

RENEWABLE ISOPRENE BY DEHYDRODECARBOXYLATION OF MEVALONOLACTONE

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Abstract

A novel process for the production of renewable isoprene has been developed by converting carbohydrate-derived mevalonolactone, dehydromevalonolactone, and mevalonic acid via a combination of fermentation and thermocatalytic reaction pathways. The conversion of these aqueous fermentation derived intermediates was studied in batch, semi-batch and continuous reactors using a variety of heterogeneous acid catalysts. Isoprene selectivity greater than 90% could be achieved in the batch and semibatch reactors at a molar yield of 26 – 55%, while 68% molar yield of isoprene was obtained in the continuous reactor.

Keywords

Isoprene, mevalonolactone, mevalonic acid, heterogeneous catalysis, fermentation

Introduction

Isoprene (2-methyl-1,3-butadiene) is a terpenoid moiety, used as a starting material for manufacturing of a plethora of synthetic polymers. Globally, the annual demand of isoprene is on the order of 1 million ton, predominantly used in making polyisoprene, a precursor to synthetic rubber. In addition, use of isoprene as a co-monomer with a variety of olefins continues to gain importance. Isoprene is mainly produced by the cracking of C5 hydrocarbons, obtained from petroleum feedstock; however, the yield of isoprene by this route is low and requires expensive and extensive separation and purification steps. Commercial on purpose production of isoprene through convergent synthetic pathways include the condensation of acetylene and acetone, dimerization of propylene followed by cracking, the Prins reaction of isobutylene and formaldehyde, oxidative coupling of isobutylene and methanol, and from metathesis derived 2-methyl-2butene (Weissmehl and Arpe 1997)(Weitz and Loser 2005).

As renewably and sustainably sourced materials are steadily gaining importance, academic as well as industrial

groups have investigated biomass based routes to isoprene and isoprenoids using naturally occurring terpenes as well as carbohydrates as feedstocks. Renewable isoprene can be produced through thermal decomposition of isoprenoids from natural resources but the overall yield from biomass is also very low. Recent activity in the area of thermocatalytic decarboxylation of lactones (Chia et al. 2012) to yield olefins inspired us to investigate options for producing isoprene from mevalonic acid (Figure 1). Mevalonic acid can be produced by various fermentation routes from glucose (Beck et al. 2014)(Cervin et al. 2012). Conversion of mevalonic acid to isoprene using sulfuric acid as a catalyst has been demonstrated but the yields are below 5% (Gasparic et al. 2003). A process of converting anaerobic fermentation products such as mevalonic acid to isoprene in good selectivity, using inexpensive catalysis technology would be highly desirable

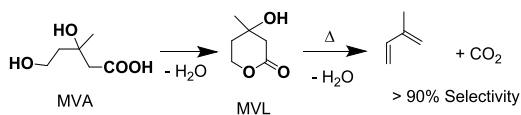


Figure 1. Synthesis of isoprene by the dehydrodecarboxylation of mevalonolactone

Materials and Methods

Initial catalyst screening was performed in a 20 ml batch screening reactor. Screening reactions were carried with 200 mg MVL (4% in water), 200 mg of heterogeneous catalyst at 250 °C for 2 h at 700 psig N₂. Isoprene was captured in tetradecane and dodecane was used as an internal standard. About 50 heterogeneous catalysts were screened including, CuO, MnO₂, Pt, Ru, WO_x on a variety of supports and/or additives (Al₂O₃, SiO₂, ZrO₂, TiO₂, zeolites, phosphotungstic acid, Cs-doped phosphotungstic acid, and supports (without metal addition). Both, acidic supports and metal catalysts seemed to promote rearrangement fragmentation reaction mechanism.

The reaction was scaled up in batch, semi-batch, and continuous reactors using the γ -alumina catalyst (BASF). Batch reactions were carried out at 1–10 wt% aqueous solution of MVL, 200 mg of heterogeneous catalysts at 200 °C for 4 h at 170 psig N₂. The reaction was carried out in semi batch mode in a 600 ml hastelloy C stirred batch autoclave (Parr) using 250 ml of dodecane as solvent and 2.5 g of catalyst under 200 psig of nitrogen pressure and at 200 °C, under constant stirring (800 rpm). 5 wt% aqueous MVL-water soln. (5 g MVL in 95 g water) was added with an HPLC pump over a 1-hr period. The reaction was run for an additional 2 hours, time on stream. Continuous MVL conversion was studied in a 1/2" stainless steel fixed bed reactor. 12.74 g of γ -alumina was used as the catalyst. The reaction was run using aqueous feed containing 4 – 5% of MVL at an LHSV of 0.5-2 ml feed/ml catalyst/hour. 10 ml/min nitrogen (inert) flow was used to sweep product from the reactor. The reaction was studied at pressure of 1000 psig and a temperature range of 150–250 °C. The liquid effluent was trapped in chilled toluene in an ice bath. The gas phase was not analyzed for these runs

Results and Discussion

Isoprene was produced in excellent selectivity from carbohydrate-derived mevalonic acid, mevalonolactone, and dehydromevalonolactone by thermocatalytic conversion over aluminum oxide and a variety of mildly acid catalysts at temperatures between 150 and 250 °C under inert conditions (N₂) in an aqueous environment. Initial results suggested that isoprene selectivity of >90% isoprene could be achieved in the batch and semibatch reactors at a molar yield of 26 – 55%, while 68% molar

yield of isoprene was obtained in the continuous reactor. Dehydromevalonolactone (DMVL) was identified as an intermediate by GC-MS analysis. We found evidence that DMVL was formed by the dehydration of mevalonolactone under acidic condition, which subsequently underwent decarboxylation to produce isoprene and CO₂; however, parallel pathways that do not involve the formal retro Diels-Alder fragmentation of a DMVL isomer may occur simultaneously.

The results from the batch, semi-batch, and continuous reactor study will be presented and a reaction mechanism for the synthesis of isoprene by the dehydrodecarboxylation of mevalonolactone will be proposed.

Conclusions

A novel process for the production of renewable isoprene has been developed by converting carbohydrate-derived mevalonolactone, dehydromevalonolactone, and mevalonic acid via a combination of fermentation and thermocatalytic reaction pathways.

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