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-2-buten (Weissermel 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
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.

References


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