Anomalous hydrocracking of triglycerides over CoMo-catalyst–influence of reaction intermediates

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MS received 15 October 2013; revised 31 December 2013; accepted 2 January 2014

Abstract. Reaction intermediates have been identified and followed to understand anomalous cracking of jathropha oil triglycerides in the presence of sulphided Co-Mo/Al₂O₃ catalyst. Undesirable C–C coupling reactions are favoured at temperatures between 320° and 340°C, giving waxy oligomerization products, whereas at temperatures above 340°C, direct hydrocracking of triglycerides to lighter and middle distillates were favoured. To minimize undesirable waxy oligomerization products, higher pressures (>80 bar) and higher H₂/feed ratios (>1500) were necessary. Aldol condensation and ketonization reactions between the reaction intermediates are counter-productive as they result in waxy long chain oxygenated products which tend to accumulate on the catalyst surface, choke the reactor and cause rapid catalyst deactivation. Reaction conditions have to be optimized to minimize condensation reaction during this process.

Keywords. Coupling reactions; hydroconversion; waxy products; reaction intermediates; triglycerides; biofuels.

1. Introduction

Currently, industry and transport sector are inherently based on costly and unsustainable crude oil sources. There is an increasingly recognized need to slow down the use of fossil fuels, since they are depleting and cause global warming and pollution. There is need to develop alternative energy fuels which must be economically competitive, technically feasible and environmentally more acceptable. One possible alternative is the fuels produced from renewable resources such as vegetable oils. Hydroprocessing of vegetable oil produces high quality renewable diesel which can replace diesel in vehicles without any major modifications of the engines, while aviation fuel produced from vegetable oils can either directly or as a blend with fossil fuel, be used for aviation purposes.^{1–4} Since biofuels do not add carbon dioxide to the atmosphere, they are carbon neutral fuel, and are also environment-friendly because they do not release nitrogen and sulphur compounds.

The most common way to produce biofuel is to transesterify triglycerides of vegetable oil with alcohol to make biodiesel, which contains oxygenated species. A better way would be to hydroprocess triglycerides to produce petroleum such as fuels. Chemically, biodiesel

consists of fatty acid alkyl esters, and the type of alkyl chain determines the quality of the product. Use of neat biodiesel requires some modification in the existing vehicle engines, and additionally it gives poor performance in cold weather. Alternatively, fuel produced from hydroprocessing is hydrocarbon-like and requires no modification in the existing engines and also has a higher cetane number (85–110) than conventional diesel fuel (51–60). This process involves hydrodeoxygenation, decarbonylation, decarboxylation, hydrocracking and isomerization or a combination of two or more for conversion of fatty acids in triglycerides into normal and/or iso-alkanes.^{5–7} The first step in plant-oil hydroprocessing for the production of hydrocarbon fuels is saturation of double bonds in the triglyceride molecule (TG), then the saturated triglyceride molecule (TG) is hydrogenated and cracked to liberate an acid (R_xCOOH)/aldehyde (R_xCHO)/alcohol (R_xOH) and a propane molecule. R_x may be either a C15 or C17 compound depending on chain length of the triglyceride molecule. The oxygen molecule may be removed by either hydrodeoxygenation (–H₂O); or hydrodecarboxylation (–CO₂); or by hydrodecarbonylation reaction (–CO).^{8–12}

The choice of catalyst is important due to its role in controlling the type of product, yield, selectivity, etc., of components present in the biofuel through hydroconversion process. Main properties of the catalyst are surface area, pore shape and size, acidity, metal

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dispersion, etc. Literature reports that various types of porous sulphided catalysts have been used for production of biofuels from vegetable oils. Acidic supports such as silica-alumina^{10,11} (for catalysts such as sulphided Co-Mo, Ni-Mo, Ni-W) and crystalline acidic supports such as hierarchical mesoporous zeolites have been successfully employed to produce cracked hydrocarbons.^{12–14} Yield of cracked products increased with increasing acidity of the catalysts. As the reactions are highly exothermic, catalyst selection based on its stability are important. Increase in acidity in reaction media due to formation of fatty acids at different processing conditions leads to formation of undesired waxy reaction intermediates via C–C coupling reactions, which further impacts catalyst life.^{13,15}

For a sustainable commercial future for biomass-derived fuels by hydroprocessing, detailed studies on better understanding of the underlying mechanisms and reaction pathways are necessary. Kráret *et al.*¹⁶ demonstrated that a CoMo/Al₂O₃ catalyst was suitable for deoxygenation of sunflower oil. Kubicka *et al.*¹⁵ demonstrated that Co–Mo supported over mesoporous alumina are active for deoxygenation of rapeseed oil. They had observed and discussed formation of oligomeric oxygenates (selectivity as high as 50%) below 280°C. Significant amounts of esters such as stearyl stearate were identified as the dominant ester at lower space velocity (1.5 h^{–1}) and lower reaction temperature (<300°C). Kumar *et al.*¹⁰ showed that sulphided Co-Mo/Al₂O₃ hydrotreating catalyst had an unusual cracking ability for jatropha oil with a high acid content. Co-Mo/Al₂O₃ despite being a low acidity catalyst gave an unexpectedly high yield (40%) of cracked hydrocarbon products. Anand and Sinha have followed the reaction pathways for plant-oil hydroconversion over a CoMo system using a low free fatty acid feed to gain an understanding into the role of acidic intermediates in cracking.¹⁷ They reported formation of insoluble waxy oligomeric products at lower conversions. At lower temperature and higher space velocities (320°C and 4 h^{–1}), concentration of oligomerized products was reported to be as high as 55%. They grouped products with similar chemical functions as lumps and used them to model kinetic behaviour of the cracking process, and kinetic parameters and activation energy were evaluated. At higher space velocities of 17.5 h^{–1} and temperatures around 350°C, Corma and co-workers¹³ reported formation of insoluble white waxy high boiling fractions (380° to 520°C fraction) product which accumulated in the reactor causing reactor plugging.

In this study, for further understanding of the reaction mechanisms, we study the formation of undesir-

able waxy intermediate, the process parameters influencing their formation and the possible reactions taking place over a Co-Mo/Al₂O₃ catalyst for hydroprocessing of *Jatropha curcus* oil.

2. Experimental

Jatropha oil (1.7% FFA (free fatty acids), having a composition of 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/Al₂O₃ catalyst. Catalysts (2.5 ml) mixed with SiC (2.5 ml) to ensure sufficient catalyst-bed length and to improve the reaction-heat transfer, were loaded into a stainless steel tubular reactor (1.3 cm I.D. and 30 cm in length) and the experiments were carried in a commercial bench-top micro-reactor (Autoclave Engineers' BTRS–Jr) with singlezonetubular furnace, for vapour phase catalyst evaluation in continuous down-flow mode. Hydrogen pressure was controlled by a back pressure regulator (Tescom), gas flow was controlled by a mass flow controller (Brooks), catalyst bed and temperatures were controlled and registered by temperature controllers and by two thermocouples. A liquid metering pump, high pressure (Eldex make) was used to maintain desired liquid flow. Liquid products were withdrawn after stabilization of reaction conditions in two-hour intervals (at each temperature) and were analysed using gas chromatography (GC: Make Varian 3800-GC-FID) to determine the activity of the catalyst. The liquid products were analysed offline after separation of the water phase. A vf-5ms column (30 m × 0.25 mm, 0.25 μm) was used for the analysis and internal standards (i.e., eicosane) were used for quantification. The results for the triglycerides were also cross checked with those from HPLC analysis after derivatization. The yield fractions were calculated on a relative basis and conversion defined as $(C_{\text{tfg}} - C_{\text{tgp}}) / C_{\text{tfg}} * 100$ where C_{tfg} and C_{tgp} are the concentrations of triglycerides in feed and reaction product.

The feed for the reaction was mixed with 0.1% DMDS (dimethyl disulphide) for maintaining catalytic activity. The triglycerides in the feed were taken as one lump and the products were lumped as heavy (from C15–C18) and oligomerized (>C18).

3. Result and discussion

Anomalous cracking of jathropha oil triglycerides in the presence of sulphided Co-Mo/Al₂O₃ catalyst¹⁷ was

studied by monitoring reaction intermediates produced at various processing conditions. Their formation and effects of various process parameters over these undesired products were understood through response surface studies. Figure 1 details the mean yield fraction of stable undesired waxy intermediate products formed during hydroconversion of triglycerides. Concentration of these stable undesired intermediates decreases with increase in residence time and reaction temperatures. At lower temperatures, i.e., 320°C and higher space velocities of 8 h⁻¹, these undesired waxy products formed are very less (4%); on decreasing the space velocity to 4 h⁻¹ the concentration of these products doubles to 8% (figure 1 and supplementary figure 1) because of increased conversion of triglycerides into these waxy products. On increasing reaction temperature to 360°C, similar concentrations of these waxy products was observed between 8 and 4 h⁻¹ which further reduced at lower space velocities (1–4 h⁻¹) as seen in chromatograms arranged in figure 2. Stable oxygenated intermediate products such as esters and some acids, alcohols, aldehydes and ethers were also confirmed by IR and NMR analyses by Anand and Sinha.¹⁷ Kubicka *et al.*¹⁵ observed large quantities of these intermediate oligomeric oxygenates (selectivity as high as 50%) below 280°C. Huber *et al.*¹³ explained the formation of these oxygenated intermediates prior to deoxygenation via the pathway TG → hydrogenation → intermediates (waxes, glycerides, fatty acids, esters) → hydrocarbons. These indicate that triglycerides are converted to waxy products at reduced residence time, but on increasing residence time, their formation decreases. These white-coloured waxy products are formed due to C–C coupling reactions such as aldol condensation, ketonization. The long chain organic acids, formed after depropanation reactions, first undergo decarboxylative coupling reactions to form ketones and alcohols which

Figure 1. Mean yield fraction of stable undesired waxy products as a function of temperature (80 bar, 1500 vol/vol).

Figure 2. Gas chromatograms' for triglycerides and stable undesired waxy product concentration, observed at varying space velocities (80 bar, 1500 vol/vol) over Co-Mo/Al₂O₃ catalyst.

further react with aldehydes formed in the reaction media using the aldol condensation, leading to long chain waxy compounds. These reactions are undesirable in hydroconversion of triglycerides, as the products formed block the reaction sites and also act as sites for coke formation on the surface of the catalyst.

Our earlier studies^{8,17} discussed various temperature-dependent reaction pathways for processing of *Jatropha*

curcus oil over Co-Mo catalytic system. After considering the product and conversion patterns, compound groups were divided into five different lumps. Here, we report the various response surfaces for depicting the multivariable effect over these different lumps and predict the optimum desired conditions for obtaining the desired product yield, complete conversions and minimum yield of undesired waxy products. Only those response surface models which satisfy the goodness of fit acceptance criteria to 95% confidence level are plotted and discussed below.

3.1 Hydrogen to feed ratio and space velocity

Different response surface graphs with the conversion of jatropha oil and yield fraction of various lumps as the response variable and hydrogen to feed ratio and space velocity as factors affecting the response variable were drawn. Figure 3 depicts the combined effect of hydrogen to feed ratio and space velocity over the conversion of triglyceride molecules. Contours for the parabolic model were slightly inclined to the horizontal, indicating a strong interaction of these variables to predict conversion of jatropha oil. The effect (figure 4) of these factors over oligomerized undesired product yield clearly shows an increase in the yield of these waxy products at higher space velocity and lower $H_2/FEED$ ratio, which was observed due to lower conversions. There was almost no interaction of space velocity and $H_2/FEED$ at higher $H_2/FEED$ ratios, but there was a slight effect of these factors on the response at lower $H_2/FEED$ ratio. Combined interaction of space velocity and $H_2/FEED$ ratio over the desired products, i.e.,

Figure 3. Conversion of triglycerides as a function of hydrogen to feed ratio and space velocity (360°C, 80 bar) over Co-Mo/Al₂O₃ catalyst.

Figure 4. Yield fraction of undesired waxy product as a function of hydrogen to feed ratio and space velocity (360°C, 80 bar) over Co-Mo/Al₂O₃ catalyst.

the heavy lump (C15–C18) is depicted in figure 5. The surface plot clearly shows 2–6 h⁻¹ and 1500 as optimum space velocity and $H_2/FEED$ for maximizing its yield fraction, this is very well-supported by the fact that at higher space velocity, there is reduced conversion because of reduced residence time; and at lower space, velocities cracking of the heavier lump took place over Co-Mo catalyst. At higher $H_2/FEED$ ratios, there was increased yield of C15–C18 product and lower yield was observed at reduced $H_2/FEED$ ratios which is very much in accordance to conversion of triglycerides and formation of unwanted waxy products. The two

Figure 5. Yield fraction of C15–C18 lump as a function of hydrogen to feed ratio ($H_2/FEED$) and space velocity (360°C, 80 bar) over Co-Mo/Al₂O₃ catalyst.

Figure 6. Conversion of triglycerides as a function of temperature and space velocity (1500 vol/vol, 80 bar) over Co-Mo/Al₂O₃ catalyst.

parameters for the response of heavy lump yield fraction interact only at extreme conditions (figure 5).

3.2 Temperature and space velocity

Response surface which depicts the combined variation for conversion of jatropha oil, with respect to temperature and space velocity is plotted in figure 6. The parabolic model satisfies the statistical criteria and has a very high F value indicating a very strong interaction between temperature and space velocity for predicting the response and conversion.

Figure 8. Yield fraction of oligomerized (>C18) lump as a function of pressure and space velocity (1500 vol/vol, 360°C) over Co-Mo/Al₂O₃ catalyst.

98.9% conversion was achieved at higher severities, i.e. 360°C temperature and 2 h⁻¹ space velocities. At lower severities, i.e., 320°C, conversion of triglycerides varied between 90 and 94% at different space velocities but with increased formation of oxygenated waxy products. With increase in temperature to 360°C, conversion increased further with increased conversion of these waxy intermediated into hydrocarbons (figures 1 and 6). At higher temperatures (360°C) the contours observed were parallel to the space velocity axis at lower space velocities (1–4 h⁻¹) and then slightly inclined at higher space

Figure 7. Conversion of triglycerides as a function of pressure and space velocity (360°C, 1500 vol/vol) over Co-Mo/Al₂O₃ catalyst.

velocities ($4\text{--}8\text{ h}^{-1}$) indicating reduced dependence of space velocities at higher temperatures for predicting conversions of triglyceride molecule. The results also concur to the temperature-dependent pathways predicted by Anand and Sinha¹⁷ for the conversion of jatropha oil over Co-Mo/ Al_2O_3 catalytic system.

3.3 Pressure and space velocity

Figure 7 details the combined interaction of pressure and space velocity over the conversion. The contours clearly depict no interactions between the factors, with reduced conversions obtained at lower pressures below 40 bar, and almost constant conversions above 55 bars. In the studied range of pressures (25–80 bar), the contours observed were parallel to the space velocity axis at 360°C , indicating enough partial pressures

of hydrogen were available at all velocities ($1\text{--}8\text{ h}^{-1}$) required for conversion of triglyceride molecule. The oligomerized product increases (figure 8) at lower pressures because of increased C–C coupling reactions favoured at lower partial pressures of hydrogen. At higher pressure ($>55\text{ bar}$), the yield of unwanted waxy product was almost constant at different space velocities at 360°C and 1500 NI/l H_2/FEED ratio. At lower pressure ($<50\text{ bar}$), the contours are inclined at higher space velocities (lower residence time and hence reduced conversions) and at lower space velocities (higher residence time and hence increased conversions); indicating a combined interaction effect of space velocity and hydrogen partial pressure over the formation of these oligomerized products at these pressures.

Mechanisms for the hydroprocessing of jatropha oil triglycerides are likely to be complex due to multiplicity

Scheme 1. Reaction mechanics for formation of unwanted waxy intermediates through C–C coupling reactions over Co-Mo/ Al_2O_3 catalyst.

Figure 9. ^1H NMR spectrum for the oligomeric intermediate compounds at 340°C, 80 bar, 1500 NL/L.

of the possible reactions of mixed triglycerides. Generally, formation of hydrocarbons proceeds through the decomposition and cleavage of the bonds and disproportion reactions. Presence of unsaturation enhances cleavage at a position α , β to the unsaturation. It is generally known that triglycerides are first saturated on their side chain and followed by cleavage of the C-O bond leading to formation of monoglycerides, diglycerides, carboxylic acids and waxes. Presence of unsaturation also leads to unwanted C-C coupling reactions which produces stable unconverted intermediates. The main reaction pathways leading to formation of these intermediates are shown in scheme 1. Oligomerization, aldol condensation, ketonization, etc. are the main reactions for the formation of these intermediates (figure 2). Presence of oxygenated species indicated by the C=O band and OH stretchings observed at 340°C temperature¹⁷ indicated presence of acidic intermediates which was also justified by increased total acid number at these conditions. To confirm the presence of these intermediates, ^1H -NMR analysis was carried out (figure 9). Chemical shifts were observed between 0.7 and 2 ppm for the sp^3 hybridized -CH with no functional group attached, indicating the presence of paraffinic carbon. Chemical shifts observed between 2.8 and 4.5 ppm indicate the presence of oxygenated sp^3 hybridized C-H present in alcohols, ethers and esters. Chemical shifts for allylic sp^3 hybridized C-H for ketones (C=O), aldehydes (-CHO), and acids (-COOH) were also observed between 1.8 and 2.8 ppm

in the ^1H NMR spectra, confirming and justifying the increased TAN and hence the C-C coupling reactions which produce these waxy intermediates.

4. Conclusion

Formation of unwanted waxy products could be minimized by minimizing the C-C coupling reactions taking place at reduced partial pressures of hydrogen and reduced conversions. Higher partial pressures could be achieved by either increasing the reactor pressure (60 bar or more) or by increasing the H_2/FEED ratio (1500 NL/l or more). Lower pressures and lower H_2/FEED ratio promotes their formation by favouring aldol condensation and ketonization reactions. As lower conversions were achieved at lower temperatures and higher space velocities; hence, higher temperatures (360°C or more) and lower space velocities (2 h^{-1} or less) were necessary for minimizing the formation of these waxy intermediates. Minimizing these intermediate reactions would enhance catalyst life and also increase selectivity of the desired reaction productive by reducing competitive reactions.

Supplementary information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

Acknowledgements

MGS and DV thank the University Grants Commission (UGC) New Delhi, India for fellowship.

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