Parametric and kinetic study for synthesis of biofuel additive using low-cost ion-exchange resin as a catalyst

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Abstract:
Levulinic acid (LA) is a valuable renewable resource that can serve as a versatile biomass-derived building block for the synthesis of organic chemicals, providing a sustainable alternative to depleting fossil fuel resources. Catalytic esterification of LA with alcohol yields levulinate esters, which find numerous applications including perfumes and fuel additives. In this study, the performance of Indion 190 as a solid acid catalyst was investigated for the esterification of LA with n-butanol to produce n-butyl levulinate (BL). The effects of reaction time, catalyst loading, temperature, and molar ratio of LA to butanol were examined One Factor at a Time (OFAT) to optimize levulinic acid conversion. The highest conversion of LA, which was 92.59%, was attained with a reaction time of 6 hours at 100 °C, utilizing a catalyst loading of 1.25 wt% Indion 190 for a molar ratio (LA: butanol) of 1:8. In the kinetic study of the reaction, an activation energy of 65.5 kJ/mol was obtained. Indion 190 proved to be a promising, cost-effective solid acid catalyst for the production of levulinate esters, providing an eco-friendly pathway for the continuous production of butyl levulinate.

Keywords: Levulinic acid; Butanol; Fuel additive; Ion-exchange

1. Introduction

The urgent need to develop sustainable and economically viable processes for biomass conversion has driven extensive research efforts worldwide. Organic esters, particularly levulinic, acid and its derivatives, have gained significant importance in various industries, such as cosmetics, pharmaceuticals, polymers, and food [1]. Levulinic acid (LA), with its ketone and carboxylic acid functional groups, serves as a versatile building block for synthesizing a wide range of organic chemicals, including levulinate esters [2, 3]. Levulinic acid offers a wide range of applications, from resins and biofuels to pharmaceutical ingredients, highlighting its potential as a valuable platform chemical [4, 5]. Particularly noteworthy is butyl levulinate (BL), a levulinate ester with remarkable properties, making it an ideal fuel additive for both gasoline and diesel [6, 7]. The synthesis of levulinate esters, especially n-butyl levulinate (BL), has attracted considerable interest due to its potential as an excellent fuel additive for gasoline and diesel [8]. BL exhibits high miscibility, excellent transport properties, low vapor pressure, and a stable flashpoint, accentuating its significance in organic process industries as a plasticizing agent, solvent, and odorant [9]. To achieve environmentally friendly and recyclable processes, the utilization of heterogeneous catalysts becomes essential. Conventional homogeneous catalysts, such as mineral and organic acids, and alkalis like NaOH or KOH, pose serious environmental concerns and necessitate intricate downstream processing. Additionally, their non-reusability and corrosive nature impose challenges in the production process [10–12].

The present work focuses on a novel heterogeneous catalyst, specifically Indion 190 resin. Leveraging the high surface area and elevated catalytic activity of Indion 190 resin, it serves as a promising alternative to homogeneous catalysts. This catalyst exhibits physical and chemical stability, no toxicity, and is environmentally compatible, enabling ease of handling, separation, and reusability [13, 14]. The versatility of Indion 190 resin extends to its consecutive reuse without compromising the yield of the desired products,
making it an attractive candidate for catalyzing the synthesis of butyl levulinate.

In this research, we explored the synthesis of butyl levulinate using Indion 190 resin as the heterogeneous catalyst. Various key parameters, reaction temperature, reaction time, catalyst loading, and initial reactant concentration, are investigated to understand their effects on the esterification process. The kinetics of the esterification reaction are analyzed using the power law kinetic model to correlate experimental data. In conclusion, this study aims to provide valuable insights into the use of heterogeneous catalysis, specifically Indion 190 resin, for the eco-friendly production of n-butyl levulinate from levulinic acid. By employing a green and sustainable approach, this research contributes to the ongoing efforts to identifying economically viable pathways for converting biomass into valuable organic chemicals on a commercial scale.

2. Materials and methods

2.1 Chemicals and reagents

Chemicals and solvents are obtained from Sigma-Aldrich. Levulinic acid (>97%) and n-butanol (98.0%), ethanol potassium hydroxide was used for the esterification process.

2.2 Catalyst

The solid acid catalyst, Indion 190, employed for the esterification reaction was generously provided by Ion-Exchange India Ltd. Indion 190 is a remarkable solid catalyst featuring cross-linked three-dimensional structures of polymeric material, which are derived through the sulfonation of a copolymer consisting of polystyrene and divinyl benzene (DVB). The catalyst exhibits a distinctive appearance, presenting as opaque, faint dark grey-coloured solid spherical beads. These beads possess superior physical and chemical stability, making them ideal for catalysing esterification reactions efficiently and selectively. With its well-defined morphology and high catalytic activity, the Indion 190 serves as a reliable and environmentally compatible catalyst, contributing to the advancement of sustainable chemical transformations. The specifications of Indion 190 catalyst are listed in Table 1.

2.3 Experimental setup and procedure

The esterification procedure was carried out using a 250 mL three-neck round-bottom flask, which was fitted with a heating rotary mantle. The rotary mantle was equipped with a temperature control knob for regulating the heating and a stirrer with an adjustable rotational speed control knob to manage the magnetic stirring rate. To effectively condense vapours and prevent any loss of reagents or products, a vertically oriented spiral condenser was connected to the reaction flask. This condenser demonstrated proficient vapour condensation capabilities, facilitating their reintroduction into the ongoing reaction mixture. For precise monitoring of the reaction temperature, a mercury thermometer was carefully inserted into the flask. The thermometer possessed a high level of accuracy, with deviations limited to within ± 0.5 K, thereby ensuring meticulous temperature measurements during the entire esterification process. Predetermined quantities of n-butanol and levulinic acid were mixed and introduced into the reactor. The reaction mixture was then heated to the desired temperature and then the calculated amount of catalyst was added to the mixture, and the time was recorded as $t = 0$. To investigate the reaction’s progress at different time intervals, samples of the reaction mixture were withdrawn at regular intervals. These samples were carefully collected and placed into a reference container for subsequent analysis. By systematically collecting samples over time, the experimental data enabled the observation and characterization of the reaction kinetics and product formation, providing valuable insights into the reaction’s behavior and performance of KOH. The quantification of the conversion of the starting material, LA was accomplished by titrating the extracted sample against a 0.05 M solution of alcoholic KOH. The product formation was confirmed using a Gas Chromatograph.

3. Results and discussions

3.1 Effect of time

Figure 1 shows a time-dependent graph of LA conversion in order to optimize the reaction time required for the conversion of LA. At time 0, LA and butanol were added in the molar ratio of 1:8. The reaction was studied over a six-hour period at a temperature of 100 °C, using a 1.25 wt% catalyst. It was observed that initially, the conversion of LA increased rapidly, reaching 45.37% and 61.11% by the end of the second and third hour respectively. But as the reaction proceeds, the conversion rate decreases, and at the sixth hour, conversion reaches to 92.59%. With further increase in time, after the 7th hour, there is not a significant increase in LA conversion. Thus, reaction time was optimized at 6 hours.

<table>
<thead>
<tr>
<th>parameter</th>
<th>specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>appearance</td>
<td>dry, opaque, grey colored beads</td>
</tr>
<tr>
<td>ionic Form</td>
<td>hydrogen</td>
</tr>
<tr>
<td>% moisture Holding capacity</td>
<td>51 to 55</td>
</tr>
<tr>
<td>% H+ ions concentration, meq/dry g.</td>
<td>4.7 min.</td>
</tr>
<tr>
<td>% whole beads</td>
<td>95.0 Min.</td>
</tr>
<tr>
<td>beads size distribution, mm</td>
<td>0.3 to 1.2</td>
</tr>
</tbody>
</table>
3.2 Effect of catalyst loading

The amount of catalyst significantly affects the conversion of the reactants. The catalyst loading was varied from 0.5 wt% to 1.5 wt% of the liquid phase reaction volume in increments of 0.25%. The reaction was carried out at 100 °C over a period of 6 hours for a mole ratio of 1:8. The conversion values obtained at various catalyst loadings after six hours are represented in Figure 2. It was observed that as the catalyst loading increased from 0.75 wt% to 1.25 wt%, conversion of LA increased significantly from 76.9% to 92.59% respectively due to the increasing availability of active sites on the catalyst. Further increase in catalyst loading to 1.5 wt% resulted in only a marginal increase in LA conversion of 93.56%. Thus, the catalyst loading was optimized at 1.25 wt%.

3.3 Effect of mole ratio

The esterification of LA by n-butanol is a second-order, reversible reaction. In order to achieve a higher conversion of LA to butyl levulinate, the rate of the backward reaction must be suppressed. According to LeChatelier’s principle, if butanol is used in excess, the reaction equilibrium will shift in the forward direction. Moreover, butanol can be easily recycled. The molar ratio of LA to butanol was varied in the range of 1:4, 1:6, 1:8, and 1:10 at constant reaction conditions of 1.25 wt% catalyst loading and a temperature of 100 °C for a period of 6 hours. LA conversion of 70%, 88%, 92.59%, and 88% was achieved for the mole ratios of 1:4, 1:6, 1:8 and 1:10 respectively at the end of the sixth hour, as shown in Figure 3. LA conversion increases from 70% to 92.59% with an increase in a molar ratio from 1:4 to 1:8 due to the use of excess butanol which favors the forward reaction. However, the conversion decreases to 88% for a mole ratio of 1:10. The reason for this may be the sharp decrease in LA concentration as compared to the amount of butanol. As a result, the available active sites on the catalyst are mostly occupied by butanol, leaving very little room for LA, thereby lowering the conversion. Moreover, although the excess butanol is expected to accelerate the forward reaction and enhance LA conversion, there may be an increase in operation cost and reactor size. Owing to the above-mentioned reasons, 1:8 is selected as the optimum molar ratio that will be used in further studies.

3.4 Effect of temperature

Since the rate constant of the esterification reaction is temperature dependent, it is important to study the effect of temperature on the reaction kinetics as well as the catalytic activity. The reaction was carried out at 80 °C, 90 °C, 100 °C and 110 °C using 1.25 wt % catalyst loading and a molar ratio of 1:8. The graph shown in Figure 4 represents LA conversion values of 67.3%, 78.16%, 92.59%, 94.74% obtained after 6 hours at 80 °C, 90 °C, 100 °C and 110 °C respectively. An increase in temperature decreases the viscosity of the reaction medium and allows the reactants to reach the catalyst active sites without much resistance and the rise in temperature also provides the activation energy needed for the reaction thus leading to better conversion of LA. It was observed that there is a sharp increase in conversion from 67.3% at 80 °C to 92.59% at 100 °C. Further increase in temperature to 110 °C resulted in only a marginal increase in LA conversion. Therefore, the reaction temperature is optimized at 100 °C.
4. Reaction kinetics

The esterification of LA with n-butanol (molar ratio 8:1 and catalyst loading 1.25 wt%) is a reversible reaction that gives the products butyl levulinate and water, as shown in equation 1.

\[
\text{levulinic Acid} + \text{butanol} \leftrightarrow \text{butyl levulinate} + \text{water} \quad (1)
\]

Assuming the entire system to be an ideal solution, and that all active sites on the catalyst are identical, the reaction rate of reaction for LA eqn. (1) is given as:

\[
-r_{LA} = k_1 C_{LA}^{\alpha_1} C_{B}^{\beta_1} - k_2 C_{BL}^{\alpha_2} C_{W}^{\beta_2} \quad (2)
\]

Since butanol is taken in excess, reaction equilibrium proceeds only in the forward direction. Therefore, the reaction can be assumed to be irreversible. This causes eqn. (2) to be reduced to eqn. (3) and (4).

\[
-r_{LA} = k_1 C_{LA}^{\alpha_1} C_{B}^{\beta_1} \quad (3)
\]

\[
C_{LA} = C_{LAO}(1 - X_{LA}) \quad (4)
\]

The Integral method of analysis is used to determine the rate constant of the reaction. Assuming that the reaction is second order, the following equation 4 is obtained [15]:

\[
-r_{LA} = k_1 C_{LAO}^2 (1 - X_{LA})(M - X_{LA}) \quad (5)
\]

Where

\[
M = \frac{C_{BO}}{C_{LAO}} , \quad k_1 = k \ln \left[ \frac{M - X_{LA}}{M(1 - X_{LA})} \right] = k C_{LAO} (M - 1) t \quad (4)
\]

A graph of \(\ln[(M - X_{LA})/(M(1 - X_{LA}))] \) versus time is plotted at 80 °C, 90 °C, 100 °C and 110 °C, for a mole ratio of 1:8 and catalyst loading 1.25 wt%, as shown in Figure 5. The slope of each line is used to calculate the k value, which is presented in Table 2.

Furthermore, in order to calculate the activation energy of the catalyst, we use the Arrhenius equation given in eq 5, Figure 6 shows a plot of \(\ln(k) \) versus \(1/T\), from which we get an activation energy of \(E_a = 65.5 \text{ kJ/mol}\).

\[
k = k_0 e^{-\frac{E_a}{RT}} \quad (5)
\]

Table 2. k values at different reaction temperatures.

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>0.2655</td>
</tr>
<tr>
<td>90</td>
<td>0.3931</td>
</tr>
<tr>
<td>100</td>
<td>0.9666</td>
</tr>
<tr>
<td>110</td>
<td>1.5156</td>
</tr>
</tbody>
</table>

5. Comparison with literature

Appaturi, J.N., et al. presented a detailed review of the synthesis of levulinate esters from levulinic acid using different heterogeneous catalysts mainly, mesoporous silicas, zeolites, metal-organic frameworks, carbonaceous materials,
Table 3. Butyl levulinate yield at optimum reaction conditions using different catalysts.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>optimized reaction conditions</th>
<th>yield (%)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA*</td>
<td>time (hours)</td>
<td>mole ratio (LA: butanol)</td>
<td>temperature (°C)</td>
</tr>
<tr>
<td>MCM-41**</td>
<td>8</td>
<td>1:5</td>
<td>120</td>
</tr>
<tr>
<td>titanate nanotube</td>
<td>8</td>
<td>1:5</td>
<td>100</td>
</tr>
<tr>
<td>LMT-SO₃H***</td>
<td>4</td>
<td>1:1.4</td>
<td>120</td>
</tr>
<tr>
<td>TiO₂ nanoparticles</td>
<td>8</td>
<td>1:10</td>
<td>120</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>4</td>
<td>1:6</td>
<td>120</td>
</tr>
</tbody>
</table>

H-BEA* - SiO₂/Al₂O₃ = 25; MCM-41** - mesoporous silica (Al/Si = 6.6); LMT-SO₃H*** - lignin-montmorillonite complex modified with sulfonic acid (LMT-SO₃H).

enzymatic catalysts, and ion exchange resins [15]. Sharieff, S., et al. used TiO₂ and WO₃ sulphonated nanocomposite as a solid acid catalyst and optimized the esterification reaction parameters as 1:8 mole ratio (LA: n-butanol), 120 °C temperature and 1.5 wt% catalyst loading, and obtained a LA conversion of 93.1% [22]. For the same reaction, Patel, A., et al. employed a Ti-ATMP catalyst and reported a conversion of 92.06% at optimum reaction conditions of 5.2 hours reaction time, 120 °C temperature, and a catalyst loading of 8.7 wt% [23]. Table 3 shows the yield of butyl levulinate obtained by employing various catalysts in the esterification of LA with butanol.

Tejero, M., et al. compared Dowex 50Wx2, a gel-type ion exchange resin, and Amberlyst 15 catalysts in the esterification of LA and butanol at optimum conditions of 8 hours reaction time, 1:3 mole ratio, 0.8% catalyst loading, and 80 °C temperature, and obtained 94% and 46% LA conversions, respectively [24]. Heterogeneous catalysts have also been employed to determine the yield of other esters such as methyl levulinate (ML) and ethyl levulinate (EL). SiO₂ catalyst modified with 3M H₂SO₄ produced 69%, 54%, and 40% yield of ML, EL, and BL, respectively [25]. Yang, F. and J. Tang obtained a yield of 99% EL using HClO₄/SiO₂ as an acid catalyst [26]. Trombettoni, V., et al. used 10 mol% of Aquivion mP98 catalyst and reported a pentyl levulinate yield of 88% [27].

6. Conclusions

In the present work, the esterification of levulinic acid with n-butanol using Indion 190 as a solid acid catalyst was studied in order to optimize the reaction parameters such as time, catalyst loading, molar ratio, and temperature. A reaction time of 6 hours, a molar ratio of 1:8 (LA: B), a temperature of 100 °C, and a catalyst loading of 1.25 wt% were found to be the optimum parametric values which resulted in LA conversion of 92.59%. Furthermore, in the kinetic study of the reaction, the rate constant values at various temperatures were used in the standard Arrhenius equation to calculate the activation energy of the catalyst, which was 65.5 kJ/mol. Thus, when compared to other catalysts, Indion 190 is an efficient and cost-effective option for esterification under mild conditions.

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Ethical Approval

This manuscript does not report on or involve the use of any animal or human data or tissue. So the ethical approval does not applicable.

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Authors Contributions

All authors have contributed equally to prepare the paper.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


