



Temperature-dependent reaction pathways for the anomalous hydrocracking of triglycerides in the presence of sulfided Co–Mo-catalyst

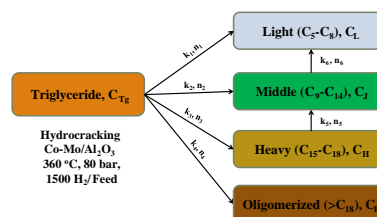
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HIGHLIGHTS

- ▶ Kinetic studies on anomalous hydrocracking of triglycerides over Co–Mo/Al₂O₃.
- ▶ Temperature has a major effect on the reaction pathways for triglyceride conversion.
- ▶ Higher activation energies for formation of light and middle than for heavy products.

GRAPHICAL ABSTRACT



Kinetic models for a shift in reaction pathways at different temperatures for hydrocracking of triglyceride molecules, with high activation energies for the formation of lighter and middle distillates and lower for the heavy and deoxygenated products, over Co–Mo/Al₂O₃ catalyst.

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ABSTRACT

Kinetic studies and product profiling was done to understand the anomalous cracking of jatropha oil triglycerides in the presence of sulfided Co–Mo/Al₂O₃ catalyst. At temperatures between 320 and 340 °C, only deoxygenation and oligomerization reactions took place whereas at temperatures above 340 °C, internal conversions between the products and direct conversion to lighter and middle distillates were favored. High pressures (80 bar) and H₂/feed ratios (>1500) were necessary to minimize oligomerization of the products and to increase the lifespan of the catalyst. Lumped kinetic models were validated with experimental results. Activation energies for the formation of lighter (83 kJ/mol) and middle fractions (126 kJ/mol) were higher than those for the heavy (47 kJ/mol) and deoxygenated (47 kJ/mol) products. Jatropha oil triglycerides hydroconversion pathways were dependent on temperature and the triglycerides could be hydrocracked to lower range hydrocarbons (C₅–C₁₄) by increasing the reaction temperatures.

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1. Introduction

Plant oils can be trans-esterified to produce biodiesel, or they may be hydroprocessed to produce petroleum-like biofuels (Bezergianni et al., 2009a,b; Donnis et al., 2009; Huber et al., 2007; Kubicka et al., 2009; Kumar et al., 2010; Lappas et al., 2009; Melis et al., 2009; Šimáček et al., 2009).

The first step in plant-oil hydroprocessing is the saturation of double bonds in the triglyceride molecule (TG) then the saturated

triglyceride molecule (TG) is hydrogenated and cracked to liberate an R_x acid (R_xCOOH) and a propane molecule. R_x may be either a C15 or C17 compound depending on the chain length of the triglyceride molecule. The R_x acid can follow three different reaction pathways for the removal of the oxygen atom to yield C15–C18 compounds.

Hydrodeoxygenation gives a water molecule and a corresponding hydrocarbon (R_xCH₃). Decarboxylation yields a carbon dioxide molecule and a C16 or C18 hydrocarbon (R_xH). Decarbonylation yields a carbon monoxide molecule, a water molecule and a long chain hydrocarbon molecule (R_xH) with 15- or 17-carbon chain length. The compounds produced by oxygen removal reactions

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