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Kinetics, thermodynamics and mechanisms for hydroprocessing of renewable oils

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ABSTRACT

Intrinsic kinetics, diffusivity, energy calculations and reaction mechanism studies for the conversion of plant-oil triglycerides over Ni-W/SiO_2-Al_2O_3 hydrocracking catalyst is reported. Specific insights into reaction mechanisms, are established using kinetic modeling and validated with experimental results. Diffusion studies and effectiveness factor calculations established diffusion–free intrinsic kinetics, with an activation energy of 115 kJ/mole required for triglycerides conversion. Thermodynamic calculations further established that the heat released during propane removal step (1.15 MJ/kg) was 8-times higher than that for hydrodeoxygenation step (0.14 MJ/kg) and lowest for hydrocracking reactions (0.08 MJ/kg). Such high exothermicity resulted in high temperature gradient across the catalyst bed (370 °C above the reaction temperature).

1. Introduction

Renewable resources are the key to meet the growing energy needs of the world in a sustainable as well as environment friendly way [1,2]. In literature, hydroprocessing of various plant-derived oils like soybean oil, sunflower oil, jatropha oil, fresh and waste cooking oil, waste animal fats either directly [1–11] or via co-processing with gas oil [1,2,4,5,12–16] have been reported. Competitive reactions such as decarbonation (decarboxylation + decarbonylation) and hydrodeoxygenation along with various side reactions like water-gas shift and methanation reaction, and their effect on the main reactions for the conversion of vegetable oil into fuels, have been discussed [1,2,4,13,14,17,18]. Studies with model compounds and radioisotopic investigations have also been discussed for hydrodeoxygenation reaction pathways over various catalytic systems [19]. Effect of process parameters such as temperature, pressure, space velocity, and hydrogen-to-oil ratio on the various competitive reactions and on product patterns, during conversion of triglycerides [1,2,4,8,9,18–20] have also been discussed in prior literature. The shift in reaction mechanisms based on the changes in the concentration of various side products like carbon dioxide, carbon monoxide and water vapor have also been predicted [21]. As these reactions are highly exothermic with water as a reaction by-product, hydrothermal stability, catalyst life, along with regenerability and desired product patterns are key issues yet to be discussed in detail in the open literature, during the selection of the catalyst [1,18,22,23]. Very high exothermicity and hydrothermal conditions during reactions could have adverse affect on the catalyst which may collapse rapidly under these conditions, resulting in unpredictable or poor catalyst life.

Biomass derived oils contains 20–30% oxygen content and vegetable oils which predominantly contain triglyceride molecules contain about 9–11 wt.% oxygen, which is undesirable for hydrocarbon based transportation fuels. Unwanted waxy (oligomeric) oxygenated product formation is also reported during hydrotreating of these oxygenated feeds [22]. These unwanted oxygenated compounds not only tend to choke the catalyst bed, but also act as precursors for coke, and deactivate the catalyst. The enormous amount of oxygen (9–30%) in these feeds, as compared to sulphur based impurities present in conventional petroleum based feeds, necessitates severe hydrotreating with very strong hydrogenation/dehydrogenation functionality. Sulphided tungsten based catalytic systems (Ni-W) offer enhanced hydrogenation ability [2] as compared to sulphided molybdenum based catalysts (CoMo, Ni-Mo). The stronger hydrogenation ability is expected to reduce the formation of waxy oxygenated species and lead to enhanced catalytic activity, with increased catalyst life [2].

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Table 1
Catalyst loading and processing conditions.

Catalyst	4% NiO, 24%WO_3, on SiO_2-Al_2O_3
Catalyst Mass, g	2 (microreactor), 100 (pilot-plant)
Catalyst Volume, ml	2.6 (microreactor), 150 (pilot-plant)
Catalyst shape	Powdered (microreactor), Extrudates (pilot-plant)
Bed length, cm	3.5 (microreactor), 45 (pilot-plant)
Bed Volume, ml	4.64 (microreactor), 318 (pilot-plant)
Reaction Temperature, °C	340–420
Reaction pressure, Bar	20–90
WHSV, hr^{-1}	0.5–12.0
H_2/feed, Nl/L	500–2500
H_2/feed, molar ratio	21.1–105.2

WHSV—Weight Hourly Space Velocity.

Hydrodesulphurization mechanisms, and intermediates formed during these reactions have been studied in detail [23]. Detailed studies on kinetics [22,24] for hydrodeoxygenation of model compounds such as acrolein [25], tristerian (glycerol tristearate C18) [26], triolean (glucerol trioleate C18) [26], tricaprylin (octanoic acid triglyceride C8) [27], caprylic acid (octanoic acid C8) [27], stearic acid [28,29] and oleic acid [19,21,30] etc. have also been reported to understand the reaction mechanisms for the conversion of these model compounds. Studies on diffusion [31,32], detailed kinetics, reaction pathways and thermodynamics, including energy barriers predictions for hydrodeoxygenation of real bio-based oxygenated feedstocks are yet to be reported over hydrocracking catalytic system. This work reports the diffusion limitations, kinetics, reaction mechanisms and thermodynamics for jatropha oil as an oxygenated renewable feed over Ni-W/SiO_2-Al_2O_3 catalyst in a fixed bed reactor.

2. Material and 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, 77.0 wt.% C, 13.6 wt.% H, 9.4 wt.% O, 4.0 ppm S; Na: 3.2, K: 28.9, Mg: 17.3, Ca: 21.5, P: 35.6, Si: 6.4 ppmw), containing mainly triglycerides of C16 and C18 hydrocarbons was used as a feed for catalytic evaluations (Table 1). The catalyst was prepared by incipient-wetness impregnation method using nickel nitrate (Sigma-Aldrich) and tungsten chloride (Sigma-Aldrich) salts, over commercial extrudates of mesoporous SiO_2-Al_2O_3 support (Sasol). The catalyst was characterized for physico-chemical properties (SI Experimental details). Brönsted and Lewis acid sites of the catalyst sample were determined by DRIFTS (Diffuse Reflectance Fourier Transform Infrared Spectroscopy) using pyridine as a probe molecule (SI Experimental details) [33]. The feed and products were analyzed using various analytical tools (SI Experimental details). For kinetic model development (lumped kinetic models) [22,24,34], <C9 carbon range liquid products were grouped as naphtha, C9–C14 carbon range products were grouped as kerosene and >C15 products were grouped as diesel. Isothermal microreactor was used for the kinetic models, with negligible variation in T across the catalyst bed (ΔT of ± 2 °C). The isothermal conditions were assured in the reactors with three zone furnace (ATS make) for micro reactors and five zone furnace (ATS make) for pilot scale reactor, which were maintained at the reaction temperatures using auto tuned controllers. The isothermal conditions were assured (for the microreactor) by three control thermocouples touching the reactor wall (horizontally passing through the furnace) and a response thermocouple kept at the heart of the catalyst bed. To assure isothermal conditions in the pilot scale reactor three response thermocouples were placed vertically across the catalyst bed to verify the isothermal conditions (Fig. S1). And five control thermocouples were outside the reactor touching the reactor walls (passing through the furnace horizontally) (Fig. S1). Continuous temperature monitoring was done with temperature variation of ±2 °C. Details of experimental fitting of these models and energy barrier predictions [35] are given in supplementary information. The product patterns obtained on pilot scale were used for heat of reaction calculations (SI Experimental details). The experiments were carried in automated fixed bed micro-reactor (Hi-Tech Engineering Inc, Pune, India) and pilot scale reactor (Xytel India Ltd, Pune, India) with multi zone furnace 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), and temperatures of the catalyst bed were controlled by temperature controllers and registered by thermocouples. A high pressure liquid metering pump (Eldex) was used to maintain desired liquid flow. The gas-liquid reaction effluent mixture passed through the gas-liquid separator to separate gaseous fractions from liquid hydroprocessed effluent. The gaseous products were analysed online using a refinery gas analyser (RGA) details in SI experimental details. Material balance and atomic balance were performed to remove any error in experimental measurements. All reaction products were withdrawn after stabilization (8–12 h) of reaction conditions in each experiment and were analyzed once during the stabilization period and twice after the stabilization (product collection) by gas chromatography (GC) to confirm constant activity. A variation of ±2.5% in yields was considered as experimental measurement error. The yield of liquid products was calculated on a relative basis considering the entire range of products formed as 100%. The extent of each reaction and individual heats of reactions were used to calculate the overall heat of reaction for the conversion of jatropha over NiW/SiO_2-Al_2O_3 catalyst.

Diffusivity and effectiveness factor were evaluated for kinetics calculations. Effective diffusivities of the reactant and product component lumps were calculated using bulk (D_{AB}) and Knudsen (D_{KA}) diffusivities (Eq (1)). The bulk diffusion of the reactant species into the catalyst external surface was calculated using Stokes-Einstein relation (Eq. (2)). Diffusion of reacting species into the pores (the catalyst internal surface) was calculated using Knudsen diffusivity given by Eq. (3), at two different temperatures, 340 °C and 420 °C.

$$\frac{1}{D_{AE}} = \frac{1}{D_{KA}} + \frac{1}{D_{AB}} \tag{1}$$

$$D_{AB} = \frac{K_b \times T}{6 \times \pi \times r_h \times \mu} \tag{2}$$

$$D_{KA} = \frac{D_p}{3} \times \sqrt{\frac{8 \times T \times R_g}{\pi \times M_{wt}}} \tag{3}$$

Here K_b is Boltzmann constant ($1.38 \times 10^{-23}\,m^2\,kg\,s^{-2}\,K^{-1}$), T is temperature in K, r_h is reactant hydrodynamic radius [32], μ is viscosity in Pa.sec, D_p is pore diameter, R_g is gas constant and M_{wt} is the molecular weightt of the reactant. Wagner–Weisz–Wheeler modulus M_w and Thiele modulus M_T were evaluated by Eq. (4), for predicting whether the reactant had completely wetted the catalyst particle and was free from any diffusion resistance [31].

$$M_w = \frac{(L^2) \times (k_{observed})}{D_{AE}} = {M_T}^2 \times \xi \tag{4}$$

Here L is the characteristic size of the catalyst particle defined to calculate the effective distance penetrated by the reactant molecule into the catalyst internal surface; $k_{observed}$ is the rate constant of the reaction; D_{AE} is the effective diffusivity of the reactant into the catalyst; ξ is the effectiveness factor. Effectiveness factor ξ is defined as the ratio of rate with external mass transfer resistance to rate without any mass transfer resistance and its value is 1 when the kinetics measured is intrinsic.