



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

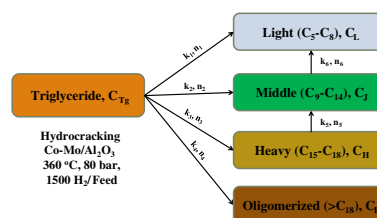
Mohit Anand, Anil K. Sinha \*

CSIR-Indian Institute of Petroleum, Dehradun 248 005, India

## HIGHLIGHTS

- ▶ Kinetic studies on anomalous hydrocracking of triglycerides over Co–Mo/Al<sub>2</sub>O<sub>3</sub>.
- ▶ 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/Al<sub>2</sub>O<sub>3</sub> 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/Al<sub>2</sub>O<sub>3</sub> 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 H<sub>2</sub>/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 (C<sub>5</sub>–C<sub>14</sub>) 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<sub>x</sub> acid (R<sub>x</sub>COOH) and a propane molecule. R<sub>x</sub> may be either a C15 or C17 compound depending on the chain length of the triglyceride molecule. The R<sub>x</sub> 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<sub>x</sub>CH<sub>3</sub>). Decarboxylation yields a carbon dioxide molecule and a C16 or C18 hydrocarbon (R<sub>x</sub>H). Decarbonylation yields a carbon monoxide molecule, a water molecule and a long chain hydrocarbon molecule (R<sub>x</sub>H) with 15- or 17-carbon chain length. The compounds produced by oxygen removal reactions

\* Corresponding author. Tel.: +91 135 2525842; fax: +91 135 2660202.  
 E-mail address: [asinha@iip.res.in](mailto:asinha@iip.res.in) (A.K. Sinha).

may crack and isomerize to yield lighter distillate products (Huber et al., 2007; Melis et al., 2009).

For hydroprocessing of various plant-derived oils, acidic supports such as amorphous mixed oxides like silica–alumina (for catalysts such as sulfided Co–Mo, Ni–Mo, Ni–W) (Kumar et al., 2010; Liu et al., 2009; Tiwari et al., 2011; Verma et al., 2011), phosphate-modified silica-alumina (Verma et al., 2011), and crystalline acidic supports like zeolites (Huber et al., 2007; Kumar et al., 2010; Murata et al., 2010; Verma et al., 2011) have been successfully employed to produce cracked hydrocarbons ranging from gasoline to kerosene to diesel. The yield of cracked products increased with increasing acidity of the catalysts. As the reactions are highly exothermic, catalyst stability and selection are important (Kumar et al., 2010; Michaelsen and Egeberg, 2009).

To realize a sustainable commercial future for biomass–oil fuels by hydroprocessing, detailed kinetic studies, product profiling and a better understanding of the underlying mechanisms and reaction pathways are necessary.

With this aim, kinetic modeling was carried out in the present study using a Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. Krár et al. (2010) demonstrated that a CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst was suitable for the conversion of sunflower oil to paraffins and Kubicka et al. (2009) demonstrated that Co–Mo supported over mesoporous alumina enhanced deoxygenation activity with rapeseed oil. Kumar et al. (2010) showed that a Co–Mo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst had an unusual cracking ability for jatropha-oil with a high acid content. Co–Mo/Al<sub>2</sub>O<sub>3</sub> despite being a low acidity catalyst gave an unexpectedly high yield (40%) of cracked hydrocarbon products. The present study was carried out to identify the reaction pathways for plant-oil hydroconversion over a CoMo system using a low free fatty acid feed and to gain an understanding of the role of acidic intermediates in cracking. Lumped power law-based kinetic models (Kumar and Froment, 2007; Zhang et al., 2009) were validated with experimental data. The model which best predicted the concentration profile of various components was chosen and kinetic parameters and activation energy were evaluated. Jatropha oil which contains mainly triglycerides of C16 and C18 hydrocarbons was used as a feed stock to produce deoxygenated hydrocarbons as the main reaction products.

## 2. Methods

Jatropha oil (1.7% FFA (free fatty acids), 19.5% C16:0, 7.9% C18:0, 45.4% C18:1, 27.3% C18:2, 77.01 wt% C, 13.6 wt.% H, 9.39 wt.% O, 4.0 ppm S) was hydroprocessed in a fixed-bed reactor over a sulphided Co–Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The catalyst was prepared by impregnation of mesoporous support extrudates of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (BET surface area = 298 m<sup>2</sup>/g, pore volume of 1.1 ml/g, and BJH pore size = 6.1 nm) (Kumar et al., 2010). The catalyst was powdered and mixed with –40 + 50 mesh SiC (1:1 volume/volume) and loaded into a stainless steel tubular reactor with a 1.3-cm internal diameter and a heated zone length of 30 cm, with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> extrudate layers above and below the catalyst bed. The reactions were performed in a commercial bench top micro-reactor (Autoclave Engineers' BTRS-Jr<sup>®</sup>) (Kumar et al., 2010). Liquid products were withdrawn after stabilization of reaction conditions in two-hour intervals (at each temperature). The liquid products were analyzed thrice during the stabilization period by gas chromatography (GC) to determine if the activity of the catalyst was constant. The liquid products were analyzed offline after separation of the water phase and diluting 100-fold in CCl<sub>4</sub>, using a gas chromatograph (Varian 3800-GC) equipped with a flame ionization detector and a thermal conductivity detector. The liquid products were analyzed in a vf-5ms column (30 m × 0.25 mm, 0.25  $\mu$ m) for hydrocarbons, free fatty acids and triglycerides. Internal standards (i.e., eicosane) were used for quantification. The quantitative results for the triglycer-

ides were compared with those from HPLC analysis after derivatization. Injection temperature was set at 340 °C. A high injection port temperature was used for reliable and direct quantification of fatty acids and triglycerides without chemical derivatization (Fu et al., 2010; Peng et al., 2012). The temperature program was: from 35 to 150 °C (rate: 3 °C/min and holding time for 5 min), increase to 300 °C (rate: 12 °C/min and holding for 5 min) and increased to 320 °C (rate: 15 °C/min and holding time for 15 min). The vapor phase was analyzed online by a gas chromatograph (Agilent 7890A, RGA) with 2-TCD detectors, 1-FID and six columns (5 packed columns and 1 capillary column from Agilent). The yield fractions were calculated on a relative basis considering the entire range of products formed as 100%. A complete mass balance was calculated for the entire reactor and was always >99% accurate for all the components before and after the reaction.

Table 1 details the processing conditions for the kinetic analysis of the hydrotreatment of jatropha oil to understand the effects of temperature, pressure, H<sub>2</sub>/feed ratio (NI/I) and space velocity on product patterns. Deactivation of the catalyst during the runs was estimated by repeating the same experiment again after 2 days of continuous operation to confirm, and if the change in activity was more than 2%, fresh catalyst was loaded and used.

The feed for the reaction was of low TAN (Total Acidity Number) and mixed with 0.1% DMS (dimethyl disulfide) for maintaining catalytic activity and to minimize the cracking tendency observed in high TAN feed (Kumar et al., 2010). The feed was taken as one lump and the products were lumped in four lumps, i.e. heavy (from C15–C18), middle (from C9–C14), light (<C9) and oligomerized (>C18). The Levenberg–Marquardt algorithm (LMA) was used for estimating the kinetic parameters (Alvarez and Ancheyta, 2008; Kumar and Froment, 2007). The values of the predicted kinetic rate constants were analyzed using CHI Square test ( $\chi^2$ ) for goodness of fit, with a level of significance of 95%. The lumped models which did not satisfy the  $\chi^2$  criteria were rejected. The rate constants were used to calculate the activation energy and frequency factor using the Arrhenius equation (Callejas and Martinez, 2000).

### 2.1. Model development

Lumped kinetic models were developed considering various product patterns observed during the reactions (Kumar and Froment, 2007; Zhang et al., 2009). Various possibilities were considered for the formation of different primary and secondary reaction products (Scheme 1).

Differential rate equations were framed for the formation of these lumps and solved simultaneously for each scheme separately to obtain a system of non-linear equations, for various concentrations of lumps (detailed methodology in Supplemental Information). The equations were reduced to the form  $Y = A_1 e^{ax} + B_1 e^{bx} + C_1 e^{cx} + D$  where  $x$  is space time and  $Y$  is the concentration of individual lumps (Supplemental Table 1).

**Table 1**  
Catalyst loading and processing conditions.

Catalyst	4% CoO, 16%MoO <sub>3</sub> , 1%P <sub>2</sub> O <sub>5</sub> on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Catalyst mass, g	2
Catalyst volume, ml	2.4
Catalyst shape	Powdered
Bed length, cm	2.8
Bed volume, ml	3.7165
Reaction temperature, °C	320–360
Reaction pressure, bar	20–90
LHSV, hr <sup>-1</sup>	0.8–8.0
H <sub>2</sub> /FEED, NI/I	500–2000
H <sub>2</sub> /FEED, molar ratio	21.1–84.4

LHSV, liquid hourly space velocity.

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