



Hydro-co-processing *Jatropha* oil and crude oil blend with Ni-Mo-supported Al_2O_3 catalyst to produce hybrid fuels: the effect of catalyst particle size

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Abstract

The present research is focused on elucidating the effect of the catalyst particle size during the hydro-co-processing of a mixture of *Jatropha oil* and fossil crude oil at initial pressure of 60 bar, 4 h of reaction time, stirring at 700 rpm; catalyst-to-feedstock ratio of 1:20 (wt:wt); and reaction temperatures from 360 to 390 °C. Hydrodesulfurization extent was determined by using ASTM D4294; hydrodeoxygenation was accounted for using Fourier transform infrared spectroscopy and H-nuclear magnetic resonance; while hydrocracking was evaluated by availing simulated distillation (ASTM D2887), and also electrospray ionization mass spectrometry followed by liquid bulk density (ASTM D4052). ASPEN HYSYS was employed to account for the distillable cuts. The powder sized catalyst exhibited the highest hydrodesulfurization activity at all temperatures showing the maximum conversion of 62.6% at 390 °C. Hydrodeoxygenation conversion was almost of 100% for reaction products as evidenced by disappearance of the FTIR bands at 1168 cm^{-1} , 1710 cm^{-1} , and 1743 cm^{-1} and further confirmed by HRMN, independently of reaction temperature and particle size. Regarding hydrocracking, the light gas oil yield was about 40% for both sizes of the catalyst particles at the four reaction temperatures, and naphtha and kerosene increased as the temperature did, disregarding particle size.

Keywords Hydrotreating · Vegetable oil · Petroleum · Hydrodesulfurization · Hydrodeoxygenation

Introduction

Energy drives the economy of countries, being considered as indicator of the degree of development. The main sources of energy are the so-called fossil fuels, accounting for more than 80% of the global produced energy (Energy Institute 2024). However due to depletion of conventional fossil fuel resources and environmental concerns, research must be conducted to look for a cleaner production of conventional fuels and also allowing to open the gates to alternative

energy sources (Han et al. 2019). For the case of fossil fuel technologies, hydroprocessing is a conventional and mature technology used to refine and upgrade crude oils and petroleum fractions. The hydroprocessing implies a number of chemical reactions consisting in removal of heteroatoms and reducing boiling points; the process requires high hydrogen pressure (2–6 MPa) and high reaction temperature (360–390 °C); the employ of solid catalyst to direct chemical reactions to the desired products is mandatory (Speight 2019). In general, the hydroprocessing reactions involve the hydrotreating and hydrocracking, and also alkylation, and isomerization reactions (Palos et al. 2019; Ibarra et al. 2019). Consequently, the intrinsic properties of the catalysts (i.e., acidity and metallic character) play an important role on the catalytic upgrading process of petroleum feedstocks.

Hydroprocessing has been also used to convert vegetable oil and animal fat to produce green fuels such as green diesel (Li et al. 2018). For the last, the reaction conditions and type of catalyst are similar to those employed in hydrotreating petroleum fractions, but due to high concentration of oxygen in renewable oil sources, some disadvantages are

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observed, mainly the loss of catalytic active sites (Li et al. 2018). Hydro-co-processing of vegetable oil or animal fat with petroleum-derived feedstocks can be a good alternative because this process allows removing sulfur and oxygen from petroleum fractions and bio-oil, respectively, while the catalyst activity is maintained (Kubička and Horáček 2011).

Hydro-co-processing can be made by employing a bifunctional catalyst (acidity and hydrogenation properties) such as the Ni-Mo- and Co-Mo-supported catalysts (Vonortas et al. 2014; Vonortas and Papayannakos 2016). Regarding hydrotreating of vegetable oil and its mixtures with petroleum feedstocks, the use of Ni-Mo/ γ -Al₂O₃ sulfided catalyst during the hydroprocessing of blend of 20 wt.% of wasted cooking oil (WCO) or animal fat, and straight run gas oil (SRGO) was carried out at 350 °C, 5.5 MPa, and LHSV of 2 h⁻¹, demonstrating that paraffin yield reached a maximum of 85% as function of the type of green source (Paz et al. 2019). On the other hand, (El-Sawy et al. 2020) tested a catalytic bed formed by Ni-Mo/ γ -Al₂O₃ and Ni-Mo/SiO₂-Al₂O₃ for the hydro-co-processing WCO or wasted lubricating oil (WLO) and vacuum gas oil (VGO) at 380–440 °C, 7 MPa, and a LHSV of 1.5 h⁻¹. The resulting products such as kerosene and diesel yields varied depending on the type of oil during hydroprocessing. WLO showed the highest diesel-like fraction yield at 400 °C.

A key factor in heterogeneous catalysis is the size of the catalyst particle. Regarding that, it is well-known that diffusional mass transfer limitations (external and internal) must be reduced to attain better performance of the catalyst (Kagami et al. 2005). As a result, several authors have research on the field and reporting their findings as follows: by employing a CoO-MoO₃/Al₂O₃ during the hydrocracking (HCK) of Athabasca bitumen, (Köseoglu and Phillips 1988) demonstrated the increased the yield of aromatics from 10.9 to 22.9%, when using 3.2 mm and 0.3 mm of catalyst particle size, respectively. Similarly, (Kobayashi et al. 2007) reported the effect of particle size during the oil hydrocracking to favor middle distillate production employing USY zeolite-supported SiO₂-Al₂O₃ catalyst. The smaller the catalyst particle size (less than 300 nm), the higher the HCK activity was. (Contreras et al. 2016) reported that the hydrodesulfurization (HDS) of a vacuum gas oil was the highest at 13 nm of catalyst particle size, while increasing the particle size decreased HDS activity. Nanometric particles sizes double the hydrodesulfurization activity compared with micrometric particle size catalyst. Finally, (Melo-Banda et al. 2022) tested NiFeMo and NiCoMo nanocatalysts during the hydroprocessing of heavy crude oil, finding that a catalyst particle size less than 100 nm and metals relation played an important role in hydroprocessing. The NiCoMo catalyst was the best in terms of middle distillate production (29%) and naphtha (16%) at expenses of decreasing VGO and residue fractions to 27% and 28%, respectively.

It should be noted that, despite the improvement of catalyst activity through particle size reduction, in hydroprocessing practice, the use of powder is prohibited; instead, the use of granules of different sizes and shapes is mandatory.

At present, no study has been published on the effect of industrial and powdered catalyst particle size for a mixture of crude oil and vegetable oil that includes analysis of the hydrotreating and hydrocracking processes. The purpose of this work was the testing a commercial Ni-Mo/ γ -Al₂O₃ in the hydro-co-processing of a mixture of virgin *Jatropha curcas* L. oil and a crude oil from new well using two different particle sizes: quadrulobe-type pellets and powder size (80/100 mesh). Therefore, the effect of the catalyst particle size on hydrodesulfurization, hydrodeoxygenation (HDO), and hydrocracking is elucidated and discussed, providing a deeper insight into the field of getting cleaner and greener fuels using conventional hydroprocessing technologies.

Experimental

Materials

Jatropha curcas L. oil was obtained by direct extraction of the corresponding seeds collected from nearby region, and the crude oil was recovered from a new onshore well located in the Ixachi field at Veracruz, State of Mexico. Prior the mixing, the crude oil was treated to remove water and sediments in samples. The vegetable oil and the crude oil were mixed to obtain a blend with the 20 vol% of vegetable oil as feedstock. A commercial quadrulobe-shaped Ni-Mo/ γ -Al₂O₃ (7.7 wt.% of Ni, 37.9 wt.% of Mo, S_{BET} of 174.8 m²g⁻¹, 0.75 cm³g⁻¹, and average pore diameter of 17.2 nm) was used as oxide phase precursor for the sulfided catalyst during catalytic tests. The powder size catalyst was obtained by crushing and sieving down to a particle size within the 80/100 meshes.

Characterization techniques

The *Jatropha curcas* L. oil was characterized by proton nuclear magnetic resonance (¹H-NMR) to determine the content of fatty acids in the triglyceride following a previously reported procedure (Barison et al. 2010), using a Bruker Ascend TM apparatus at 750 MHz. The feedstock and liquid products of hydro-co-processing were characterized by simulated distillation (ASTM D2887 procedure) to obtain the boiling point curve, and subsequently computing the corresponding hydrocarbons mass fractions using ASPEN HYSYS V9 as follows: naphtha, kerosene, light gas oil, heavy gas oil, and residue. Density of feedstock and liquid products at 25 °C was determined following the method ASTM D4052. Fourier transform infrared

spectroscopy (FTIR) was employed to track HDO activity using an IR spectrometer measuring absorbance within the range of 400–4000 cm^{-1} in an IR 2 IlluminatIR II JY Smiths 195 Detection apparatus coupled to an OLYMPUS BX41 optic microscope. $^1\text{H-NMR}$ was also used to confirm the disappearance of signals corresponding to C–O and C=O. Electrospray ionization mass spectrometry (ESI–MS) was employed to characterize liquid fractions using a Bruker Daltonics micrOTOF-Q apparatus scanning within the range of 50–2000 m/z and employing a positive ion polarity. Finally, sulfur content was determined according to ASTM D4294 using a SINDIE-2622–10 apparatus.

Catalytic evaluation

Hydro-co-processing experiments were conducted in batch mode using a Parr 4598 100 mL reactor at the following conditions: 360 °C, 370 °C, 380 °C, and 390 °C; 6 MPa of initial hydrogen pressure; 4 h of reaction time; stirring at 700 rpm; and 5 g of the sulfided catalysts per 100 g of the reaction mixture of feedstock. The sulfidation process was conducted prior to catalytic tests with the same batch reactor, but using 10 mL of light gas oil (1.5% sulfur) spiked with 0.14 mL of dimethyl disulfide (Aldrich, 99%) and 1 g of the oxide phase Ni–Mo/ γ - Al_2O_3 catalyst at the following reaction conditions: 350 °C, 3 h of sulfidation time, 30 bar (3 MPa) of hydrogen initial pressure, and stirring at 750 rpm.

Results

Characterization of vegetable oil, feedstock, and liquid products

Composition of the vegetable oil

Figure 1 shows the composition of carboxylic acids in the pristine *Jatropha curcas L. oil* as determined by $^1\text{H-NMR}$. Hence, the vegetable oil was mainly conformed by linoleic acid (46.3%) and oleic acid (40.3%). The remnant percentage was 12% of saturated hydrocarbons and 1.3% of linolenic acid. Accordingly, the vegetable oil was mainly composed of the triglyceride ascribed to the three fatty acids therein, which agree with the type of vegetable oil.

Boiling range distribution of petroleum fractions

ASTM D2887 distillation curve for the hydro-co-processing feedstock (*Jatropha curcas L. oil* and crude mix) is shown in Fig. 2. According to the latter, the 10% of the mixture boiled at 200 °C, at the 80% at 450 °C, indicating the occurrence of heavy oil components derived from the crude oil component in the feedstock. In addition, most of the components

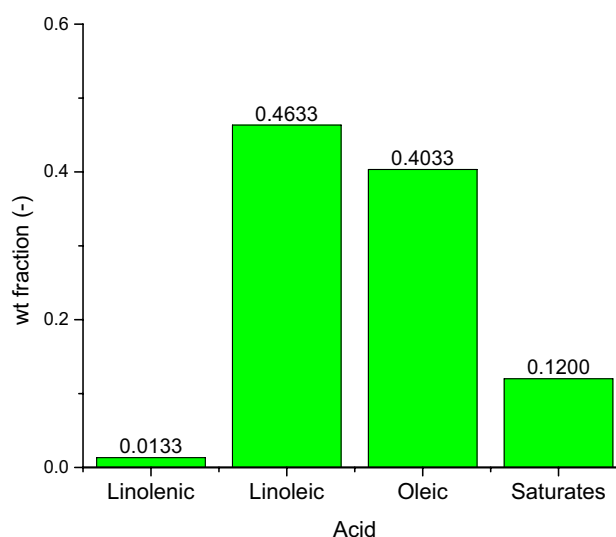


Fig. 1 Fatty acids composition in the *Jatropha curcas L. oil* by $^1\text{H-NMR}$ analysis

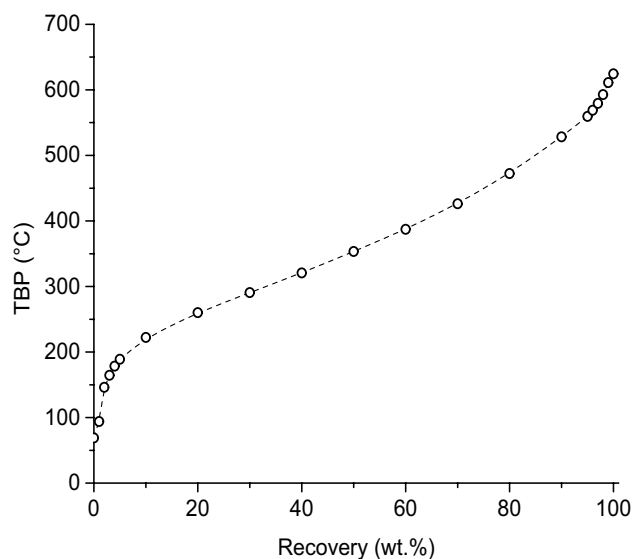


Fig. 2 TBP curve for the used feedstock for hydro-co-processing reactions according to ASTM D2887 procedure

boiled between 250 and 450 °C, which was about the 60% of recovery.

Density of the liquid products and feedstock

Figure 3 shows the density of the feedstock and the liquid products at the corresponding reaction temperature. As it can be observed, density of the liquid products decreased with the increase in reaction temperature, and deeper changes were found using catalyst in powder. Accordingly, the lighter fractions compositions increased due to the

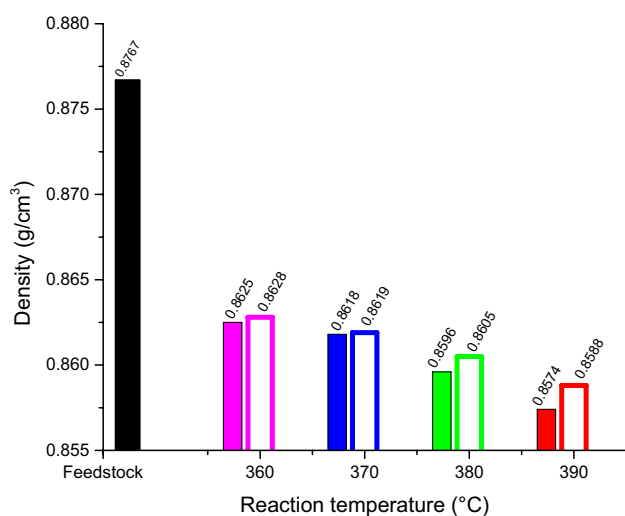


Fig. 3 Density of feedstock and liquid products employing powdered catalyst (filled bar) and particle catalyst (unfilled bar)

hydro-co-processing the mixture vegetable oil and crude. In this respect, it must be said that hydrotreating reactions (HDS and HDO) influenced the changes in density. Specifically, hydrotreating reaction mechanism involves a step of cracking of heavier molecules to selectively remove the heteroatom (S and O) via hydrogen sulfide and/or water

formation (Pérez-Martínez et al. 2011). Therefore, the more hydrotreating activity, the more occurrence of lighter fractions. Hence, decreasing the density of the final liquid product during the hydro-co-processing was mainly due to HDO.

Electrospray ionization–mass spectra for the liquid products during hydro-co-processing

On the other hand, Fig. 4 shows the ESI–MS spectra in positive ion mode, using the powder size catalyst in Fig. 4a and the particle size catalyst in Fig. 4b. As far as it can be observed, the feedstock exhibited the most intense signals at m/z between 650 and 700, ascribed to heavier components in the feedstock. Then, the occurrence followed by signals between m/z of 300 and 400. The spectra of liquid products at higher temperatures led to the increase in m/z signals between 200 and 400, and the reduction of the signals ascribed to heavier components. Accordingly, increasing the reaction temperature from 360 °C to 390 °C improved the yield of lighter fractions at expenses of decreasing the heavier ones.

By comparing ESI–MS spectra as function of catalyst particle size, it could be observed that the powder size exhibited clearer the occurrence of signals at m/z between 200 and 400. Nevertheless, changes in m/z distributions could

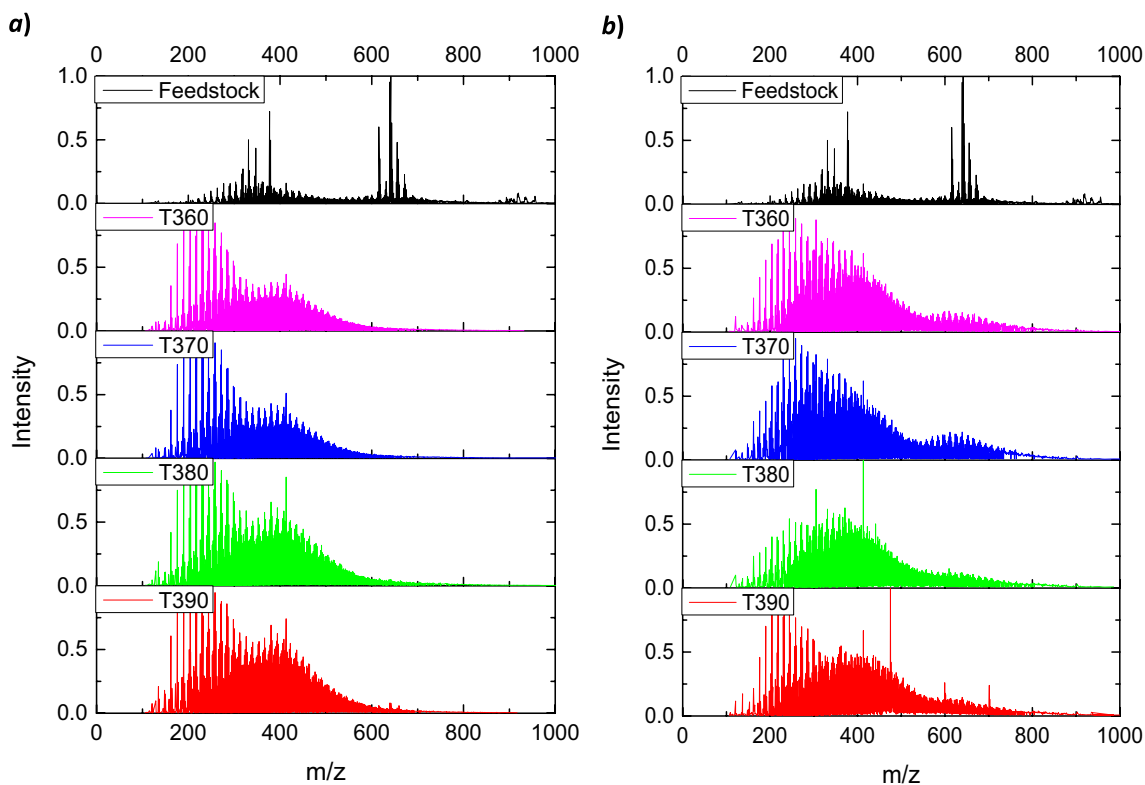


Fig. 4 ESI–MS spectra for the feedstock and liquid products at different reaction temperatures **a** powder size catalyst and **b** particle size catalyst

be considered marginal by using both catalyst particle sizes, the last due low hydrocracking reaction extent.

$^1\text{H-NMR}$ spectroscopy of the liquid products of hydro-co-processing

According to $^1\text{H-NMR}$ spectra shown in Fig. 5, hydro-co-processing the mixture *Jatropha curcas* L. oil and crude oil resulted in the hydrocarbons production via HDO of the vegetable oil components. The most intense signals are found at 0.9 ppm and 1.3 ppm in chemical shift, which corresponded to linear hydrocarbons, $-\text{CH}_2-$ and $-\text{CH}_3$. By comparing with the $^1\text{H-NMR}$ spectrum for the feedstock, it could be observed that acyl group signals were slightly evident at chemical shift of 2.04 ppm, 2.31 ppm, 2.77 ppm, 4.27 ppm, 5.28 ppm, and 5.35 ppm. The latter signals are due to concentration of the vegetable oil in the feedstock at 20 vol.%. Nevertheless, as it was previously stated, those signals disappeared almost completely by hydroconverting the reaction mixture disregarding the reaction temperature or the catalyst particle size, thus confirming almost complete conversion of triglycerides and intermediaries containing oxygen atoms bounding to carbon.

Therefore, the changes in density of the liquid products shown in Fig. 3 could be explained mainly due to the conversion of triglycerides into hydrocarbons during the HDO of the vegetable oil as inferred by ESI-MS analysis (see Fig. 4). In addition, *Jatropha curcas* L. oil could be decomposed in three fatty acids: linolenic, linoleic, and oleic acid, which were later hydroconverted in lighter saturated hydrocarbons as evidenced by the occurrence of the signals at 0.9 ppm and 1.3 ppm in the $^1\text{H-NMR}$ spectra in Fig. 5, ascribed to methyl and methylene groups. The occurrence of unsaturated compounds was undetectable.

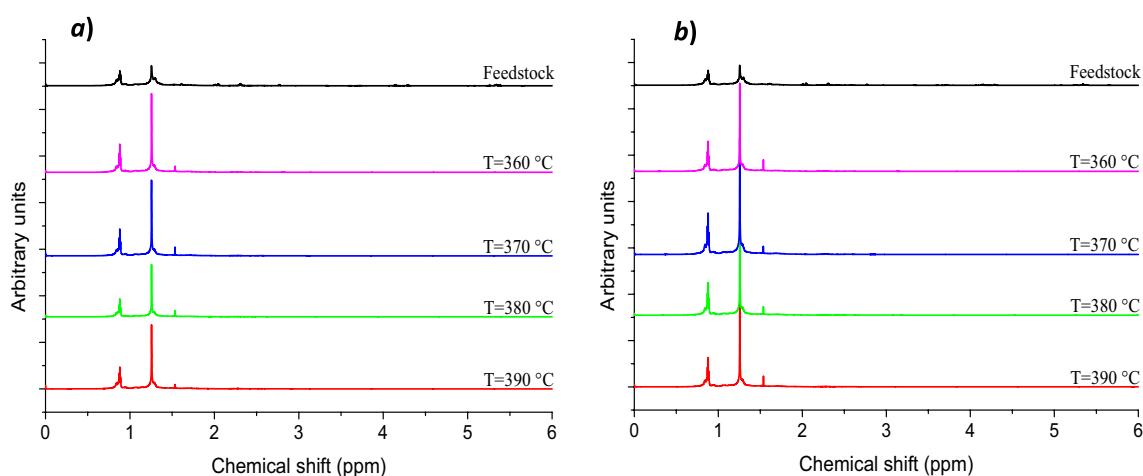


Fig. 5 $^1\text{H-NMR}$ spectra for the feedstock and liquid products at different reaction temperatures **a** powder size catalyst and **b** particle size catalyst

Boiling point distribution in function of catalyst particle size

In Fig. 6, a comparison between boiling points (BP) of products obtained by using powder and commercial catalyst size is depicted, as determined by ASTM D2887. It is observed that the difference of BP is small between products disregarding the catalyst particle size. Therefore, as it was previously stated in ESI-MS analysis (Fig. 4), no major differences in the liquid product composition could be observed by using a powdered size catalyst either a particle shape

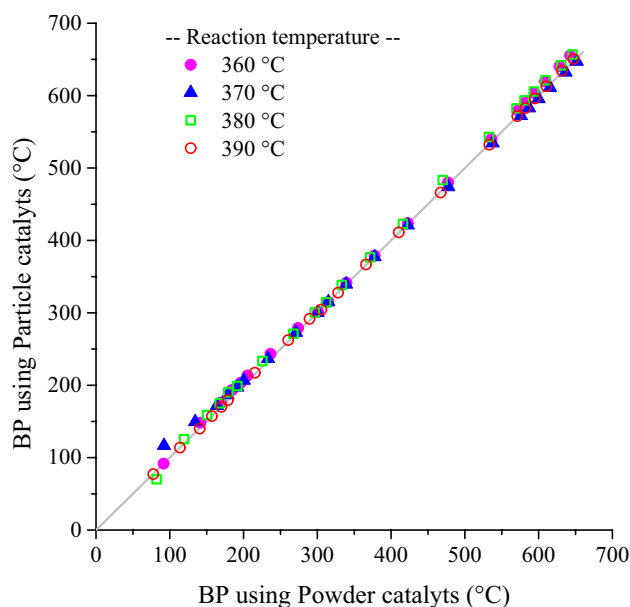


Fig. 6 Comparative chart for different catalyst particle sizes of fractions distributions by boiling point (BP) as determined by the ASTM D2887 procedure

catalyst. The latter ratifies that particle size did not significantly influence HCK reactions during the hydro-co-processing of the mixture vegetable oil and gas oil. The last can be explained because Ni-Mo/ γ -Al₂O₃ is not catalyst for HCK, rather it is a catalyst for heteroatoms removal by hydrotreating (HDT) reactions (e.g., HDS) (Korsten and Hoffmann 1996). Therefore, changes in density, product distribution, and boiling points could be attributed mainly to the hydro-conversion of the vegetable oil into the feedstock via HDO and HDS mechanisms.

The latter results are explained due to that HCK reactions are mainly promoted by acidity ascribed to chemical groups on the catalytic support (i.e., zeolites). Such acidity enhances alkylation, isomerization, and HCK reactions derived from the occurrence of strong Brønsted acid sites and an optimum Brønsted/Lewis acid sites distribution. Since the commercial catalyst used in this study was supported on γ -Al₂O₃ (only Lewis acid sites), a low HCK of heavy hydrocarbon from petroleum part is expected (Pérez-Martínez et al. 2011; Contescu et al. 1995).

Effect of the catalyst particle size and reaction temperature on the fraction compositions in the liquid products

ASTM D2887 curves were converted into lumps fractions using ASPEN HYSYS V9, thus obtaining the following fractions or lumps: naphtha, kerosene, light gas oil, heavy gas oil, and residue. Therefore, analysis was performed based on the mass fraction of each component accordingly.

Figures 7 and 8 exhibit the compositions of the fractions as function of reaction temperature using the powder size catalyst and the particle size catalyst, respectively.

Disregarding the catalyst particle size, no major changes in fractions compositions were observed as it was pointed out in Figs. 4 and 5 for ESI-MS and boiling point parity plot (Fig. 6), respectively. Accordingly, the only effect observed was that of the reaction temperature. Raising the temperature from 360 to 390 °C resulted in increasing yields of the lighter fractions (light gas oil, kerosene, and naphtha) at expenses of decreasing the heavy gas oil and residue. Specifically, a diesel-like fraction (light gas oil) increased from 33.4 to 40%. Additionally, it can be observed, at the lowest reaction temperature, the composition of naphtha and kerosene was smaller than those for the same fraction composition in the feedstock.

Therefore, the highest yields of naphtha and kerosene compositions were reached at 390 °C. One way to explain that result relied on observing that the light gas oil composition was higher at 360 °C than at 390 °C. Hence, the hydroconversion of the light gas oil enhanced the formation of naphtha and kerosene by increasing the reaction temperature. Finally, since no major differences in fractions

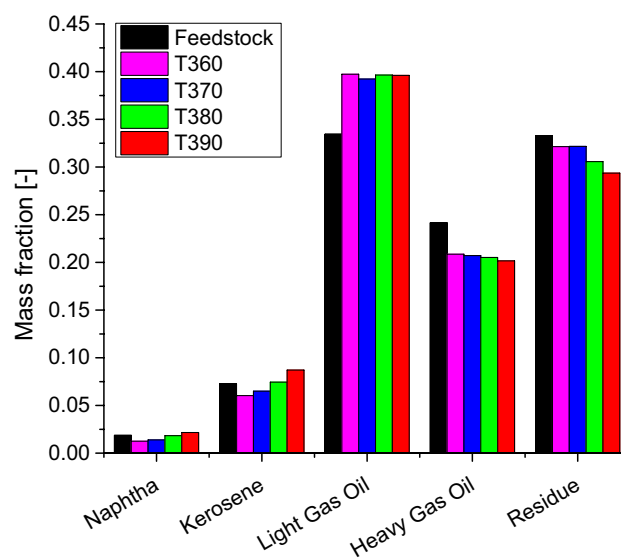


Fig. 7 Distribution of fractions compositions of the liquid products during the hydro-co-processing with the powder size catalyst

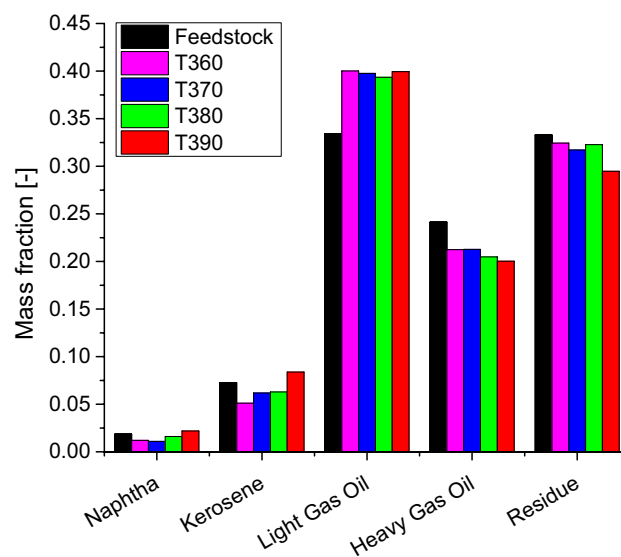


Fig. 8 Distribution of fractions compositions of the liquid products during the hydro-co-processing with the particle size catalyst

compositions were observed by testing the catalyst with different particle sizes and shapes, it could be inferred that, in addition to the thermal effect of temperature, the changes in density and product distribution relied upon the effect of active metals on HDS and HDO reactions rather than HCK, as previously argued in Sect. "Boiling point distribution in function of catalyst particle size." Specifically, HDO mechanism involved the decomposition of the triglyceride into the corresponding free fatty acids, which subsequently were hydroconverted in lighter hydrocarbons via oxygen removal of carbonyl group (Vonortas and Papayannakos

2016; Restrepo-Garcia et al. 2023; Poissonnier et al. 2022), thus reducing the average boiling point of reaction mixture.

Effect of catalyst particle size and temperature in the hydrodeoxygenation (HDO) of the vegetable oil

HDO activity was assessed by following the FTIR bands at 1168 cm^{-1} for simple carbon and oxygen bond, 1710 cm^{-1} for the carbonyl group in carboxylic acids, and 1743 cm^{-1} for the carbonyl group in triglycerides or vegetable oil. FTIR spectra for feedstock and reaction products are shown in Fig. 9. Firstly, the absence of the 1168 cm^{-1} band confirmed the oxygen removal of C-O group for both catalyst particle sizes and any reaction temperature. Secondly, disregarding the particle size and the temperature from $360\text{ }^{\circ}\text{C}$ to $390\text{ }^{\circ}\text{C}$, there were not observed signals at 1710 cm^{-1} or 1743 cm^{-1} , indicating the complete oxygen removal from the carbonyl group in the *Jatropha curcas L. oil* in the feedstock. For the latter, it is assumed the complete hydrodeoxygenation (HDO) of the vegetable oil at the reaction conditions and catalysts evaluated. Finally, the bands between 1250 cm^{-1} and 1500 cm^{-1} , and 2750 cm^{-1} and 3000 cm^{-1} corresponded to $-\text{CH}_2-$ and $-\text{CH}_3$, respectively. The latter results agreed the $^1\text{H-NMR}$ analysis of liquid products. In addition, FTIR results allowed to ratify that the more HDO, the more occurrence of lighter fractions in the liquid product of the hydro-co-processing of the reaction mixture (vegetable oil and gas oil). A complete removal of oxygen from feedstock enhanced the formation of lighter hydrocarbons via degradation of carbonyl group compounds in the vegetable oil.

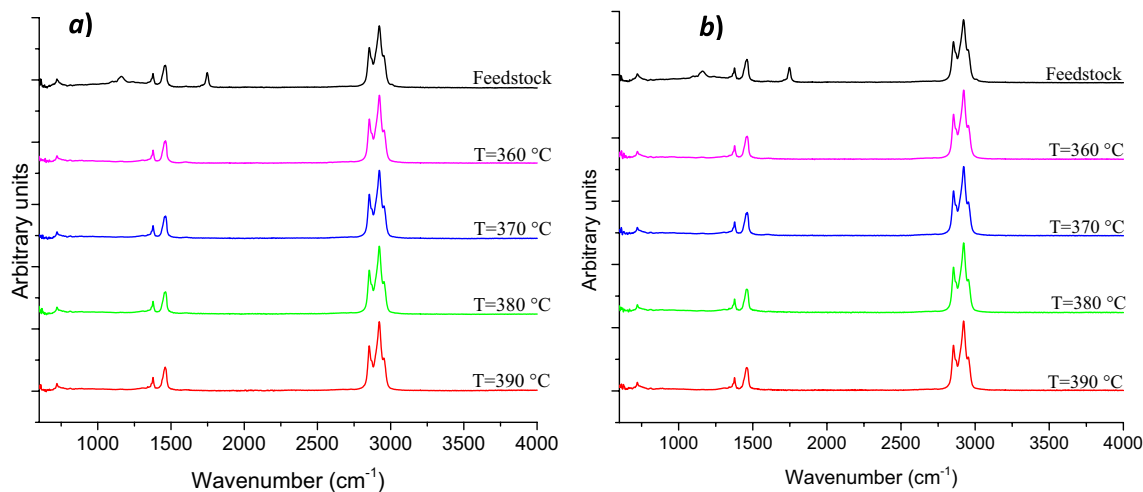


Fig. 9 FTIR spectra of the liquids products during the hydro-co-processing **a** powder size catalyst and **b** particle size catalyst

Effect of the catalyst particle size and temperature in the hydrodesulfurization (HDS) of the mixture vegetable oil and crude oil

As shown in Fig. 10, sulfur removal increased with the temperature, from 35.35% ($360\text{ }^{\circ}\text{C}$) to 54.85% ($390\text{ }^{\circ}\text{C}$) for the particle size catalyst, and from 50.86% ($360\text{ }^{\circ}\text{C}$) to 62.57% ($390\text{ }^{\circ}\text{C}$) for the powder size catalyst. Hence, particle size clearly influenced HDS activity as well as the reaction temperature.

Additionally, increasing sulfur removal (HDS) improved the transformation of heavier molecules into lighter ones reducing the density as shown in Fig. 3 as previously reported (Melo-Banda et al. 2022). HDS reactions require

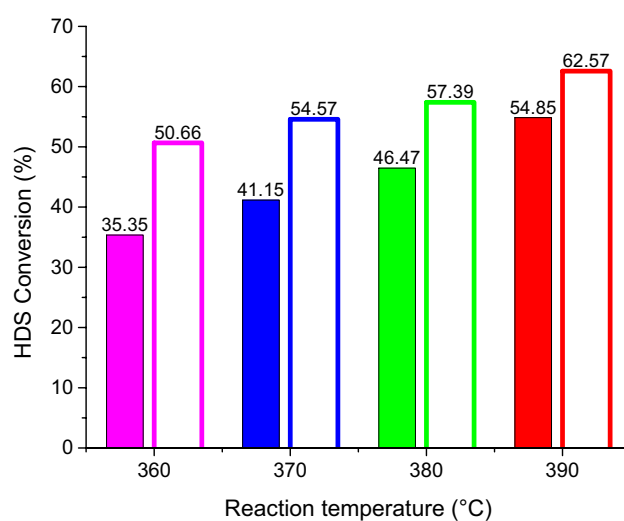


Fig. 10 HDS conversion during the hydro-co-processing using powder size catalyst (filled bar) and particle size catalyst (unfilled bar)

the selective removal of sulfur via cracking of larger molecules into shorter ones via hydrogenolysis and hydrogenation mechanisms. Hence, increasing the concentration of lighter compounds in the final hydrodesulfured liquid products was a consequence of HDS extent.

In summary, using Ni-Mo-supported alumina catalyst in both pellet and powder size did not affect in significant manner, the removal of oxygen atoms from vegetable oil blended with crude oil, at the reaction conditions employed in the current study. Regarding hydrocracking, increasing temperature improved the yield light fractions, but mainly it was due to breaking triglycerides into free fatty acids and further converted into linear hydrocarbons. Finally, HDS was the most affected reaction by changes in particle size due the organic sulfur is contained in complex molecules in petroleum feedstock, thus undergoing difficulty to enter in pores of catalyst particle, being thus favored by using small particle sizes, while the dependence of removal of sulfur on reaction temperature was in line with the previous reported works (Korsten and Hoffmann 1996). The competence between HDO and HDS can also affect the extent of the last reaction, which is slower than HDO at the same reaction conditions.

Conclusions

The catalytic activity of a commercial Ni-Mo/ γ -Al₂O₃ sulfided catalyst was screened during the hydro-co-processing of a mixture *Jatropha curcas L. oil* and crude oil. The catalyst activity was measured in terms of the corresponding hydroprocessing reaction: hydrodesulfurization, hydrodeoxygenation, and hydrocracking. HDS activity was the highest (62.6%) for the powder size catalyst, and the highest reaction temperature (390 °C) in experiments conducted in a batch reactor during 4 h of reaction time and 60 bar of initial pressure of hydrogen. Removal of oxygen from feedstock was almost the 100% using both particle sizes as ratified by disappearance of FTIR bands at 1168 cm⁻¹, 1710 cm⁻¹, and 1743 cm⁻¹ for C-O bond and carbonyl group in carboxylic acid and triglyceride, respectively. The latter disregarding the catalyst particle size and reaction temperature. Finally, HCK activity measured as the change in hydrocarbon compositions in the liquid products indicated that, disregarding the catalyst particle, size mass fraction of the cuts underwent few changes among products, and increasing the reaction temperature enhanced the formation of lighter fractions (naphtha and kerosene). The highest yield (about 40%) was attained for a diesel-like fraction. The present results imply that mixtures of vegetable oil and petroleum-derived feedstocks can be hydroprocessed in a typical HDS industrial reactor using commercial particle size, involving no major changes to the existing infrastructure and achieving almost

100% conversion of the vegetable oil part and acceptable levels of HDS conversion.

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Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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