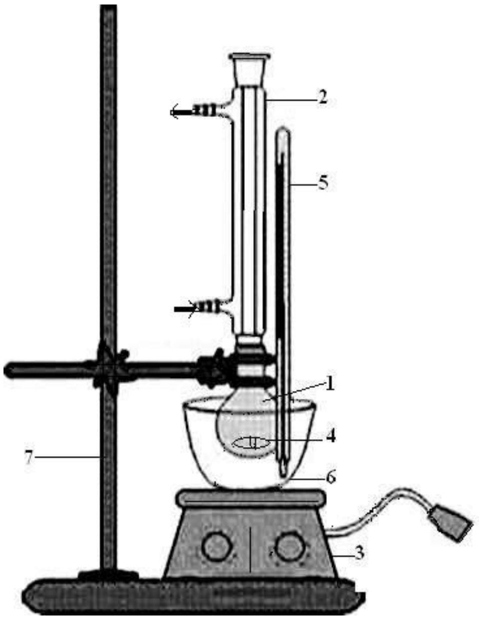

Figure 1: Experimental setup for batch reaction: (1) round bottom flask; (2) condenser; (3) hot plate with stirring; (4) magnetic stirrer; (5) thermometer; (6) heating oil; (7) stand.

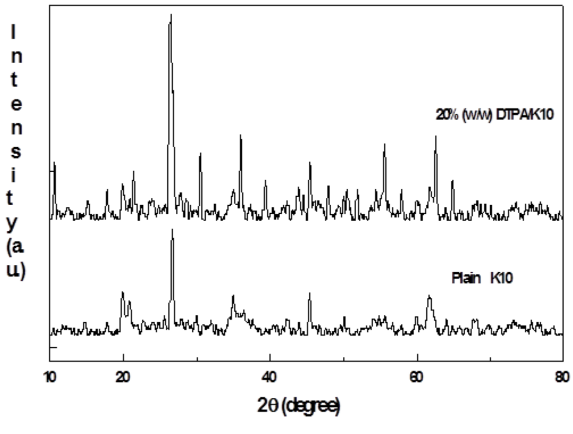

Figure 2: Powder X-ray diffraction (XRD) for plain K10 and 20% (w/w) DTPA/K10

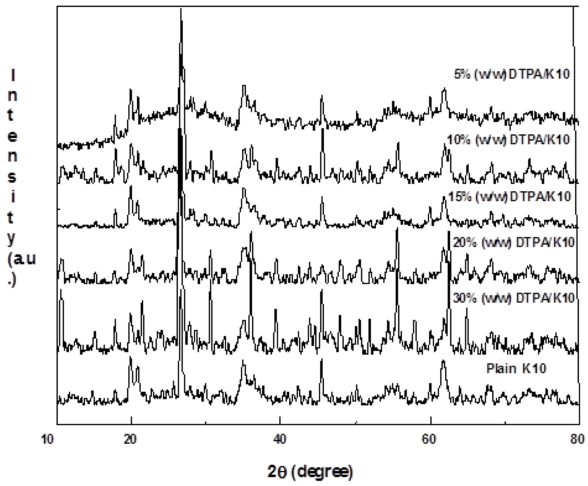

Figure 3: Powder X-ray diffraction (XRD) for different loading of DTPA on K10

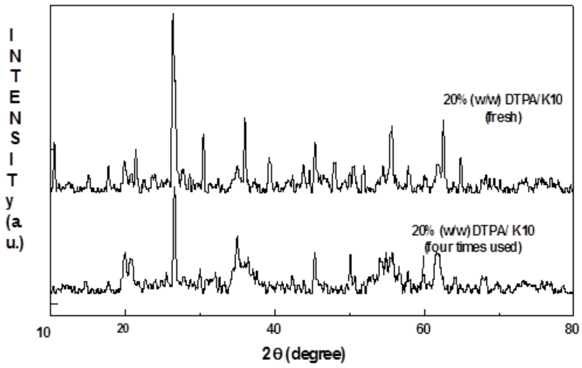

Figure 4: XRD pattern for fresh 20% (w/w) DTPA/K10 and four times used 20% (w/w) DTPA/K10

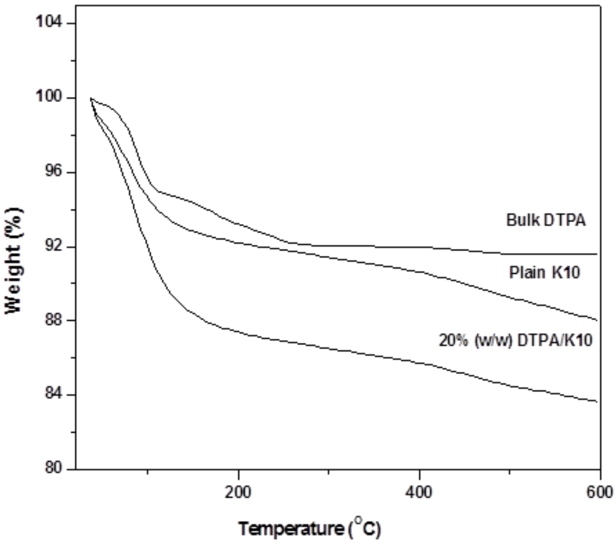

Figure 5: Thermal gravimetric analysis of bulk DTPA, K10 (plain), and 20% (w/w) DTPA/K10

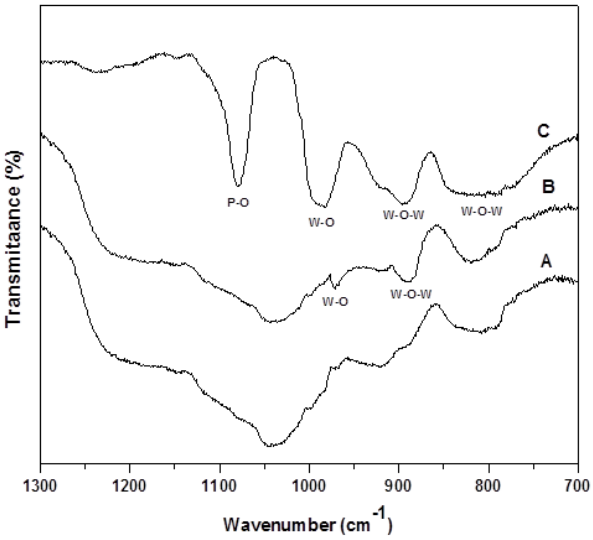

Figure 6: FTIR of (A) K10 (plain); (B) 20% w/w DTPA/K10, and (C) bulk DTPA

2.5 Analysis of feed and product

The liquid reaction products were analyzed by using gas chromatography (GC−1000) (packed column, liquid phase 5% SE-30, solid support CHW-HP, 1/8’ diameter × 8’ length) with nitrogen as a carrier gas and programmable temperature range of 40 to 200 0C. The reaction products were also confirmed by GC-MS (Shimadzu-QP 5000).

3. RESULTS AND DISCUSSION

In general, the esterification reaction follows pseudo first order kinetics in which one of reactant act as limiting reactant. In present case, we used levulinic acid as limiting reactant and ethanol is in excess as, levulinic acid is expensive than ethanol.

3.1 Catalyst characterization

3.1.1 Powder X-ray diffraction

The XRD patterns for all of the prepared samples are shown in Fig. 2 and Fig. 3. The XRD analysis confirmed that all synthesized catalysts are well crystalline in nature. From several synthesis runs, samples are selected on the basis of different percentage of DTPA loading. Fig. 2 and Fig. 3, show the differences in the nature of the phases for DTPA at different loading. The powder XRD pattern of K10 has shown a little crystallinity, whereas the DTPA loaded catalyst sample is observed to be more crystalline than plain K10 (Fig. 2). This additional intensity confirmed that the DTPA is properly deposited on the K10. Fig. 3 gives the trend of an increase in phase crystallinity with an increase in the percent DTPA loading on K10, which gives proportionately more active acid sites for the reaction.

Fig. 4 reveals the XRD patterns for fresh 20% (w/w) DTPA/K10 and four-times-used 20% (w/w) DTPA/K10. The used catalyst showed reduction in crystallinity vis-à-vis fresh catalyst, but it is not amorphous.

3.1.2 Nitrogen adsorption

The measured surface areas of all prepared samples are shown in Table 1. The micro pore surface area obtained from low-temperature nitrogen adsorption data is found to decrease in nonlinear fashion with an increase in DTPA loading on K10 (Table 1). This decrease in surface area may be due to the catalyst contains the highest amount of DTPA could be incorporated into the pores of K10 and remains in the mouth of the pores, reducing surface area. Entry 7 in Table 1 shows that there is further decrease in surface area on reuse of the catalyst.

3.1.3 Temperature programmed ammonia desorption (TPAD)

For temperature programmed ammonia desorption (TPAD) 0.1 g of sample is loaded and activated at 500 0C, in a quartz cell, in helium flow (20 mL/min) for the period of 2 h. Presaturation is accomplished by passing 10% (v/v) ammonia in helium for 1 h at ambient temperature.

Then the sample is flushed with helium for 1 h at 50 0C to remove excess ammonia. The adsorbed ammonia is desorbed in helium flow (30 mL/min) with a heating rate of 10 K/min, and the temperature is raised from 50 to 750 0C. Thermal conductivity detector (TCD) detects the desorbed ammonia. The TPAD profile is subjected to deconvolution by using Gaussian line shapes for quantitative estimation. Typically, DTPA when heated alone goes into the so-called lacunary form, but it still does not lose its acidity. DTPA supported on a K10 is maintained stability up to 500 0C. In this study, it is seen that desorption of ammonia is negligible beyond 500 0C, indicating all acidic sites are free of ammonia.

The variation in the number and distribution of acid sites as a function of DTPA loading is estimated by TPAD (Table 2). The nonlinear increase in acid site concentration with increase in DTPA loading on K10 from 5 to 30% is observed. The marginal increase of 0.3% in acid sites is observed with 30% (w/w) DTPA/K10 as compared to 20% (w/w) DTPA/K10. This may be due to blocking of the channels at select junctions, thereby rendering them inaccessible to the probe molecule.

Table 2: Total acidity of the catalysts prepared by TPAD

Sr.No.	Catalyst	Weak Acidity (mmol g^{-1})	Strong Acidity (mmol g^{-1})	Total Acidity (mmol g^{-1})	Increased of acid sites concentration after heteropoly acid loading (%)
1	Plain K10	0.120	0.019	0.139	-
2	5% (w/w) DTPA/K10	0.057	0.132	0.189	5.00
3	10% (w/w) DTPA/ K10	0.068	0.174	0.242	10.3
4	15% (w/w) DTPA/ K10	0.097	0.231	0.328	18.9
5	20% (w/w) DTPA/ K10	0.142	0.281	0.423	28.4
6	30% (w/w) DTPA/ K10	0.145	0.281	0.426	28.7
7	20% (w/w) DTPA/ K10 (four times used)	0.132	0.212	0.344	20.5

3.1.4 Thermal gravimetric analysis (TGA)

The thermal gravimetric analysis (TGAs) of DTPA show a weight loss of about 7% up to a temperature of 200 0C indicating loss of free and adsorbed water (Fig. 5). According to a study, the gradual weight loss of about 2% up to 500 0C corresponds to the mass loss due to the reaction between acidic protons and structural oxygen from phosphotungstic acid releasing water followed by decomposition to WO3 and POx species [31]. The thermal data of K10 show a steady loss of weight of about 10% up to 500 0C, which is attributed to the loss of physisorbed and interlayer water and also due to de-hydroxylation caused by the breaking of structural OH groups of the support. The TGA of supported DTPA onto K10 shows about 13% weight loss within the temperature range of 80–150 0C due to the loss of adsorbed water molecule. There was gradual weight loss of about 4% up to 500 0C and thus it indicated an increase in thermal stability of DTPA on the K10 support. This may be due to the formation of intermolecular bonding between the support and DTPA, and it indicated the presence of chemical interaction between the K10 and DTPA.

3.1.5 Fourier transform of infrared (FTIR)

Bulk DTPA shows the characteristic IR bands at 1080 cm-1 (P–O in central tetrahedral), 984 cm-1 (terminal W=O), 894 and 801 cm-1 (W–O–W) associated with the asymmetric vibrations of the Keggin poly-anion supported on K10. Some of the characteristic Keggin bands are observed at 982, 940, and 840 cm-1, and other bands are merged up with the K10 bands (Fig. 6). Fourier transform infrared (FTIR) of 20% (w/w) DTPA/K10 indicates that the primary Keggin structure is preserved after supporting it on K10.

3.2 Selection of catalyst

The montmorillonite K10 and DTPA on K10 are screened for the esterification of levulinic acid (LA) with ethanol at identical process parameters of 78 0C for 4 h, Molar ratio (ethanol: levulinic acid) of 6, catalyst loading of 20% (w/w) with respect to levulinic acid. The esterification of levulinic acid (LA) with ethanol occurs even in absence of catalyst, because the LA is able to catalyze the reaction itself. For this reason, thermal reaction is performed at 78 0C and a conversion of 3% of levulinic acid is achieved after 4 h. DTPA loaded sample showed better activity compared to plain K10 (Fig. 7). The activities are well correlated with the XRD, surface area, and acidity measured by ammonia TPD. Hence, the study is extended for the optimization of DTPA loading on K10.

3.3 Optimization of process parameters

3.3.1 Effect of DTPA loading on K10

The effect of DTPA loading on the K10 was studied systematically in the levulinic acid esterification reaction, under an identical set of experimental conditions (Fig. 8). When the DTPA loading on the K10 support is increased from 5 to 20% (w/w), there is an increase in conversion. This is well correlated with the corresponding increase in strong acidity with DTPA loading (Table 2). However, with further increase from 20 to 30% (w/w) DTPA/K10, there is decrease in conversion. This may be due to the presence of almost equal acidity of the catalyst above 20% (w/w) DTPA loading (Table 2). This would suggest that there is an onset of intra-particle diffusion beyond 20% (w/w) loading. It appears that the decrease in conversion to ethyl levulinate is due to narrow channels of the 30% (w/w) DTPA/K10 catalyst. However, in all cases the selectivity of ethyl levulinate remains 100%. 20%(w/w) DTPA/K10 catalyst is further investigated for the optimization of the catalyst loading for the reaction.

3.3.2 Effect of catalyst loading

The effect of 20% (w/w) DTPA/K10 catalyst was studied for the optimization of catalyst loading for same reaction (Fig. 9). The amount of 20% (w/w) DTPA/K10 catalyst was varied from 7 to 25% (w/w) of levulinic acid to assess its effect on the conversion of levulinic acids at a temperature of 78 0C, reaction time of 4 h and ethanol to levulinic acid molar ratio of 6. Fig. 9 shows that the conversion of levullinic acid increased with increase of catalyst loading. At higher catalyst loading, the equilibrium achieved sooner and accelerated the conversion due to increase of total number of acid sites available for the reaction (not shown in Fig. 9).

An increasing trend of levulinic acid conversion from 56 to 79% is observed with an increase in catalyst loading from 7 to 20%. In present case, catalyst loading of 20% is observed to be optimum. The LA conversion is also observed to increase from 79 to 79.2%, up to catalyst loading of 25% (Fig. 9). Research showed this marginal increase in conversion may be due to diffusional resistance in catalyst pores and less accessibility of active sites [32].

3.3.3 Effect of molar ratio of ethanol to levulinic acid

The esterification of levulinic acid with alcohol is a reversible reaction. High conversion could only be achieved if the backward reaction is minimized. The rate of backward reaction can be reduced by removing the product water simultaneously or by using excess of ethanol. In present reaction system, it is not easy to remove water, as the boiling point of ethanol (78 0C) is much lower than the boiling point of water (100 0C). Hence, the ethanol is used in excess to accelerate rate of forward reaction.

The ethanol to levulinic acid ratio was varied between 4 and 10 over 20% (w/w) DTPA/K10 catalyst at constant reaction temperature of 78 0C and catalyst loading of 20% (Fig. 10). Fig. 10 shows the effect of ethanol to LA ratio over 20% (w/w) DTPA/K10 catalyst. The LA conversion increased with increase of ethanol to LA ratio and maximum value approached to 79%.

In present case, molar ratio of ethanol to levulinic acid of 6 was observed to be optimum. The LA conversion was observed to decrease from 79 to 75% up to molar ratio of ethanol to LA of 10. At higher concentration of ethanol, multilayer formation of alcohol over active catalyst surface reduces the mass transfer with chemical reaction rate between LA and ethanol at active catalyst surface that leads to decrease in LA conversion.

3.3.4 Catalyst stability with reaction temperature

The reaction temperature was varied from 351 to 357 K in a batch reflux system over 20% (w/w) DTPA/K10 catalyst at ethanol to levulinic acid ratio of 6 and catalyst loading of 20%. Fig. 11 shows the effect of reaction temperature on levulinic acid conversion. Based on a study, esterification reaction of fatty acid with alcohol is an endothermic reaction [33,34]. Hence, at higher temperature less reaction time is required to achieve the maximum conversion of levulinic acid. The catalyst was active within temperature range of 351 to 357 K with reaction time of 4.5 h. The highest conversion was up to 79% when being esterified at 351 K (the boiling point of ethanol).

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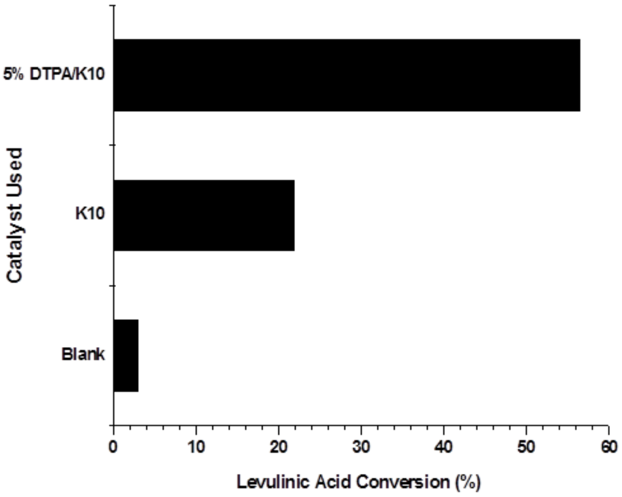

Figure 7: Conversion of levulinic acid esterification with ethanol for thermal reaction (blank); K10 and 5% (w/w) DTPA/K at reaction conditions: temperature: 78 0C; mole ratio (ethanol to levulinic acid) of 6; catalyst loading: 20% (w/w) of levulinic acid; reaction time: 4 h.

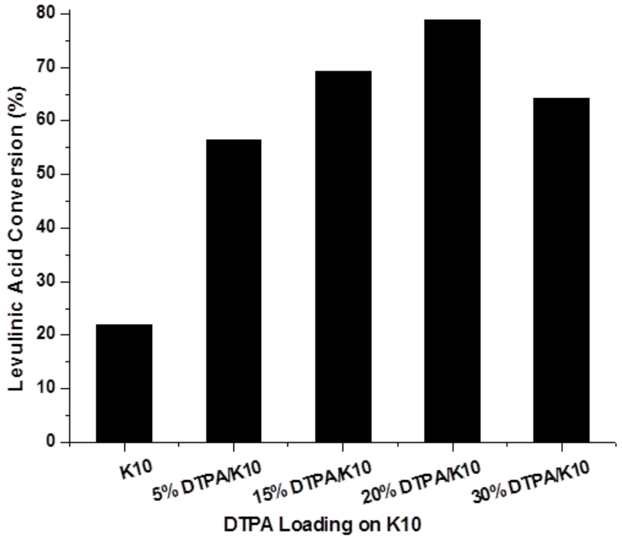

Figure 8: Effect of different percent DTPA loading on K10 on conversion of levulinic acid esterification with ethanol at reaction conditions: temperature: 78 0C; mole ratio (ethanol to levulinic acid) of 6; catalyst loading: 20% (w/w) of levulinic acid; reaction time: 4 h.

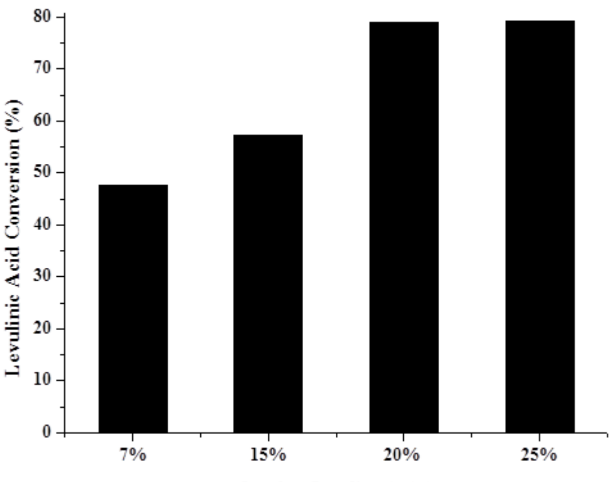

Figure 9: Effect of catalyst loading on esterification of levulinic acid by ethanol at reaction conditions: temperature: 78 0C; mole ratio (ethanol to levulinic acid) of 6; reaction time: 4 h.

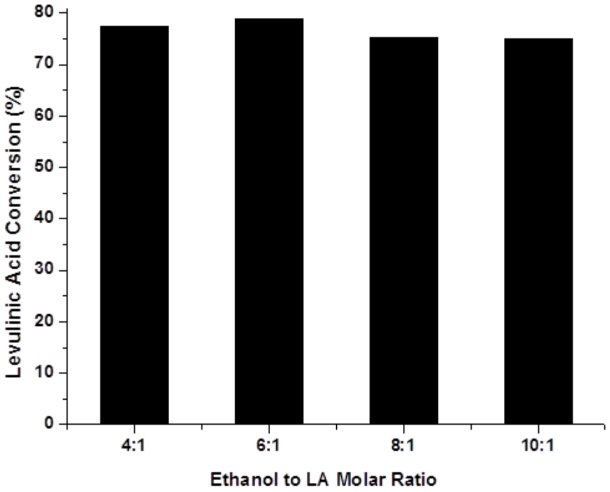

Figure 10: Effect of ethanol to levulinic acid molar ratio on esterification of levulinic acid at reaction conditions: temperature: 78 0C; catalyst loading: 20% (w/w) of levulinic acid; reaction time: 4 h.

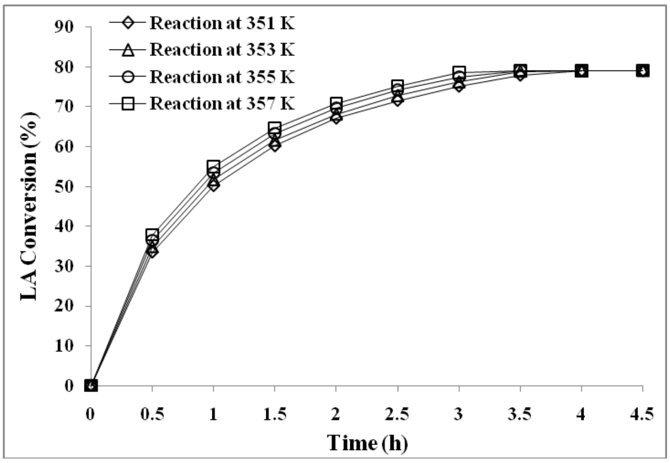

Figure 11: Catalyst stability with temperature: Catalyst: 20% (w/w) DTPA/K10 in levulinic acid esterification with ethanol at optimized process parameters: mole ratio (ethanol to levulinic acid) of 6; catalyst loading: 20%(w/w) of levulinic acid.

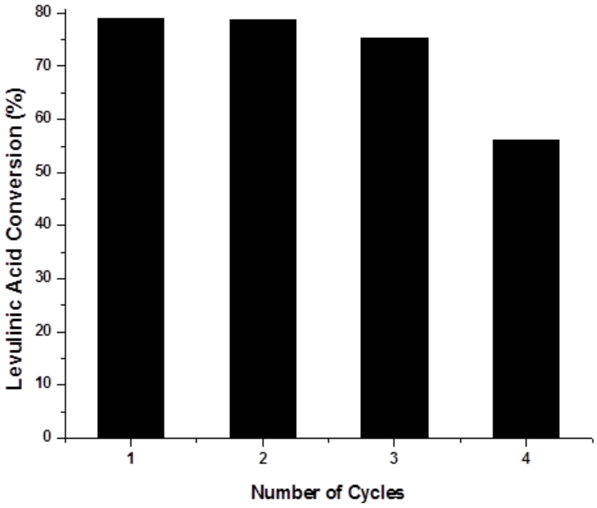

Figure 12: Reusability study of 20% (w/w) DTPA/K10 in levulinic acid esterification with ethanol at optimized process parameters: temperature: 78 0C; mole ratio (ethanol to levulinic acid) of 6; catalyst loading: 20% (w/w) of levulinic acid; reaction time: 4 h.

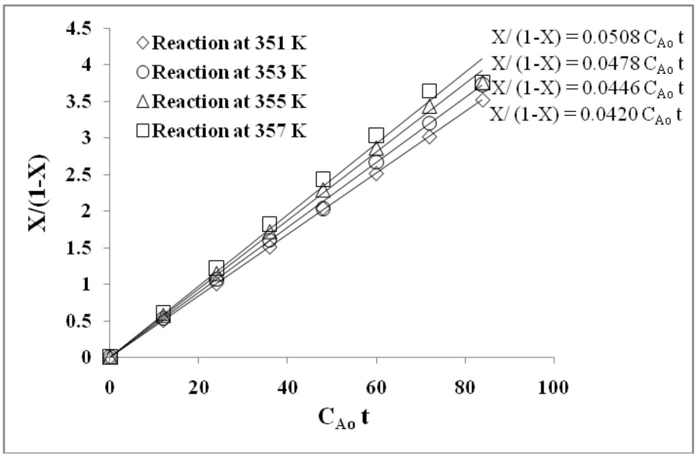

Figure 13: P-H model plot of X/(1-X) vs CAot to obtain reaction rate constants at different reaction temperatures.

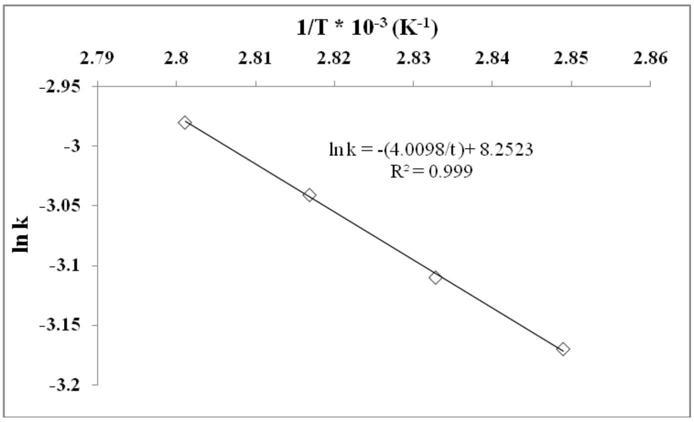

Figure 14: Arrhenius plot to obtain activation energy and pre-exponential factor.

3.4 Catalyst reusability

The reusability of 20% (w/w) DTPA/K10 was studied 4 times using identical experimental conditions of 78 0C, ethanol to LA molar ratio of 6 and reaction time of 4 h. After completion of each reaction, the catalyst was filtered and used without any post treatment.

As can be seen from Fig. 12, the catalyst activity is observed to be stable for two cycles (fresh and one reuse). After two cycles, the catalyst activity decreased marginally (third cycle) and then substantially (fourth cycle), giving LA conversion of 56%. The used catalyst is subjected to detailed characterization by various techniques such as XRD (Fig. 4), nitrogen adsorption (Table 1) and TPAD (Table 2). The results are well correlated with the experimental data. The used catalyst has shown a decrease in XRD crystallinity, surface area and acidity, but the catalyst is not completely deactivated.

3.5 Kinetic Modeling

The esterification reaction of levulinic acid (A) with ethanol (B) for producing ethyl levulinate (E) and water (W) in the presence of solid acid catalyst is given as follows:

$$aA + bB \leftrightarrow eE + wW$$

The kinetic model of this work was built on the following assumptions [35-38]:

(1) The rate of the non-catalyzed reactions is negligible compared with the catalyzed reactions;

(2) The catalytic activity of all sites on the solid catalyst surface is the same.

(3) The whole reaction system is assumed as an ideal solution Under these conditions, the reaction is assumed to be pseudo-homogeneous (P-H model), second-order in the forward and reverse direction.

The reaction rate can be described as:

$$-\left(\frac{dC_A}{dt}\right) = k\,C_A{}^{a}\,C_B{}^{b} - k'\,C_E{}^{e}\,C_W{}^{w} \tag{1}$$

Where *CA, CB, CE, CW* denote the concentration of levulinic acid, ethanol, ethyl levulinate and water, respectively; *a, b, e, w* refers to their reaction orders; *k* and *k'* are kinetic constants for the forward and reverse reaction, respectively.

kCA^{a} can be a constant as the concentration of ethanol is much higher than that of other components in our experimental conditions. k is far larger than *k'*, so Eq. (1) can be simplified as follows:

$$-\left(\frac{dC_A}{dt}\right) = kC_A{}^{n} \tag{2}$$

$$C_A = C_{Ao}(1-X) \tag{3}$$

X and *CAo* refer to the conversion and the initial concentration of levulinic acid. Eq. (3) can be converted to Eq. (4)

$$-\left(\frac{dX}{dt}\right) = \frac{k}{C_{Ao}}[C_{Ao}(1-X)]^{n} = k_1\,[C_{Ao}(1-X)]^{n} \tag{4}$$

Where,

$\left(\frac{k}{C_{Ao}}\right) = k_1$ when n≠1 Eq. (4) is integrated to,

$$(1-X)^{1-n} = 1+(n-1)k_1 t\, C_{Ao}{}^{n} \tag{5}$$

Table 3: Rate constants and R^2 values for esterification reaction at different reaction temperatures

Reaction temperature (K)	351	353	355	357
Rate constant k ($dm^3\ mol^{-1}\ h^{-1}$)	0.0420	0.0446	0.0478	0.0508
R^2	0.999	0.999	0.997	0.988

Thus, Eq. (5) can be changed to Eq. (6).

$$\frac{X}{(1-X)} = k\,C_{Ao}\,t \tag{6}$$

By solving the model and optimizing the objective function, the kinetic parameters for each experiment are determined. The reaction rate constant is performed by a linear regression. Fig. 13 shows a linear relationship between X/(1-X) and CAot. The reaction rate constant k is obtained from the slope of each straight line as shown in Table 3. The reaction rate constants k increased with an increase in reaction temperature. Besides, the straight line fitted well with the experimental data (Fig. 13). This is a clear indication that the P-H kinetic model is valid.

To consider the effect of reaction temperature on the kinetic model, the Arrhenius equation is listed as:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \tag{7}$$

Where R= gas constant (8.31 J mol^{-1} K^{-1}).

The plots of ln k can be used as a function of the reciprocal temperature:

$$lnk = \left(-\frac{E_a}{RT}\right) + lnA \tag{8}$$

Both the frequency factor A, and the activation energy Ea, were obtained by non-linear regression.

The dependence of the reaction constants on reaction temperature is described by the Arrhenius equation (Eqs. (7) and (8)). A straight-line (Fig. 14) represents the plot of ln k vs. 1/T and the activation energy (Ea) is obtained from the slope of the line. The pre-exponential factor (A) is found to be 3836.44.

The activation energy found for the esterification of levulinic acid with ethanol over 20% (w/w) DTPA/K10 catalyst is 33.32 kJ/mol which implies the esterification reaction is kinetically controlled owing to the high activation energy. According to a study, the activation energy obtained in present study is less than the reported value (Table 4) [39,40]. The difference could be due to the difference system and catalyst used in the present study.

Table 4: Kinetic studies on esterification reaction

Substrate	Solvent	Catalyst	Activation Energy (kJ mol^{-1})	References
Oleic acid	Methanol	*p*-TSA	67.1	[33]
Palmitic acid	Isopropanol	ZnA/SC	36.02	[34]
Palmitic acid	Isopropanol	*p*-TSA	40.77	[34]
Oleic acid	Methanol	CCM	35.97	[37]
Palmitic acid	Isobutyl alcohol	Sulfuric acid	58	[39]
Levulinic acid	*n*-butanol	Sulfuric acid	54.27	[40]
Levulinic acid	Ethanol	15%(w/w)DTPA/K10	33.34	Present case

4. CONCLUSION

Esterification of levulinic acid (LA) with ethanol to ethyl levulinate is systematically studied in batch process using heteropoly acid on K10 as solid acid catalyst. 20% (w/w) Dodecatungstophosphoric acid (DTPA) on K10 is found to be the most active solid acid catalyst, with 79% levulinic acid conversion and 100% selectivity towards ethyl levulinate at optimized process parameters. The study is further extended to see the potential of 20% (w /w) DTPA/K10 by investigating various process parameters such as DTPA loading on K10, catalyst loading, ethanol to LA molar ratio etc. The catalyst is observed to be reusable for two cycles (fresh and one recycle) and then there is a marginal decrease during third cycle and substantial decrease during the fourth cycle. Thus, 20% (w /w) DTPA/K10 is an efficient catalyst for the esterification of levulinic acid (LA) with ethanol to ethyl levulinate. A P-H kinetic model is also developed to predict the kinetics of the esterification using 20% (w/w) DTPA/K10 catalyst. The experimental results follow second order reaction rate. This work reveals the use of DTPA/K10 as potential solid acid catalyst for esterification of LA to ethyl levulinate in order to make the process eco-friendly and economical.

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