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# **Evaluation of the hydroconversion reactions of** *Jatropha curcas* **L. oil on hydrodesulfuration catalysts**

# Evaluación de las reacciones de hidroconversión de aceite de *Jatropha curcas* L. sobre catalizadores de hidrodesulfuración

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#### Abstract

In this study evaluated the catalytic activity of two commercial catalysts Ni-Mo/Al<sub>2</sub>O<sub>3</sub> and Co-Mo/Al<sub>2</sub>O<sub>3</sub> for the biofuels production under the hydrodesulfurization process (HDS). The process is performed on *Jatropha curcas* oil, due to its excellent flow properties, allowing the effluent mixing with commercial hydrocarbon cuts. Catalysts have the characteristic of the hydrodeoxygenation reactions of fatty acids present in *J. curcas* vegetable oil for the generation of chemically similar hydrocarbons to those of fossil origin. The effect of the main reaction parameters as pressure, temperature and Weight Hourly Space Velocity (WHSV) were evaluated. HDS process activity with pure *J. curcas* oil and 20% mixture with n-hexadecano was appraised. The results indicate that Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst showed increased conversion of triglycerides and fatty acids to linear-chain hydrocarbons, being greater than 85%, compared to the Co-Mo/Al<sub>2</sub>O<sub>3</sub>-based catalyst, which had a conversion of close to 82%. Blends of *J. curcas* oil with n-hexadecane shows that the process is selective towards diesel production with high conversion of 98.5%. The selectivity can be oriented towards gasoline cuts by changing HDS process parameters *Keywords*: Biofuels, hydroconversion, bifunctional catalysts, *Jatropha curcas*, catalytic selectivity.

#### Resumen

En este estudio se evaluó la actividad de dos catalizadores comerciales Ni-Mo/Al<sub>2</sub>O<sub>3</sub> y Co-Mo/Al<sub>2</sub>O<sub>3</sub> para la producción de biocombustibles bajo el proceso de hidrodesulfuración (HDS). El proceso se realiza sobre aceite de *Jatropha curcas*, debido a sus excelentes propiedades de flujo, lo que permite su mezcla con cortes de hidrocarburos comerciales. Los catalizadores tienen la característica de las reacciones de hidrodeoxigenación de ácidos grasos presentes en el aceite vegetal de *J. curcas* para La generación de hidrocarburos químicamente similares a los de origen fósil. El efecto de los principales parámetros de reacción como presión, temperatura y velocidad especial peso hora (WHSV) fueron evaluados. La actividad del proceso de HDS con aceite de *J. curcas* puro y en mezcla al 20% con n-hexadecano fue evaluado. Los resultados muestran que el catalizador Ni-Mo/Al<sub>2</sub>O<sub>3</sub> mostró mayor conversión de triglicéridos y ácidos grasos a hidrocarburos de cadena lineal, siendo superior al 85%, en comparación con el catalizador basado en Co-Mo/Al<sub>2</sub>O<sub>3</sub>, que tuvo una conversión cercana al 82%. Las mezclas de aceite de *J. curcas* con n-hexadecano muestran que el proceso es selectivo hacia la producción de diésel con una alta conversión del 98,5%. La selectividad se puede orientar hacia los cortes de gasolina cambiando los parámetros del proceso de HDS.

Palabras clave: Biocombustibles, hidroconversión, catalizadores bifuncionales, Jatropha curcas, selectividad Catalítica.

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## 1 Introduction

Nowadays there is a worldwide problem due to the excessive usage of fossil fuels which generate greenhouse gases derived from fossil fuels burning, all of the issues have led to a search of new renewable energy sources. Natural fats and oils are potential sources of feedstock for the production of biofuels (Díaz de León-Cabrero and Sánchez-Castillo, 2016). Currently, edible and non-edible vegetable oils are the main feedstock sources for biodiesel production. the combination of naphtha mixture (Sánchez-Olmos *et al.*, 2020). However, the yields of the different hydrocarbon cuts and their selectivity under the current conditions of the Mexican refinery (PEMEX) processes have not yet been studied.

The use of biomass as a raw material to produce renewable fuels does not increase the concentration of  $CO_2$  in the atmosphere, since this gas released during combustion is removed from the environment through photosynthesis during the production of biomass. Among the methods by which energy can be obtained from biomass are: direct burning, pyrolysis gasification and anaerobic digestion (Teo *et al.*, 2017; Gupta and Demirbas, 2010).

### 1.1 Mechanisms of triglyceride deoxygenation reaction

The reaction mechanism eliminate the to oxygen atoms present in oils is carried out in the hydroconversion process. Hydrogenated triglycerides form free fatty acids, diglycerides and monoglycerides, from the C=C bonds of unsaturated vegetable oils (Huber and Corma, 2007). Oxygen removal can be carried out through three ways: decarboxylation (Kubičková et al., 2005) decarbonylation and hydrodeoxygenation (Sankaranarayanan et al., 2011). Huber et al. (2007) They proposed a triglyceride reaction mechanism shown in Figure 1 where the reaction mechanism of the first stage is represented; triglyceride is hydrogenated, followed by a hydrolysis of triglycerides in fatty acids and glycerol (Berenblyum et al., 2010).

The requirement for molecular hydrogen in the hydroconversion process is greater in the hydrodeoxygenation reaction (Eq. 1) in which the number of carbons of the fatty acid is conserved, in the case of decarboxylation (Eq. 3) the hydrogen is not required, those linear chains can be broken and produce lower molecular weight alkanes and isomerized (Huber *et al.*, 2006). The operating conditions of the process are very important because the secondary reactions depend on great measure of these.

# 1.2 Operating conditions required for the vegetable oil hydroconversion process

Hydroconversion studies of vegetable oils are based on hydrotreatment conditions used in oil refineries, which can reach temperatures of 150 - 425 °C, pressures of 100-3000 psia, space velocities (LHSV) of 0.1-10 h<sup>-1</sup> (Ramírez-Corredores and Borole, 2011). In the case of hydrodisintegration, the temperatures range go from 350 - 450 °C, space velocities (LHSV) from 0.3 -2.0  $h^{-1}$ . The catalysts used for these purposes are NiMo and CoMo type supported in alumina, they can contain an acidic part such as zeolites, which provides the molecules breaking activity (Islam et al., 2015). An important parameter is the partial pressure of hydrogen since it improves hydrogenation and keep clean the surface of the catalyst from coke residues, on the other hand, the rate of rupture and isomerization reaction decreases when this parameter is increased (Pinho et al., 2015). The hydroconversion process of vegetable oils is based on operation conditions of hydrodisintegration and hydrotreatment; several research groups have applied different conditions, among which are: Kubičková et al. (2009) used temperatures of 300-360 °C and pressures of 246.5-580 psia, the obtained conversions were 32-100% a clear effect of temperature is shown, they also evaluated the effect of the partial pressure of hydrogen, being this of 10.1-187.1 psia, showed that at higher pressure the formation of aromatic compounds is avoided.

$$R - CH_2 - COOH \rightarrow R - CH_3 + CO_2$$
(a)  

$$R - CH_2 - COOH + H_2 \rightarrow R - CH_3 + CO + H_2O$$
(b)  

$$R - CH_2 - COOH + 3H_2 \rightarrow R - CH_2 - CH_3 + 2H_2O$$
(c)

Fig. 1. Mechanisms for reaction of fatty acids to linear hydrocarbons (a) hydrogenation; (b) decarbony; (c) decarboxylation. (Huber *et al.*, 2007).

Hancsók *et al.* (2007) evaluated temperatures from 280 to 370 °C, pressures of 507.5-1160 psia, LHSV 1-4 h<sup>-1</sup>, H<sub>2</sub> hydrocarbon ratio 250-400 Nm<sup>3</sup>/m<sup>3</sup>, it was obtained a yield of 94% with a higher proportion of i-paraffins at 350 °C and higher production of n - paraffins at 300 °C, thus make note that temperature is a key factor in the hydroconversion process of vegetable oils.

Huber et al. (2007) evaluated temperatures of 300-450 °C, pressures of 725 psia, LHSV of 4.97 h<sup>-1</sup>, H<sub>2</sub> hydrocarbon ratio, 1600 mL H<sub>2</sub> /mL of feed liquid, it was observed that at high temperatures the alkanes linear chains were isomerized, at high space velocity waxes were formed and at low space velocity there was no polymerization from product obtained, mainly alkanes. Bezergianni and Kalogianni, (2009) used hydrotreatment parameters with temperatures of 350-390 °C. They evaluated the removal of heteroatoms that also is favored with temperature, it was observed that the hydrogenation of olefins is initially favored, but with increasing temperature it decreases. The operation parameters were: 1999 psia pressure and LHSV =  $1.5 \text{ h}^{-1}$ ,  $\text{H}_2/\text{oil} = 1068 \text{ Nm}^3/\text{ m}^3$ , it was observed that the process has greater selectivity towards diesel production. Temperature is a key parameter because this increases the catalyst activity and promotes the conversion, due the hydro-disintegration activity increases, however, the saturation decreases. Therefore, the advisable temperatures range from 300 to 390 °C, hydrogen high pressures as well as low H<sub>2</sub>/oil and LHSV ratios of  $1-4 h^{-1}$ . For this process to be carried out, it is necessary to use bifunctional catalysts and adequate operating conditions that can promote hydrotreating of vegetable oils.

### 2 Materials and methods

The operating profile of the hydroconversion experiment (table 1) began with the pressurization

of the reactor with nitrogen at 200 mL/min until reach 400 psia of pressure, the temperature was programmed at 300 °C, when the ideal conditions were reached in stable state, the nitrogen flow was modified by hydrogen to 120 mL/min. The liquid feed rate was established with an equimolar sulfation mixture  $(C_5H_{12}/CS_2)$ , with a flow of 6 mL/min during 4 h to activate the catalyst. Once finished this stage, the mixture was modified with J. curcas L. Oil, with a flow rate of 18 mL/min h. after hydrotreating, the liquid sample was collected and its yield was measured. This hydroconversion experiment was carried out at temperatures of 300-360-390 °C, and pressure of 145 to 400 psia. Sampling was done in triplicate. The hydroconversion process was carried out using two different loads, the first J. curcas L. oil was used to 100% purity, and the other, feed an oil mixture in n-hexadecane ratio 20-80%.

Catalytic activity experiments were performed in a continuous flow tubular reactor (30 cm length, with internal diameter of 1 cm) assisted by HP150 software control. Experiments were conducted under conditions similar to the HDS operating process with a temperature range of 300-390 C, a pressure of 145-400 psia, and residence times of 0.5 and 2.0 min (WHSH -60 h<sup>-1</sup> and 30 h<sup>-1</sup>)

#### 2.1 Analysis method

The effluent analysis of the hydroconversion was done by gas chromatography coupled to mass spectrometry (GC/MSD), the equipment is Agilent 7890A-5975C chromatograph with ChemStation software for data acquisition. A capillary column with 30 m length HP-5MS was used, by means of a simulated distillation method in splitless mode with triple quadrupole detector, with an injector temperature of 250 °C, helium carrier gas with a flow of 1 mL/min. The determination of the conversion and selectivity was made by comparing the retention times of the standard and the sample by means of the Nist 2.0 library getting an 90% quality or higher.

	Oil 0,3 mL/min H <sub>2</sub> 120 mL/min		
Feed flow to reactor			
Pressure	145 psía		400 psía
Residence time 1/WHSV	0.5 min		2.0 min
Temperature	300 °C	360 °C	390 ℃
Type of catalyst	NiMo	CoMo	

Table 1. Evaluation parameters in hydroconversion reactions with Jatropha curcas oil.

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The hydroconversion of the vegetable oil liquid effluent was analyzed based on chain length, and molecular weight to determine the three global hydrocarbon cuts (i.e., gasoline (<10 carbon atoms); jet fuel ( $\leq 10$ -15 > carbon atoms); and diesel ( $\geq 16$  carbon atoms) to quantify conversion and yield (Zambrano *et al.*, 2019).

### 2.2 Oil extraction from J. curcas L.

Extraction experiments of J. curcas L. oil were made from seed with husk to evaluate the extraction yields, since by previous references it is known that the presence of husk can be important for the accumulation of pressure within the press that favors the operation (Vaknin et al., 2011). 3 kg of seed were submitted, obtaining the extraction yields presented in table 2. Yields were lower than those reported by other paper (Martínez-Herrera et al., 2006), where a 55-60% percentage of oil was obtained through the press extraction method with from Yautepec, Morelos seeds. No reports of oil with husk yields were found, however, it is not advisable to use this method because the efficiency is lower as in a 19%, in addition to that, when remove the husk, the oil contains less impurity presence, so the press extraction method without husk seed represents the best option.

Table 2. Jatropha curcas oil extraction yield
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Seed	Extraction yield
WITHOUT HUSK	25.8%
WITH HUSK	31.9%

### **3 Results and discussion**

### 3.1 Conversion and selectivity results for catalyst

Selectivity and conversion results for both catalysts evaluated are shown in the Figure 2, this activity is established at short residence times but with characteristic of the study of the HDS process. The conversions for both catalysts evaluated at three temperatures are observed, the increases in the conversion as the temperature rises.

NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst show greater conversions, however, the percentage difference is low at 390 °C, being 2.6% with respect to CoMo/Al<sub>2</sub>O<sub>3</sub>, the variances analysis, shows that there is no significant difference between NiMo and CoMo from HDS. At 360 °C NiMo/Al<sub>2</sub>O<sub>3</sub> is higher with a conversion of 74% compared to 50.2% for CoMo. Finally, at 300 °C a greater it is observed a greater range of conversion in the NiMo catalyst over CoMo, with a difference in percentage of 30.5%, statistically NiMo show significant difference compared to CoMo catalyst. The CoMo catalyst has greater desulfurization activity but is less selective towards other heteroatoms; as oxygen, NiMo is selective as well as towards other heteroatoms and also sulfur (Pinho et al., 2015), with what favors the conversion of J. curcas L. oil (Teo et al., 2019). Liquid fuels are produced by hydroconversion reactions are gasoline, taking into consideration a range of 4-10 carbon atoms, jet fuel with chains of 10-16 carbons, and finally diesel with molecules containing more than 16 carbons in its structure.



Fig. 2. Catalyst conversions at 400 psía, and retention time of 2.0 min for both catalysts.



Fig. 3. Selectivity for catalysts evaluated at 390 °C, 400 psia with 2.0 min of retention time.

The selectivity results for the two catalysts at the best temperature of 390 °C, residence time of 2.0 minutes and 400 psia are presented in Figure 3. It can be observed a greater selectivity towards diesel for both tested catalysts, it is shown a greater production using NiMo compared to CoMo catalyst. In jet fuel the production is quite similar with differences in values of less than 2%. In gasoline production, CoMo presented a greater value as of 33.7%. It is evident that the reaction benefits the production of diesel over jet fuel and gasoline, which coincides with the existing reports, these catalysts have low acidity and therefore the breakdown of molecules is less. Hydrotreating catalysts are designed to remove heteroatoms and have minimal cracking activity (Donnis et al., 2009; Huber et al., 2007). Among the main products obtained in the diesel cut are heptadecane, octadecane, 7-octadecane, 8-heptadecane, hexadecane, 7-hexadecane, pentadecane-3-methyl, in smaller quantities hydrocarbons such as 1-nonadecene, 5-nonadecene, eicosan, 1,3,12-nonadecatriene. As for jet fuel, compounds such as decane, tetradecane, pentadecane, 1-tetradecene, 4-tridecene, among others, were obtained. In the gasoline cut the compounds obtained were octane and hexane.

#### 3.1.1 Reaction kinetics

Commercial CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts were evaluated at 2 residence times of the HDS process, 0.5 and 2.0 min (WHSV of 60 and 30 h<sup>-1</sup>, respectively). The conversion results at those residence times for the first catalyst indicate that at 360 °C the conversion increases from 17.3 to 46.3% at 145 psia passing from 0.5 to 2.0 min, at 400 psia, it goes from 13.6 to 50.2%.



Fig. 4. Selectivity kinetics for CoMo/Al<sub>2</sub>O<sub>3</sub> at 390 °C and 145 psía (grey lines) and 400 psía (black lines).

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Fig. 5. Effect of Residence Time on NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (The first legend value represents the temperature in degrees Celsius and the second the pressure in psia).

At 390 °C the conversion increases by 400 psia the initial value is 32.6% and it increases up to 83.4% with increasing residence time. As expected, the overall conversion increases with respect to the residence time. Figure 4 shows the behavior of the selectivity towards the different fuel cuts according to the residence time for the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at a temperature of 390 °C.

Considering a residence time of 0.5 min this process is mainly oriented to the production of diesel followed by jet fuel and finally gasoline, which indicates that at this temperature there are oxygen removal reactions, and cracking reactions so that the larger molecules are fractionated in order to obtain smaller ones which are considered in rage of gasoline and jet fuel (Ooi et al., 2019). When increase the residence time, it is observed that the production of diesel and jet fuel decreases, this benefit the selectivity towards gasoline, with these results it can be established that longer residence time benefits the catalytic cracking process therefore a greater production of lighter hydrocarbons as gasoline, which increases from 5.7 to 33.7% at 400 psia and from 18.9 to 24.8% at 145 psia.

The Results for the NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst are shown in Figure 5, the residence time bring a positive effect on conversions, at 360°C the conversion went from 22.8 to 46% and from 17.7 to 74.5% at 145 and 400 psia, respectively. For the temperature of 390 °C the initial conversion was 43.1% and it was increased as of 75.9% at 145 psia, when increases the pressure to 400 psia the conversion was as of the double, getting a final value as of 86.1%. The residence time is a very important parameter in the hydroconversion process, it is evident the increases in the conversion when it went to a higher residence time, so, the hydroconversion products increase (Bezergianni *et al.*, 2012).

NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst presented a similar trend to the previous catalyst in terms of selectivity, results indicate that at 0.5 min the selectivity towards diesel is greater with a difference in percentage of 46.5% on jet fuel and 66.6% over gasoline, these results can vary in a low percentage as of 5% in both pressures because selectivity were very likely. The results at 2.0 min in selectivity are similar at 0.5 min, however, there is a percentage of gasoline greater as of 3 times that obtained in 0.5 min in both pressures, as of jet fuel there is a slight decrease at 400 psia of 1%, at 145 psia this decreases to 10 the percentage. The diesel percentage decreases by 10% to 400 and by 5%to 145 psia. It can be concluded that there is a cracking step for diesel molecules and jet fuel producing a greater percentage of gasoline.

When assessing temperature of 350 °C the selectivity tendency is not different to the previous ones, the conversion is as of 55% at 145 psia and 79.9% at 400 psia, this at 2.0 min. At 0.5 min conversion is 24.2 and 46.5% at 145 and 400 psia. it can be seen that the conversion in greater in high pressure, which coincides with the results goes from 0.5 to 2.0 min. The selectivity towards diesel decreases in 5% at 400 psia in less than 0.3% at 145 psia, jet fuel decreases in a 2% and 5% at 400 and 145 psia, finally the selectivity towards gasoline increases from 3.35 to 10.7% at 400 psia and from 2.8% to 8.4% at 145 psia. It is confirmed that at high pressure there is greater

diesel cracking in order to generate more gasoline than jet fuel, this is contrary to 145 psia where the jet fuel molecules undergo a breaking process in order to get gasoline, leaving the selectivity towards diesel without any changes. The results show that diesel production with both catalysts is greater compared to the one of jet fuel and gasoline respectively, being the gasoline with lower percentages obtained. Temperature and residence time are very important parameters that affect the selectivity of the reaction, when both values increase there are a greater production of lighter fuels among gasoline range, diesel tends to decrease because those molecules break, the same phenomena can be observed in the selectivity towards jet fuel. These results coincide as of the ones reported previously, the increases in residence time increase cracking reactions and this favored with the temperature used (Bezergianni et al., 2009; Donnis et al., 2009; Huber et al., 2007).

#### 3.1.2 Temperature effect on hydroconversion process

Hydroconversion temperature has an effect over the conversion rate for both catalysts, for CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst the results are shown in Figure 6, it shows a maximum conversion of 83.4% at 390 °C and 400 psia, evaluated in a residence time of 2.0 min.

The selectivity is greater towards diesel at low temperatures, as the temperature increases there is greater selectivity towards gasoline, this indicates the molecules in the order of diesel and jet fuel suffer a catalytic cracking process, this is originated from triglycerides which contain fatty acids of 18 carbons as oleic and linoleic acid, followed by the palmitic acid of 16 carbons that through cracking produce hydrocarbons from the order of decane, octane, hexane, among others. This phenomenon has been highlighted by different authors who have gotten similar previous data.



Fig. 6. Effect of temperature on selectivity of samples treated with CoMo/Al<sub>2</sub>O<sub>3</sub> at 2.0 min and pressures of 145 psia (grey lines) and 400 psia (black lines).



Fig. 7. Effect of temperature on selectivity of samples treated with NiMo/ Al<sub>2</sub>O<sub>3</sub> at 2.0 min and pressures of 145 psia (grey lines) and 400 psia (black lines).

Bezergianni *et al.* (2012) reported the oil-used selectivity, where every cut of hydrocarbons is modified as the temperature increases and it is oriented towards gasoline fractions. At 145 psia is observed a gasoline production which is 4 times greater than initial, jet fuel has an increase of 23.3 to 31.5%, diesel shows a decrease of 31.5%. Huber *et al.* (2007) report the same performance for sunflower oil where the diesel fraction decrease from 70 to 58% and the cuts of jet fuel and gasoline increase to 10.72% and 5.48% respectively, from 300 to 400 °C.

For NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, selectivity showed a similar tendency to the CoMo catalyst, in Figure 7 it is observed the decrease of the selectivity towards diesel, especially at 400 psia. The greater gasoline production can be gotten at higher temperature and pressure of 145 psia with 18.5%. The selectivity towards diesel is greater using this catalyst due to it does not have a high acidity and therefore the catalytic cracking is low, when temperature increased diesel selectivity decrease in 6%, giving an increase in jet fuel of 22% and gasoline of 3.3%, as it can be seen that for this catalyst produces fuels related to diesel and in low proportion, jet fuel and gasoline.

#### 3.1.3 Pressure effect on hydroconversion process

To assess the effect that the pressure has in the hydroconversion process, the oil was subjected to both catalysts, pressures of 145 and 400 psia and residence times at 0.5 and 2.0 min. The pressure shows a positive effect on the majority of evaluated temperatures, the effect is observed in Figure 8 for CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. Gasoline production increases slightly at 400 psia and 390 °C, while at 145 psia

and 300 ° C there is greater selectivity towards diesel. For the same catalyst, jet fuel production is favored at 390 °C with a value of 34.9% when the working pressure was increased at the same temperature. As the temperature decrease to 360 ° C and 300 °C, the selectivity did not have statistically significant effects when modifying the pressure from 145 to 400 psia. For NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst (Figure 9) the pressure exerts a positive effect on the conversion, at 300 °C goes from 24.5 to 41.7%; for 360 °C goes from 46% to 74.5% and for temperature of 390 °C it ends with a value of 86.1%. This positive effect on conversion as the pressure increases coincides with their data reported by Hancsók et al. (2007), where it showed that pressure favors the deoxygenation reactions on sunflower oil, it can be observed that at 300 °C by increasing the pressure from 453 to 1160 psia, the conversion increased from 31 to 48% and at temperatures of 360 °C conversion rise of 94 to almost 100% for the same pressure range.

For NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst the selectivity towards jet fuel is favored with high temperatures and pressure of 145 psia. The greater selectivity as seen for both catalysts goes towards diesel cuts, for pressures of 400 psia and 360 °C.

#### 3.2 Oil-hydrocarbon mixing experiments

Blends of *J. curcas* L. oil with n-hexadecane in a ratio of 20-80 (v/v), for HDS process using CoMo and NiMo catalysts, at residence times of 0.5 and 2.0 min, with temperatures of 360 and 390 °C, at 400 psia of pressure, these operation conditions simulate the hydrotreatment process at an industrial level.







Fig. 9. Effect of pressure on selectivity of samples treated with NiMo/Al<sub>2</sub>O<sub>3</sub> at 2.0 min.



Fig. 10. Selectivity kinetics for CoMo/Al<sub>2</sub>O<sub>3</sub> at 390 °C (black lines) and 360 °C (grey lines) in mixture of 20% *J. curcas* oil in n-hexadecano.

As seen before residence time and temperature are the most important parameters in the process that affect directly the conversion oil, for the CoMo catalyst, high conversion values are obtained even at low residence time, at 0.5 min the conversion at 360 °C and 390 °C is 95.7% and 98.5% respectively, when the residence time increased the conversion is in a 100% in the range of temperature used, which shows that the operation conditions applied are appropriate to carry out the process (Figure 10).

This behavior in mixtures has been reported previously by authors such as *et al.* (2011) reported diesel mixtures with sunflower oil in an 80-20 proportion, greater conversions were obtained of 95% at temperatures of 320 °C and 100% at 350 °C, at a WHSV of 2 h<sup>-1</sup>, however, it was reported that at 320 °C when increases the WHSV the conversion was less than 65% Blend of *J. curcas* oil with nhexadecane was carried out brought high conversions in short residence time, when assessing selectivity, it is clear that diesel production is far superior to jet fuel and gasoline (Figure 9), the tendency in selectivity of diesel as of a temperature of 390 °C it is higher than 90%, which decrease in a 2% with residence time increase. Selectivity gasoline cuts increases less than 2% and jet fuel increases by 2.5% when residence time increase from 0.5 to 2.0 min at 360 °C, the behavior changes for diesel, as the residence time increased, the selectivity increases in a 63.4%, for gasoline is as of 5% less as in diesel, this is at 0.5 min.

Selectivity at temperature of 390 °C towards diesel is greater compared to 360 °C in the two residence times evaluated, which coincides to the results reported by Huber *et al.* (2007), diesel selectivity increase from 22 to 33% by increase the temperature from 350 to 450 °C, the selectivity towards to gasoline and jet fuel cuts increases, however, these values are less than 10%. For the NiMo catalyst the results are very similar to the previous ones, the conversion is 98.4% at 360 °C and 100% at 390 °C, as in 2.0 min of residence time, this catalyst had a better performance in oxygen removal in J. curcas oil It is important to be aware of the importance of temperature and residence time as the better suitable conditions are gotten, resulting in a complete process as in mixtures. Bezergianni et al. (2009) conduced mixtures at 30% of used cooking oil with hydrocarbon cuts, getting a percentage of oxygen removal greater than 70% at 350 °C. The fact that in mixtures the conversion is higher it is attributed to the low quantity of oil, there are more vacant catalytic sites and therefore the greater part of triglycerides can react and generate free oxygen- compounds (Negm et al., 2018).

NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst report high selectivity values towards diesel compared to jet fuel and gasoline in both tested temperatures. The selectivity increases towards gasoline when residence time increased, at 360 °C the gasoline production increased as of 19% and decreases to 9.4%, from 0.5 to 2.0 min, while the jet fuel production maintains near to 1% in both residence times, at 390 °C the selectivity towards jet fuel is greater than for gasoline, being 15.5%.

The selectivity of the hydroconversion reaction in oil mixtures with n-hexadecane shows that the process is selective towards diesel production. Based on the results obtained by gas chromatography, it was observed hydrocarbons production as: octadecane and heptadecane, these products show that oxygen removal reactions are carried out through decarboxylation and hydrodeoxygenation. the highest production of gasoline was at temperature of 360 °C and residence time of 0.5 min, with both catalysts. This can be associated with more drastic operating conditions, that can be polymerization of small molecules by the dimerization process.

### Conclusions

The NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts typical of the hydrodesulfurization process, were suitable to carry out the *J. curcas* L. oil hydroconversion reactions, getting higher conversion levels than 80% inside the operation range HDS. However, the process tends to be more selective towards the production of

diesel with yields greater than 60%. Hydroconversion reactions are highly dependent from the operation conditions, mainly due to the temperature and residence time which are key parameters during the process.

Catalytic activity increases proportionally to temperature and residence time for both catalysts which conversion to a low temperature evaluated showed 20% and increased nearly 80% due its bifunctional acidic and metallic activity, HDS catalysts were able to carry out the deoxygenation reactions to required conversion levels so this biofuel can be used without alter the quality of the final fuels.

The complete deoxygenation of the mixture of hydrocarbons and *J. curcas* L. oil at 20% produce an excellent opportunity to diminish the content of contaminants such as sulfur contained in liquid fuels and mainly the partial replacement of fossil based liquid fuels in a short an and long term. When using *J. curcas* L oil. it resulted to be the adequate because it had better testing results. It can be observed when adding hydrocarbons cuts, the conversion is fully complete in the oil.

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