

Effect of reaction conditions on the production of synthetic middle-distillates via catalytic dimerization of biomass-derived olefins

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Introduction

Conversion of biomass to fuels remains one of the most promising approaches to support our energy needs. It has been previously demonstrated that biomass-derived synthesis gas can be used to produce fuels like methanol and dimethyl ether (DME)¹. However, the use of methanol and DME is limited due to the fact that they have low energy densities, poor lubricity and lower viscosity when compared to long-chain hydrocarbons^{2,3}. Consequently, the petroleum-derived hydrocarbons remain as the main constituent of middle-distillate based fuels. One way to increase the share of biofuels in middle-distillates is to use methanol/DME as building blocks for producing renewable, energy-dense hydrocarbons. One way to achieve this is by catalytically converting DME and methanol to light olefins, followed by oligomerization to higher molecular weight premium alkanes, which can directly be used as kerosene/diesel fuels.

Here, we report the catalytic dimerization of biomass-derived deoxygenated olefins into transportation fuel-range hydrocarbons under liquid-phase stirred-batch conditions. Specifically, the effect of operating conditions, such as reaction temperature, solvent-type, reaction duration and olefin-structure, on the conversion, selectivity and kinetics of dimerization of triptene (2,3,3-trimethyl-1-butene) were investigated. Triptene, as previously reported, is one of the major products of the DME-homologation reaction over a BEA zeolite⁴. We show that triptene can be converted to high quality middle-distillates using a commercially available ion-exchange acid resin, Amberlyst-35 (dry) by the process of catalytic dimerization.

Materials and Methods

Batch-dimerization of triptene was carried out at atmospheric pressure, at three different temperatures (60, 80, 100°C) and with two separate solvents for various durations. Amberlyst-35 (dry), a macro-porous, sulfonated polystyrene-based ion-exchange resin was supplied by Rohm & Haas. The technique of Gas Chromatography-Mass Spectrometry (GC-MS) was used for identification of reaction products. The boiling range of the final product was determined using the ASTM-D2887 method. The high heating value (HHV) was measured following ASTM-D240. The product fractions, as primary, secondary, tertiary and quaternary carbon species, were determined using ¹³C NMR spectroscopy, which enabled the estimation of the cetane value of the final product.

Results and Discussion

Figure-1 compares the conversion of triptene at three different temperatures. The rate of dimerization increased with increasing temperature; however, the production of cracking products also increased. The selectivity for dimers was higher at lower temperatures

(maximum > 90% at 60°C) at the expense of lower reaction rates. The best case scenario was achieved at 100°C, with nonane as the solvent, that resulted in production of the desired dimerized hydrocarbon product (2,2,3,5,5,6,6-heptamethyl-3-heptene or di-triptene) with a conversion of approximately 50% and a selectivity greater than 70%, within the first 3 hours of reaction. The solvent, in which the feed olefins were dissolved, also affected the selectivity and the overall conversion, with lower molecular weight solvent affording higher yield. Performance of triptene dimerization was compared with that of other C₆-C₈ olefins having different skeletal structure, including 2,3-dimethyl-1-butene, 1-heptene and 2,4,4-trimethyl-1-pentene. The role of olefin properties, such as extent of branching and chain length, was examined. Triptene (2,3,3-trimethyl-1-butene) was found to be most reactive towards dimerization-specific reaction pathways due to the formation of more stable reaction intermediate.

The final product mixture was evaluated for its potential to be used as a middle distillate-range transportation fuel (See Table-1). Approximately, 85% of the final product is in the boiling range of 164 to 340°C. Much lower cloud point (-81°C), adequate cetane index (42) & high heat of combustion (46.5 MJ/kg) confirm that the product mixture is well-suited for applications as blend-stock for jet/diesel based fuel.

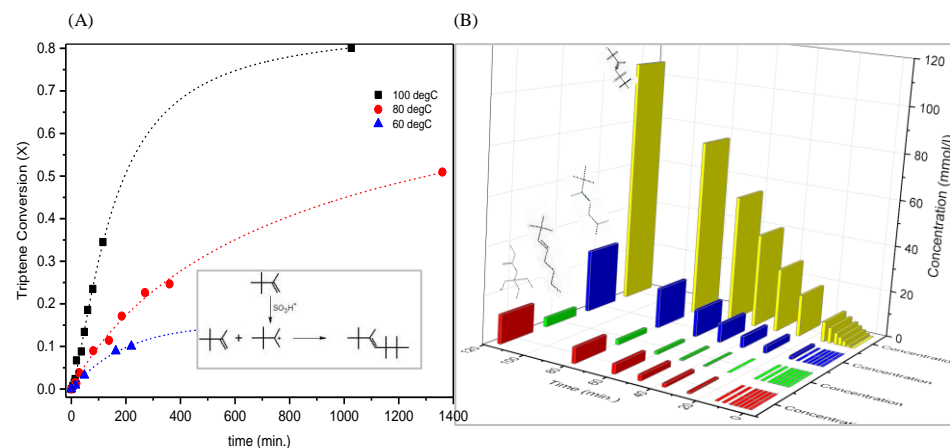


Figure-1. (A) Conversion-time profiles for triptene at different reaction temperatures with nonane as solvent. Insert shows a schematic of the reaction path involved in dimerization of triptene over Amberlyst. (B) Plot showing product distribution at different times for triptene dimerization at 100 °C

References

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