



# Catalytic hydrotreating of jatropha oil into non-isomerized renewable diesel: Effect of catalyst type and process conditions



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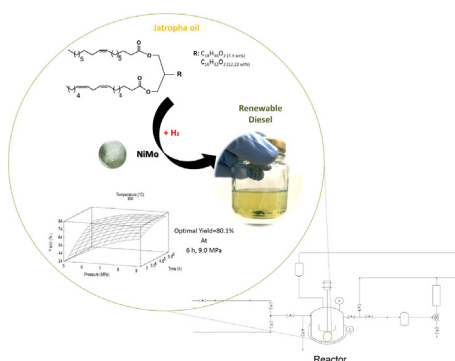
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## HIGHLIGHTS

- Ni-Mo is a better catalyst than Co-Mo for hydrotreating of jatropha oil.
- Ni-Mo has higher amount of sulfided sites at the reaction temperatures.
- Ni-Mo has higher metal dispersion than Co-Mo.
- Main reaction pathway is the decarboxylation/decarbonylation route.
- Highest product yield was ca. 80 wt%, at 300 °C, 9.0 MPa and 6 h with Ni-Mo.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The selective production of renewable diesel through the hydrotreating of jatropha oil was investigated to determine the effects of the catalyst type (Ni-Mo and Co-Mo) and of the variables temperature (300–370 °C), pressure (5.0–9.0 MPa) and time (3–6 h). Reactions were carried out in a high-pressure reactor operated in semi-batch mode. The experiments also allowed to establish the reaction pathway and to optimize the response variable (yield). A thorough characterization of the catalysts was carried out using the techniques XRF, TPR coupled to a mass spectrometer, CO-chemisorption, XRD, N<sub>2</sub>-sorptionometry and TGA/DTA. Results indicate that temperatures as high as 370 °C should be avoided because they induce the formation of unwanted by-products by cracking or polymerization reactions, and NiMoS was more sensitive to this effect. At intermediate temperature (350 °C), both catalysts behaved nearly the same. However, at the lowest temperature (300 °C) NiMoS was clearly more active than CoMoS. Amongst all the characterizations performed to the catalysts, only the chemisorption analyses (TPR and CO-chemisorption) showed relevant differences. TPR analyses showed that the amount of stronger sulfided sites, the ones still present at the reaction temperature, were higher in NiMoS, compared to CoMoS. Besides, CO-chemisorption revealed that Ni-Mo had a metal dispersion 75% higher than Co-Mo. Hence, these two factors could be the responsible for the better performance of NiMoS over CoMoS. The main reaction pathway was the decarboxylation/decarbonylation route. A clear optimum value for the yield of 80% (97% of theoretical) could be obtained at 300 °C, 9.0 MPa and 6 h with NiMoS. The variable temperature had a negative effect on yield while pressure and time had a positive effect. NiMoS did not lose activity after five re-uses.

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## 1. Introduction

Liquid biofuels, obtained from different types of biomass, are promising substitutes for fossil fuels used in transportation, heating services and the generation of electric energy [1]. Nowadays, commercial biofuels obtained from oleaginous plants, like biodiesel (fatty acid methyl esters) and renewable diesel (paraffins), are used. The latter has competitive advantages over biodiesel, such as: a) better oxidative stability in storage [2], b) oils used as raw material for renewable diesel do not require a high degree of refining, c) renewable diesel can totally or partially replace fossil diesel, d) renewable diesel has a heating value of 46 MJ/Kg, while that of biodiesel is approximately 39 MJ/Kg, e) renewable diesel process doesn't produce glycerin as by-product, instead, it produces propane that has a wider market.

The current commercial technologies used for the production of renewable diesel (Ecofining, NExBTL, H-BIO, Bio-Synfining) involve a two-stages process [3]: i) a first catalytic hydrotreating stage to obtain linear paraffins, in which unsaturations and the oxygen present in the oil are removed by hydrogenation and deoxygenation reactions (hydrodeoxygenation, decarboxylation and decarbonylation), respectively, obtaining at this point a product with poor cold flow properties (pour point of +16 °C), as long as there are no collateral reactions of cracking; ii) a second catalytic isomerization step, carried out from the linear paraffins obtained in the previous step, through which a mixture of iso-paraffins are obtained; this stage is mainly done to improve the cold flow properties, obtaining a product with cloud points lower than -10 °C.

Some authors have put forward the applicability and the evaluation of the quality of non-isomerized renewable diesel (NIRD), which only includes the first hydrotreatment stage aforementioned [2,4–6], based on the following considerations: i) commercial mixtures of NIRD with a light petrochemical diesel have good cold flow properties (e.g. cloud point below -15 °C) at low contents of NIRD, ii) NIRD can totally substitute biodiesel from highly saturated oils, such as palm oil, in tropical countries that use biodiesel-diesel blends, like Colombia (B10) and Indonesia (B20), because palm-oil biodiesel and NIRD have very similar cold-flow properties, iii) the isomerization stage significantly decreases the product yield in ca. 20% [7].

In this research, jatropha oil was used as raw material because it is a promising feedstock for the production of renewable diesel, given its low agricultural production costs, high oil content of its seeds, non-edible character and its potential to generate new production niches that stimulate agricultural development [8]. This is a highly unsaturated oil (ca. 80%) comparable with other widely used oils like rapeseed oil (ca. 90%).

The use of commercial nickel and cobalt catalysts with molybdenum (Ni-Mo and Co-Mo) has been reported for the production of renewable diesel by deoxygenation reactions. These catalysts were transferred from the petrochemical industry that mainly use them in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions of petroleum fractions, and in a minor level in oxygen-removal reactions (HDO) [9–11]. In HDS reactions, the Co-Mo catalyst has shown higher activity than Ni-Mo at temperatures up to 350 °C, while at higher temperatures the Ni-Mo performs better [12]. Other authors reported that, in general, the Co-Mo catalyst exhibits a better sulfur-removal performance than the Ni-Mo catalyst [13]. In the case of HDO reactions of vegetable oils, Ni-Mo catalysts has shown, in general, a better performance than Co-Mo catalysts, but there are also contradictory results depending on the oil and reaction conditions.

For instance, Zhang et al. [14] reported high yields of diesel-like hydrocarbons from canola oil when using an unsupported NiMoS (sulfided Ni-Mo) catalyst in a batch reactor at 9.0 MPa of hydrogen, 375 °C, 1000 rpm and 8 h, whereas an unsupported CoMoS catalyst showed undesired hydrocracking that led to gasoline-like bioliquid fuel and polymerization reactions. Hancsók et al. [8] reported the hydro-treatment of rapeseed oil and sunflower oils in a continuous reaction

system using alumina-supported Ni-Mo, Co-Mo and NiW as catalysts, at 280–380 °C, 2.0–10.0 MPa, and liquid hourly space velocity (LHSV) of 0.75–3.0 h<sup>-1</sup>. They obtained a fuel for diesel engines with a paraffin content of 99.95% with all catalyst and oils. The paraffins yields were 75–85% of the theoretical value and in the order Co-Mo > Ni-Mo > NiW. The product mass yield never surpassed 71.5 wt%. In this work, the sulfidation of catalysts was not reported, and a very high H<sub>2</sub>:oil ratio of 450 Nm<sup>3</sup> m<sup>-3</sup> was employed, thus casting doubts about its economic feasibility. Besides, no further explanation on the higher activity of the Co-Mo catalyst was given in this work.

Since the rapeseed oil is around 10% more unsaturated than jatropha oil and has a higher content of linolenic acid (14% more), it is expected rapeseed oil to be more chemically unstable than jatropha. This lower stability is mainly due to the conjugated double bonds that easily undergo cracking and polymerization reactions. Therefore, the behavior of jatropha oil towards the renewable diesel production is expected to be quite different. The deoxygenation of jatropha oil with both catalysts Ni-Mo and Co-Mo, both sulfided, has not been reported so far. There are few reports on the deoxygenation of jatropha oil with other catalysts.

Ramya et al. [15] reported the deoxygenation of jatropha oil in a continuous system (quartz reactor) at 400 °C, using catalysts based on microporous and mesoporous zeolites. The composite AlMCM-41/ZSM-5 based catalyst was the most active catalyst for the cracking of jatropha oil as it showed 99% conversion with 70% yield of bioliquid fuel and 61% selectivity towards gasoline-like fraction. AlMCM-41 based catalyst converted only 65% of jatropha oil, yielding 39% of bioliquid fuel with 47% and 36% selectivities towards green diesel and green gasoline, respectively. This study was also aimed at the optimization of temperature and reaction time toward the cracking of jatropha oil, but the influence of the pressure was not taken into account, nor reported. Romero et al. [16] deoxygenated jatropha oil using commercial hydrotalcite (Pural MG70) and alumina (Puralox SBa200) as catalysts, in the temperature range of 350–400 °C, 3–6 h and pressure between 4.0 and 11.0 MPa in a batch system. They obtained 99% conversion with 83% of hydrocarbon content with the hydrotalcite at 400 °C and 11.0 MPa, of which the majority are C8–C18, divided in 52% of gasoline range (C8–C11), and 47% of diesel range (C12–C18), and yields of liquid product obtained exceeded 80 wt%. The use of alumina did not improve significantly the process; on the contrary, a higher amount of acid compounds were obtained when alumina was used as catalyst (around 19% more than with no-catalyst). Gong et al. [17] hydro-treated jatropha oil over PtPd/Al<sub>2</sub>O<sub>3</sub> catalyst and sulfided NiMoP/Al<sub>2</sub>O<sub>3</sub>, under conditions of 330–390 °C, 3 MPa and 2 h<sup>-1</sup> in a fixed-bed reactor. When using NiMoP/Al<sub>2</sub>O<sub>3</sub>, they obtained a product yield up to 83.8% of liquid hydrocarbons, containing mainly n-paraffins of C15–18, small amounts of alkanes of C4–14 and iso-paraffins of C15–18. This catalyst allowed low cracking reaction level, resulting in a product with low acid number, suitable density and viscosity, and quite high cetane index. The main drawback of this system is the very high H<sub>2</sub>:oil ratio required (600 mL/mL). Likewise, under a surplus of hydrogen (H<sub>2</sub>:oil = 1200 mL/mL). Chen et al. [18] achieved a complete conversion of jatropha oil in a fixed-bed flow microreactor at 350 °C, 3 MPa and 0.5 h<sup>-1</sup> LHSV, using the catalyst Pt/SAPO-11. They obtained 83% yield of a liquid hydrocarbon mixture (diesel-like) containing mainly C15–18 hydrocarbons (with a high content of iso-paraffins). Nevertheless, the product oil phase also presented trace amounts of free fatty acid (stearic acid and palmitic acid), fatty alcohol (octadecanol, heptadecanol, hexadecanol, pentadecanol) and esters (stearyl stearate). In addition, monoglycerides, diglycerides and unreacted triglycerides were also detected in the oil phase. Verma et al. [19] hydroprocessed jatropha oil over sulfided Ni-Mo and NiW catalysts supported on hierarchical mesoporous SAPO-11 at 375–450 °C, 6.0–8.0 MPa and 1 h<sup>-1</sup> in a fixed-bed reactor. A high yield (ca. 84 wt%) of liquid hydrocarbon product was obtained with all the catalysts. The product distribution was 40% diesel, 40% aviation kerosene and 20% lighter gasoline range

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