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Hydroprocessing of crude palm oil at pilot plant scale

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ABSTRACT

High cetane index renewable diesel can be obtained by hydroprocessing of palm oil using conventional hydrotreating catalyst (NiMo/γAl_2O_3). At 40–90 bar hydrogen pressure crude palm oil (CPO) can be deeply converted into paraffins in the diesel range. However, at lower pressures hydrodeoxygenation cannot be fully reached and the appearance of intermediates as C16–C18 alcohols, C16–C18 acids and esters were preliminary identified in the reaction product. Times of stream (TOS) experiments have shown that conventional hydrotreating catalyst suffers of slight deactivation as the reaction proceeds.

1. Introduction

The option of using vegetable oils as an alternative diesel fuel is restricted by their high viscosity. Several routes have been tried for reducing this viscosity, such as diluted vegetable oil with diesel fuel, microemulsification with alcohols, pyrolysis, and transesterification [1]. In recent years, hydroprocessing technology has been used to convert lipid feedstocks into distillate fuels [2–7]. The two main products consist of a liquid distillate fuel with very similar properties to petroleum diesel, and propane in the gas phase stream. This fuel is incorporated into EPAct05 biodiesel definition as non-ester renewable diesel (NERD) in "thermal depolymerization" technology that can become a most effective tool in reducing the carbon footprint [8]. The primary advantages of this fuel over first-generation biodiesel technology are: (1) the cold weather properties are superior; (2) the propane byproduct is preferable over glycerol byproduct; (3) the heating content is greater; (4) the cetane number is greater; and (5) capital costs and operating costs are lower [9].

Under high hydrogen pressure and relative high temperature vegetable oils can be converted into paraffins (from n-C15 up to n-C18) having water, propane and CO_x gases as by-products. Intermediates as monoglycerides, diglycerides, ketenes, aldehydes, acrolein and carboxylic acids have been proposed [2,10], these are formed in the initial step and subsequently hydrogenated or broken down via decarboxylation, decarbonylation or hydrodeoxygenation. In addition to the main reactions mentioned above, cyclization and aromatization reactions can take place especially when fatty acids that compose the triglycerides in the vegetable oil are polyunsaturated as linoleic and linolenic acids [11].

Although in principle common industrial hydrotreating catalyst can be used for this purpose their stability to the presence of by products as water and CO_x has not been established yet [12]. In this paper experiments at pilot plant scale combined with chromatographic methods has been conducted with the purpose of studying of reaction variables as hydrogen pressure and time of stream, the latter with the objective to observe the stability of the catalyst to the reaction by-products. Additionally experimental information has been compared with data obtained by an equilibrium reactor model.

2. Experimental

Hydrogenation of crude palm oil (CPO) using an industrial hydrotreating catalyst (NiMo/γAl_2O_3, Haldor Topsøe 217) intended to sulfur and metal removal was carried out. The catalyst particles are in the trilobe form and have an average equivalent size of 1.8 mm, a length of 4.1 mm, and are mixed (diluted) with spherical and inert SiC particles of different sizes, with the purpose of improving the flow pattern and help to achieve isothermal conditions. The hydrotreating activity experiments were conducted in a trickled-bed reactor unit continuously operated using pure CPO as feed. The catalyst was previously activated by a standard procedure using straight-run gas oil containing 3 wt% dimethyl disulfide for sulfiding [13]. After catalyst activation, reaction conditions were adjusted. Two process variables were investigated, i.e., hydrogen pressure and time on stream (TOS). They were varied as follows: pressure = 15–90 bar and TOS = 0–14 days using in all experiments a volume (STP) ratio hydrogen/CPO = 484 (20:1 molar). Product samples were collected and analyzed for cetane index (ASTM D-4737), kinematic viscosity at

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Table 1
Properties of crude palm oil (CPO).

Property	Units	CPO
Cetane index	Cetane units	–
Kinematic viscosity at 40 °C	mm^2/s	40.33
Density at 15 °C	g/mL	0.9139
API gravity	°API	23.3
Flash point	°C	275
Cloud point	°C	23
Pour point	vC	12
BSW	vol%	0.3
Bromine number	$g Br_2/100 g$	52.9
Acidity	mg KOH/g	7.392

40 °C (ASTM D-445), density (ASTM D-4052), flash point (ASTM D-93), cloud point (ASTM D-2500), pour point (ASTM D-97), Corrosion (ASTM D-130), Color (ASTM D-1500), acidity number (ASTM D-664), thermal stability (ASTM D-6468), carbon and hydrogen (ASTM D-5291), bromine number (ASTM D-1159), simulated distillation (ASTM D-7213) using an Agilent 6890 GC equipped with a fused silica 10 m × 0.53 mm × 0.9 μm column and a calibration mixture from C3 to C60; Properties of CPO provided by a local extractor plant are given in Table 1.

After reaction products are separated in a biphasic separator where the reaction pressure is reduced to almost atmospheric pressure. Liquid products are collected in the separator and gases are measured with a Ritter TG-3 and collected in a stainless steel container. The liquid products, i.e., aqueous phase and the less dense organic phase (hydroprocessed product) are then separated by decantation.

In addition to all analysis previously described, the hydrogenated product was analyzed by GC–MS using a gas chromatograph Agilent 6890 connected with a mass spectrometer Agilent 5973N equipped with a HP5-MS 60 m × 0.25 mm × 0.1 μm column. The temperature in GC oven was programmed from 30 to 300 °C at a heating rate of 3 °C/min. The reaction gases were analyzed using an Agilent 6890N GC equipped with FID/TCD detectors using multidimensional chromatography.

3. Results and discussion

3.1. Hydrogenation of CPO varying hydrogen reaction pressure (P)

GC–MS analysis of hydrogenation products varying the hydrogen pressure are shown in Fig. 1. As it can be seen the reaction pressure P has an appreciable influence on product selectivity. As the P is decreased not only the yield of products with higher boiling points (retention time longer than 34.7 min that corresponds to the n-C18 paraffin) increases but also the yield of products with lower boiling points (retention time shorter than 28.0 min time that corresponds to the n-C16 paraffin). At lower retention times lighter products would correspond to the paraffin series from C3 to C14. At longer times (>34.7 min) a higher yield of heavier products as the reaction pressure decreases is observed. Along with this behaviour the main peaks corresponding to the n-paraffins C15–C18 become broader indicating that co-elution of isomers of these products and other reaction products, is occurring. A zoom of the chromatogram on this range of retention times shows clearly the effect of decreasing the hydrogen pressure in the reactor (see zoom right). Only the two extreme pressures are plotted, i.e., 15 and 90 bar. As observed the number of products increases dramatically as the pressure is reduced. Unfortunately the peak purity for some of these compounds at low hydrogen pressure was very low and they could not be identified.

We have combined quantitative information from GC-FID techniques and semi-quantitative analysis from GC–MS, especially considering the higher peak resolution of GC–MS compared to distillation chromatography obtained from GC-FID analysis, to interpret the results of this study. Thus, we have used fraction yields in terms of gasoline (IBP-221 °C), middle distillate (221–344 °C) and 344 °C+.

Between the reaction products obtained at low pressures, and preliminary identified by GC–MS, and observed at higher retention times (>34 min) are octadecenes (35 min), octadecanol (36.2 min), n-hexadecanoic acid (37.8 min), octadecanal (38.9 min), and hexadecyl hexadecanoate (58.5 min), and octadecyl hexadecanoate.

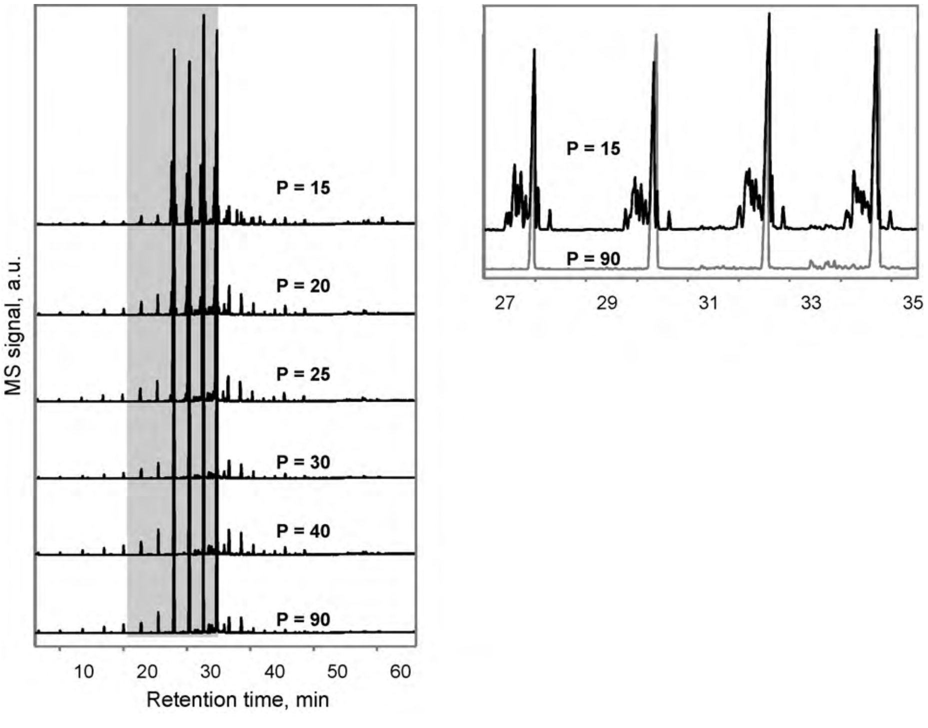

Fig. 1. GC–MS of CPO hydrogenation products varying reaction pressure from 90 to 15 bar.

These compounds are not formed (or at very low concentrations) at 90 bars. These compounds are very likely the intermediates formed by the thermal decomposition of the triglyceride where from a triglyceride molecule, a fatty acid, an aldehyde or long chain alcohols can be formed. At this point it can be presumed that the high molecular esters observed at low pressure are the result of the reaction between a fatty acid and a long chain alcohol that are possible intermediates of the involved reactions in this process. In contrast at higher hydrogen pressure the formation of fatty acids and other oxygenated compounds is reduced and therefore high molecular esters are not observed in the reaction products.

It is also important to remark that in the product composition where observed cycloparaffins and aromatics but mostly at pressures lower that 25 bar. While at 90 bar approximately 0.5 wt% of cycloparaffins and 0.0 wt% of aromatics were observed, at the lowest studied pressure (15 bar) the content of these secondary reaction products increased in case of cycloparaffins to 8.6 wt% and aromatics to about 0.2 wt%. In comparison to the results observed by Da Rocha [11] where highly polyunsaturated vegetables as those from maracuja and soybean and hydroprocessed at 360 °C and at even at a much higher pressure (140 bar), a higher content of cycloparaffins and aromatics were reported. This can be interpreted in terms of the fatty acid composition of the vegetable oils. In palm oil the content of linoleic (C18:2) and linolenic (C18:3) acids is about 12 wt% while in maracuya and soja is of the order of 71 and 64 wt%, respectively. This leads to a higher production of these secondary products when a vegetable oil with high concentration of polyunsaturated fatty acids is hydroprocessed. Thus, palm oil has the advantage to be easier to process and probably to conduce to lower hydrogen consumption.

In order to evaluate these analytical results in terms of chemical equilibrium considerations, the hydroprocessing of triacylglicerides was simulated.

Mass balances of all these experiments were evaluated. All reaction effluents, organic and aqueous liquid phases and gases, have led to satisfactory mass balance results. Based on the series of reactions proposed [11,14] we have simulated in Aspen Plus 2006.5 simulator an equilibrium reactor based on stoichiometric approach varying operational conditions as total pressure, reaction temperature and hydrogen/CPO ratio. Joback's contribution method was used to estimate the standard Gibbs free energy of formation of some compounds which are not in the simulator database such as cycloalkanes and olefins (Table 2). PSRK (predictive Soave–Redlich–Kwong equation of state) was used as thermodynamic model of phase equilibrium [15]. The set of reactions can be seen in Table 2, where initial reactions represent the degradation of triglycerides; hydrogenation reactions represent the saturation of double bonds of fatty acids; cyclization reaction indicate the formation cycloalkanes from fatty acids with double bonds; decarboxylation and decarbonylation reactions represent the production of C17 and C15; reduction reactions indicate the production of C18 and C16; and reactions 17–20 represent the formation of oxygenated products as alcohols and esters.

In order to represent the fatty acid distribution of the CPO, triolein (45 wt%), tripalmitin (43 wt%) and trilinolein (12 wt%) were used as representative molecules of triglycerides for CPO. Considering that decarboxylation and decarbonylation reactions lead to, n-paraffins with a one carbon less than those present initially in the fatty acids chains that compose the triacylglicerides, molar ratios C17/C18 and C15/C16, were calculated. Results simulated at 350 °C are presented in Figs. 2 and 3 for two different H_2:CPO ratios (12.5:1 and 20:1) and compared with experimental data obtained using a ratio H_2:CPO = 20:1. As observed there is a reasonable agreement with calculated results at a 12.5:1 ratio that indicates a deficiency in effective hydrogen if these reactions were in chemical equilibrium. It can be suggested that under these conditions the reaction can be restricted by hydrogen diffusion or triglyceride diffusion to the active sites [16] or by hydrogen spillover effect [17] which can occur on catalysts as the used in this study. In spite of this conventional catalyst consists of a large pore system provided by the γ alumina and is currently used to process vacuum gas oils and other high molecular weight feedstocks, the bulky triacylglycerides molecules cannot diffuse properly into this pore system. However, as triacylglicerides are thermal unstable compounds, thermal cracking of these molecules occurs simultaneously favoring their processability in this catalytic system [10].

As observed in Fig. 2 C17/C18 and C15/16 ratios decrease with reaction pressure indicating that decarboxylation and decarbonylation reactions are diminished. In terms of process profitability

Table 2
Reactions included in simulation of equilibrium reactor.

Reaction no.	Stoichiometry	
1	TRIOLEIN + $3H_2 \leftrightarrow$ 3 OLEIC ACID + PROPANE	Initial reactions
2	TRIPALMITIN + $3H_2 \leftrightarrow$ 3 PALMITIC ACID + PROPANE	
3	TRILINOLEIN + $3H_2 \leftrightarrow$ 3 LINOLEIC ACID + PROPANE	
4	OLEIC ACID + $H_2 \leftrightarrow$ ESTEARIC ACID	Hydrogenation
5	LINOLEIC ACID + $H_2 \leftrightarrow$ OLEIC ACID	
6	LINOLEIC ACID + $2H_2 \leftrightarrow$ ESTEARIC ACID	
7	OLEIC ACID + $3H_2 \leftrightarrow$ DODECYL-CYCLOHExANE + $2H_2O$	Cyclization
8	ESTEARIC ACID $\leftrightarrow$ n-C17 + CO_2	Decarboxylation
9	PALMITIC ACID $\leftrightarrow$ n-C15 + CO_2	
10	OLEIC ACID $\leftrightarrow$ C17= + CO_2	
11	ESTEARIC ACID + $H_2 \leftrightarrow$ n-C17 + CO + H_2O	Decarbonylation
12	PALMITIC ACID + $H_2 \leftrightarrow$ n-C15 + CO + H_2O	
13	OLEIC ACID + $H_2 \leftrightarrow$ C17= + CO + H_2O	
14	ESTEARIC ACID + $3H_2 \leftrightarrow$ n-C18 + $2H_2O$	Reduction
15	PALMITIC ACID + $3H_2 \leftrightarrow$ n-C16 + $2H_2O$	
16	OLEIC ACID + $3H_2 \leftrightarrow$ C18= + $2H_2O$	
17	ESTEARIC ACID + $2H_2 \leftrightarrow$ OCTADECANOL + H_2O	Formation of alcohols
18	PALMITIC ACID + $2H_2 \leftrightarrow$ HExADECANOL + H_2O	
19	2 ESTEARIC ACID + $2H_2 \leftrightarrow$ OCTADECANOATE OCTADECYL + $2H_2O$	Formation of esters
20	2 PALMITIC ACID + $2H_2 \leftrightarrow$ HEXADECANOATE HExADECYL + $2H_2O$	

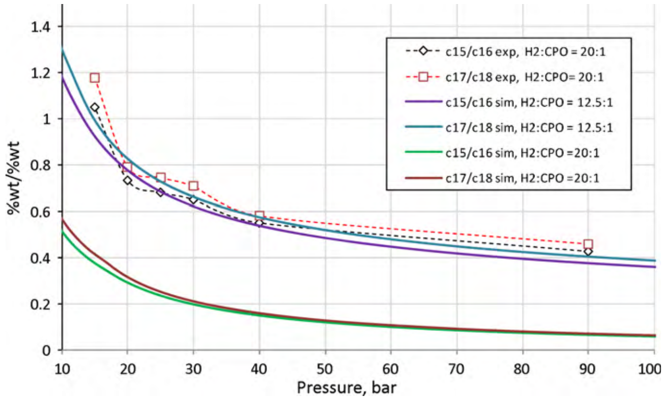

Fig. 2. Equilibrium and experimental c15/c16, c17/c18 profiles at 350 °C as a function of reactor pressure.

that would imply higher hydrogen consumption as reaction pressure is increased.

In order to monitor the effect of pressure on hydrogen consumption, this parameter was calculated from simulation. In Fig. 4 hydrogen consumption is presented as a function of pressure. As it can be seen hydrogen consumption in this system increases exponentially with pressure. For instance, at a H_2:CPO ratio of 12.5 and pressures of 20, 40 and 90 bar hydrogen consumption is of the order of 1342, 1448 and 1541 scf H_2/bbl CPO, respectively. Considering that decarboxylation and decarbonylation routes decreased with pressure and that in itself, without considering subsequent reactions as water gas shift and methanation, they would conduce to a lower hydrogen consumption in comparison to the deoxyhydrogenation reaction of the fatty acid intermediates, it would be attractive to hydroprocess palm oil at pressures close to 40 bar. In such a case decarboxylation and decarbonylation are favored and less hydrogen is also consumed due to the lower pressure. However, taking into account the experimental results where a lost in selectivity to the main products in the range of diesel (221–344 °C) was observed, a pressure higher than 40 bar is more proper in order to reduce the formation of heavy oxygen containing compounds.

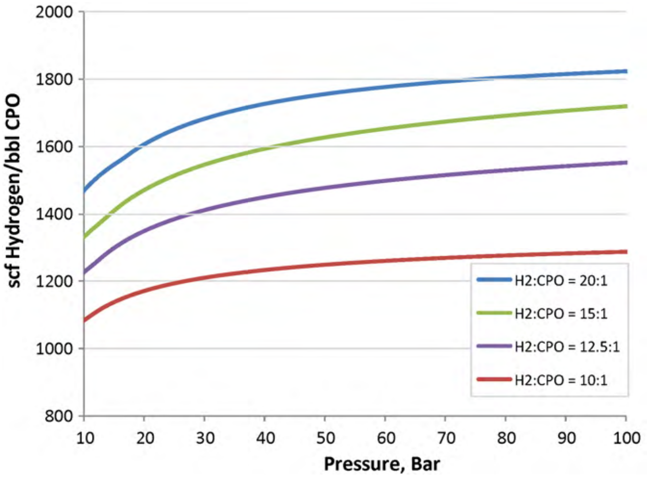

Fig. 4. Hydrogen consumption at 350 °C, LHSV of 2 h^{-1} as a function of reactor pressure and H_2:CPO ratio.

3.2. Hydrogenation of CPO varying time on stream (TOS)

Hydrogenation of CPO was monitored at different time on streams. Reaction conditions were 350 °C, pressure 40 bar, LHSV of 2 h^{-1}, feed flow 180 mL/h and hydrogen flow 87.07 L/h. Chromatograms of hydrogenation products at different TOS resulted very similar to that presented in Fig. 1, where C15–C18 paraffins have predominated. Based on the calibration mixture used for obtaining the simulated distillation reaction products were grouped by their boiling points in three groups of interest. In Table 3 products with boiling points between IBP and 221 °C (gasoline range), 221–344 °C (diesel range) and 344 °C and FBP are shown. Figures are expressed in volume % basis.

As can be observed the most remarkable changes are obtained in the products with boiling points higher than 221 °C. At low TOS higher volume % of products with boiling points in the diesel range are formed while as the reaction proceeds the selectivity to these products decreases and products with higher boiling points (>344 °C) increases from 4.8 vol% in the first day to 8.2 vol% at

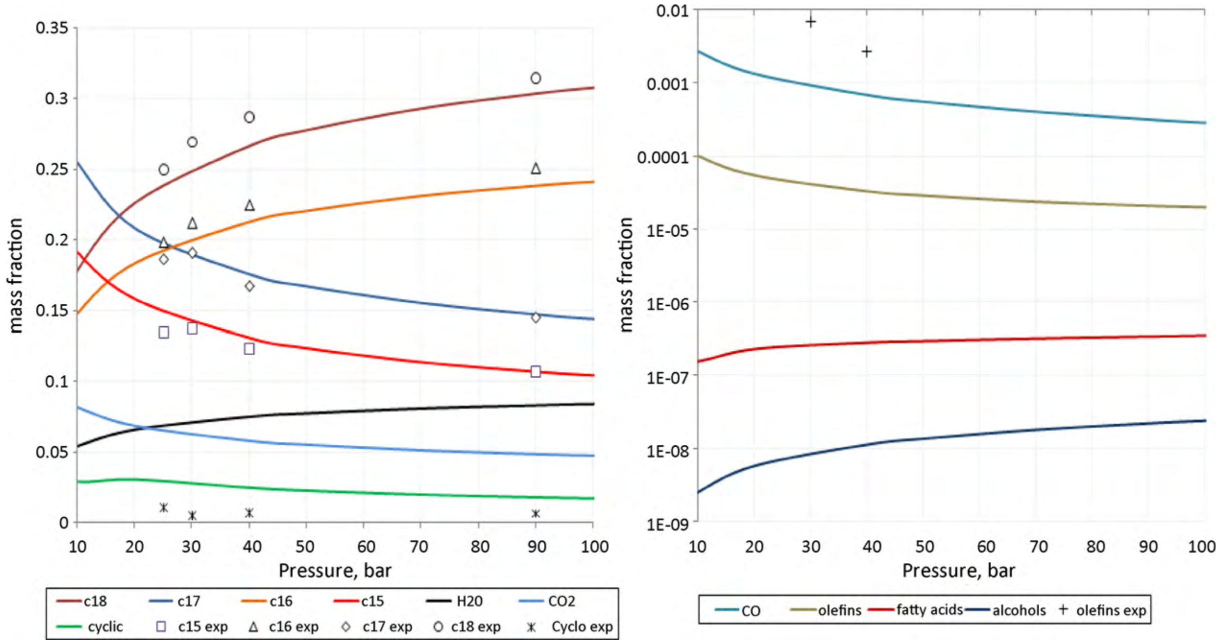

Fig. 3. Equilibrium mass fractions profiles at 350 °C and H_2:CPO = 12.5:1 as a function of reactor pressure and experimental data at 350 °C and H_2:CPO = 20:1.

Table 3
Simulated distillation cuts of hydrogenation products obtained at different time of streams.

Distillation cuts	Simulated distillation yields in volume % basis at TOS from 1 to 14 h					
	TOS1	TOS4	TOS6	TOS9	TOS11	TOS14
IBP–221.0 °C	0.9	0.1	0.3	0.9	0.9	0.9
221.0–344.0 °C	93.3	95.3	92.2	92.6	90.6	89.9
344.0 °C–FBP	4.8	3.6	6.5	5.6	7.6	8.2

Table 4
Properties of crude palm oil (CPO) and hydrogenation products at different time on stream.

Property	Units	CPO	TOS1	TOS4	TOS9	TOS11	TOS14
Cetane index	None		96.1	95.1	94.4	93.4	92.5
Kinematic viscosity at 40 °C	mm^2/s	39.8423	3.3931	3.523	3.5464	3.627	3.6918
Density at 15 °C	g/mL	0.9152	0.7839	0.7855	0.7856	0.7872	0.7882
API	°API	23.0	48.9	48.6	48.6	48.2	48.0
Color	None	5.5	0.6	0.6	0.7	0.8	0.7
Thermal stability	% reflectancy	98	99	99	98	99	99
Bromine number	$g\,Br_2/100\,g$	Not measured	3.85	4.28	5.05	6.26	5.75
Acid number	mg KOH/g	7.40	0.21	0.77	1.01	1.51	1.50

the 14th day. Light paraffinic products (<221 °C) remains approximately constant with TOS.

In terms of composition these results of time of stream are very similar to those obtained when hydrogen pressure was decreased, i.e. higher concentration of heavier products and preliminary assigned to reaction intermediates as octadecanol, n-hexadecanoic acid, octadecanal, and secondary products as hexadecyl hexadecanoate and octadecyl hexadecanoate; higher degree of isomerization of main products C15–C18; and higher concentration of long chain olefins. The influence of the presence of these compounds in the properties of the whole reaction product is presented in Table 4.

As can be seen from this data the decrease in the selectivity to normal paraffins C15, C16, C17 and C18 leads to a product with lower cetane index and to a parallel increase in the acid and bromine numbers, viscosity, and density. As discussed above the increase in the acid number is due to the presence of free fatty acids formed from the CPO that cannot be fully deoxyhydrogenated at these reaction conditions. Besides at this stage esterification, probably catalysed by the acid sites of the alumina used as support in this type of catalysts, between octadecanol or hexadecanol and hexa- or octadecanoic acids present in the reaction mixture can occur and produce the high molecular weight esters preliminary identified in the product. The occurrence of this reaction is an indication that catalyst deactivation can gradually occur at higher time on stream. As mentioned in the paper of Krause and Viljava [18] possible causes for the deactivation of the sulphide active phase of the catalyst during deoxyhydrogenation is the presence of high molecular weight reaction products of oxygen-containing molecules and the replacement of the catalytic sulphur with oxygen, since the adsorbed oxygen-containing compounds can polymerise to high molecular weight species decreasing the activity of the catalyst. In addition it should be taken into account that when feed consists of pure CPO as is the case in this study, non-sulphur containing species are available and this can lead to a gradual lost of the catalytic sulphide metal. However, at present most renewable diesel can be obtained by co-processing of vegetable oils in conventional hydrotreating facilities blended with petroleum diesel. Thus, when co-processing vegetable oils at low percentages, this problem can be overcome. In stand-alone plants in principle no conventional catalyst can be directly used [19]. However, it is important to consider at this point that TOS experiments were conducted at a pressure of 40 bar and as it was previously shown, when the reactor pressure is increased up to 90 bar, deoxyhydrogenation of palm oil can be further enhanced. Thus, for a long-term commercial usage of conventional hydrotreating catalysts, two options can be used to minimize the lost of activity as the one observed in this work (for instance, 3.4% selectivity to diesel range hydrocarbons 221–344 °C were lost): one would be by adjusting the system pressure and the other one by co-processing crude palm oil with crude oil diesel.

Finally from Table 4 can be also inferred that the product even at the longest TOS monitored consists of a fuel that fulfills most of the specifications required for a diesel, i.e. high thermal stability, low viscosity, low bromine and acid numbers being the last two properties closely related to the oxygen containing compounds that were not fully deoxyhydrogenated at the studied conditions but produce at low concentrations. This high cetane index renewable diesel obtained from crude palm oil is registered in Colombia by the mark Biocetano®.

4. Conclusions

GC–MS analysis of the hydrogenation product of CPO varying reactor pressure or time on stream has permitted to preliminary identify the components of the fraction 344 °C+ of the product. Similar compositions of the renewable diesel obtained from crude palm oil when either reactor pressure is decreased or the reaction is permitted to proceed for long times on stream were observed. Components as octadecanol, n-hexadecanoic acid, octadecanal, and the esters hexadecyl hexadecanoate and octadecyl hexadecanoate were identified. However, plenty confirmation of these products could be reached by running the samples in the SIM mode and combining Kovats indexes with appropriate standards.

The presence of these heavy oxygen containing components has been interpreted as a slight deactivation of the catalysts that leads to a gradual lost of selectivity to the main C15–C18 products that constitute the renewable diesel. However, for an industrial application this can be overcome by operating the plant at higher pressures and by co-processing with crude oil diesel. Both strategies will permit to use conventional catalyst as the one tested in this study in the existing hydrotreating facilities at the refineries.

Hydroprocessing of crude palm oil has resulted in a highly paraffinic renewable diesel (Biocetano) with excellent cetane index even when operating at low reaction pressures or after reaction times as long as 14 days under the studied conditions.

Experimental data to different pressures were compared with calculated results of simulation model based in chemical equilibrium, resulting in reasonable agreement with experimental data when decreasing the hydrogen CPO ratio of the simulated case.

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