**Liquid-phase synthesis of *sec*-butyl levulinate by esterification of levulinic acid with 1-butene over Amberlyst-15**

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**Highlights**

* Esterification of levulinic acid with 1-butene over Amberlyst-15 is technically feasible
* The proposed reaction pathway entails very low byproducts formation
* High temperature and excess of levulinic acid gives high yield of sec-butyl levulinate
* Amberlyst-15 is a promising catalyst for the *sec*-butyl levulinate production

**1. Introduction**

Liquid-phase synthesis of *sec*-butyl levulinate (SBL) by esterification reaction of levulinic acid with 1-butene over an acidic ion-exchange resin (Amberlyst 15) has been studied in a batch reactor. The use of SBL in transportation fuels formulation is of interest due to some of its properties, which make SBL a potential candidate for blending in both diesel and gasoline fuels. For instance, when blended in diesel, butyl levulinates reduce vapor pressure and improve the lubricity, conductivity, and cold flow properties of the fuel, which leads to cleaner combustion, and are completely soluble below the diesel cloud point (around −25.8 °C) [1]. However, levulinates exhibit low cetane numbers, which entails that their inclusion in diesel formulation requires additional cetane-enhancing additives. With respect to gasoline, high blending octane quality is achieved by adding butyl levulinates. For instance, blending values of RON and MON of 107 and 98, respectively, have been reported for 10 %vol. addition of SBL [2].

On the other hand, since levulinates are synthesized from levulinic acid (LA), which is a non-edible lignocellulose derivative, SBL can contribute in achieving the biofuel target in current EU legislation, which sets a minimum 10 %vol. of biomass-based oxygenates to improve fuel automobile quality by 2020 [3].

Conventional production of butyl levulinates is achieved by: 1) esterification of LA with butanol, 2) furfuryl alcohol-butanol alcoholysis, and 3) direct butanolysis of saccharides or polysaccharides; all of which are acid-catalyzed reactions. In most cases, ester formation is limited due to side reactions responsible for the formation of, for instance, dialkylether, water and polymerization products. Alternative pathway synthesis for butyl levulinates involves replacing the alcohol for an olefin as the esterification agent, which poses lower byproducts formation than conventional pathways. In addition, residual refinery streams containing “spent” C4 compounds, which are usually regarded as low-value streams, can be re-valorized by using them as the olefin source, taking advantage of the fact that these streams are usually rich in linear butenes, butane, and isobutane.

Therefore, and given the scarce number of literature references on the proposed synthesis reaction using ion-exchange resins as catalysts, the present work is aimed at determining the optimal reaction conditions for the batch-mode liquid-phase synthesis of *sec*-butyl levulinate over Amberlyst-15, in terms of temperature and initial reactants concentration.

**2. Methods**

Reactants were LA (>98 %wt., Across Organic) and 1-butene (>99.9 %GC, Air Liquide). Amberlyst‑15 (The Dow Chemical Company) was used as the acidic ion-exchange resin catalyst (acid capacity of 4.81 meq H+/g, BET surface area of 42.1 m2/g, BET pore volume of 0.328 cm3/g, and maximum operating temperature of 393 K).

Experiments were performed following a two-factor face-centered experimental design in which temperature ranged from 323 to 373 K and initial AL to olefin molar ratio was varied between 0.5 and 2.0. The catalyst load was set at 5 g (about 3 %wt.). All experiments were carried out in a 200 cm3 stirred-tank reactor equipped with a six-blade magnetic stirrer operated in batch mode. The pressure was set at 2.5 MPa by means of N2. Samples were taken in-line at different reaction times and analyzed by GC-MS using a capillary column (HP-PONA 19091S-001, J&W Scientific; 100% dimethylpoly-siloxane, 50m×0.20mm×0.50 μm). The typical duration for every experimental run was of 5 h, at least.

**3. Results and discussion**

Almost complete conversion of 1-butene was achieved in all of the experiments, whereas some LA remained unreacted at the end of the runs. In fact, 1-butene readily isomerizes to *cis*- and *trans*-2-butenes, which in turn react with LA to give the corresponding ester, SBL. Results showed only minimal side reactions extension regardless of the assayed experimental conditions, being the sum of all formed byproducts, mainly 2-butanol and olefin dimers, always below 5 %GC. Table 1 lists main results in terms of yield towards SBL from 1-butene. As seen in the table, higher yield is achieved at high temperature and high initial molar ratio.

**Table 1.** Yield (Y) of SBL from 1-butene.

|  |  |  |
| --- | --- | --- |
| ***T* (K)** | ***R*°A/O** | Y a **(%)** |
| 323 | 0.5 | 21 |
| 323 | 2.0 | 54 ± 6 |
| 373 | 0.5 | 88 |
| 373 | 2.0 | 98 |
| 348 | 1.0 | 89 |
| a Yield calculation is based on GC areas. |

**4. Conclusions**

The feasibility of the proposed chemical reaction pathway is strongly supported by the low amount of formed byproducts, which is the main drawback of conventional synthesis of butyl levulinates. The highest assayed temperature (373 K) and an excess of levulinic acid in the reactants mixture favors the formation of the desired product. Amberlyst-15 is a promising catalyst for the proposed reaction, since it allows high conversions at relatively low temperature while being an inexpensive catalyst.

**References**

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