

Octyl levulinate biolubricant liquid-phase synthesis from levulinic acid and octanol over acidic ion-exchange resins.

Rodrigo Soto^{1*}, Jordi-Hug Badia, Eliana Ramírez, Roger Bringué, Carles Fité, Montserrat Iborra, Javier Tejero

1 University of Barcelona. Department of Chemical Engineering and Analytical Chemistry, Martí i Franquès 1-11, 08028, Barcelona, Spain

**Rodrigo soto: r.soto@ub.edu*

Highlights

- Octyl levulinate was produced from levulinic acid and 1-octanol esterification over acidic resins.
- All the resins were active with LA moderate conversions around 54-67%.
- The OL initial formation rates ranged from 0.042-0.166 mol/(s·kg cat) being Dow2 the most active resin.
- The resin morphology in swollen state allows to explain the catalytic activity.

1. Introduction

The biorefinery concept is based on the development of necessary technology infrastructure using biomass feed as raw material to substitute current refineries using oil. Alkyl levulinates are bioderived materials with great potential as fuels and additives to conventional fuels. They can improve engines efficiency by high octane ratings, reduce overall harmful emissions, low freezing point and entail lubricating capability [1]. Moreover, they present multiple applications in the chemical industry, e.g., as green solvents, additives to polymers and perfumes, flavoring preparations and latex coating compositions. Among alkyl levulinates, octyl levulinate (OL) offers profitable advantages such as a high viscosity index that makes it an efficient lubricant, its low freezing point and low volatility [2]. OL synthesis can be carried out by esterification of levulinic acid (LA) with 1-octanol (OcOH), Figure 1, over acid catalysts, e.g. acidic ion-exchange resins (IERS) and zeolites. Since both LA and OcOH can be produced from biomass, OL encompass the feature of being a fully biomass derived compound, being therefore a green alternative to current lubricants. This work aims to shed light into the IERS properties that can maximize their catalytic activity for the synthesis of OL, which are still unclear to the best of our knowledge.

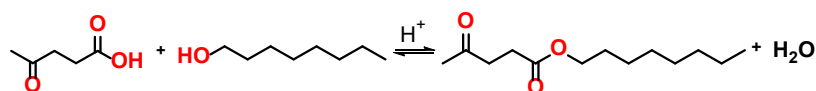


Figure 1. Reaction scheme for the production of octyl levulinate.

2. Methods

Levulinic acid and 1-octanol were used as reactants. For analytical purposes, OL was purified in our laboratories by liquid-liquid extraction (50 %vol, with water) followed by distillation in a packed column. Experimental runs were carried out isothermally, at 100 °C during 4 h, in a 250 cm³ stainless-steel batch reactor equipped with a six-blade stirrer (Autoclave Engineers, US). The reactor was heated with a jacket connected to a thermostatic bath with a mixture of dimethyl sulfoxide and thermal oil, controlled within an accuracy of ± 0.1 °C. The stirrer speed was set at 750 rpm and the reactor pressure to 30 bar. Initial molar ratio OcOH-to-LA ($R_{OH/LA}^0$) was set at 1 for all the runs using 3 g of dry catalyst mass. A variety of acidic commercial ion-exchange polystyrene-divinylbenzene sulfonated resins was selected in order to cover a great range of morphological properties: Macromolecular resins Amberlyst™ 15 (A15), Amberlyst™ 16 (A16), Amberlyst™ 39 (A39), Amberlyst™ 36 (A36), Amberlyst™ 35 (A35), Macronet™ MN500 (MN500), and gel-type ones, Dowex 50Wx2 100-200 mesh (Dow2), Dowex 50Wx4 100-200 mesh (Dow4), and Dowex 50Wx8 100-200 mesh (Dow8). The reactor

hourly product distribution was analyzed in line by a coupled GC/MS system (Agilent 7890B GC/5977B GC/MSD).

3. Results and discussion

No byproducts were detected under the conditions explored, being OL and water the only products detected. LA conversion reached values of 54-67% at the end of the runs for all the tested catalysts, being this the corresponding equilibrium conversion at the explored temperature (Table 1).

Table 1. Catalytic activity of tested resins in terms of LA conversion at $t = 4$ h and of initial OL formation rate.

| Catalyst | X_{LA}^a [%] | $r^0 \times 10^3^a$ [mol/(s·kg)] |
|----------|-------------------|-------------------------------------|
| A15 | 54 | 42 |
| A16 | 64 | 45 |
| A35 | 57.9 ± 0.6 | 73 ± 5 |
| A36 | 56 ± 2 | 56 ± 12 |
| A39 | 55 | 111 |
| MN500 | 67.0 ± 0.5 | 132 ± 26 |
| Dow2 | 64 | 166 |
| Dow4 | 63.3 ± 1.1 | 116.7 ± 0.6 |
| Dow8 | 62.1 ± 0.4 | 99 ± 7 |

^a Standard deviation is shown for replicates.

As for the catalytic activity, all the resins evaluated were active with OL initial formation rates ranging 0.042-0.166 mol/(s·kg cat), being A15 the least active resin and Dow2 the most active, followed by MN-500. These activity results were correlated to the different catalyst properties as measured in dry state by BET (N₂ physisorption) and in swollen state by Inverse Steric Exclusion Chromatography (ISEC), finding that steric effects are the most relevant factor for this reaction given the relatively large molecular volumes of OcOH and OL. Resins with high surface area values (macroporous type) or those with broad cavities in the gel-phase when swollen in the reaction medium (low DVB content) show the best catalytic performance toward the alkyl levulinate synthesis. This fact allows to infer that the availability of convenient spaces within resins for accommodating bulky molecules is crucial.

4. Conclusions

Octyl levulinate has successfully produced from levulinic acid and 1-octanol esterification over acidic resins at 100°C using an initial molar ratio OcOH-to-LA of 1. No byproducts were detected under the conditions explored, being OL and water the only products detected. LA conversion at 200 min reached moderate values (54-65%). Among resins tested, A15 was the least active resin and Dow2 the most active, followed by MN-500. The catalytic activity results were rationalized through resins morphology in swollen state.

References

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Keywords

Octyl levulinate, esterification, acidic ion-exchange resins, catalyst screening, morphological properties.