



Full Length Article

Co-processing of straight run gas oil with used cooking oil and animal fats

H. De Paz Carmona^{a,*}, O. de la Torre Alfaro^b, A. Brito Alayón^a, M.A. Romero Vázquez^c, J.J. Macías Hernández^d

^a University of La Laguna (ULL), Faculty of Chemistry, Chemical Engineering Department, Con. San Frco. de Paula, s/n, 38206 San Cristóbal de La Laguna, Spain

^b Cepsa Tower, Product Technology and Biofuels/Refining Development, Paseo de la Castellana, 259 A, 28046 Madrid, Spain

^c Cepsa Research Center, Av. Punto com, 1, 28805, Alcalá de Henares, Madrid, Spain

^d Cepsa Refinery Tenerife, Av. Manuel Hermoso Rojas, 3, 38005 Santa Cruz de Tenerife, Spain

ARTICLE INFO

Keywords:

Co-processing
Used cooking oil
Animal fat
Hydrotreatment
Hydrodesulfurization
Hydrodenitrogenation

ABSTRACT

Co-processing experiments of straight run gas oil (SRGO) with used cooking oil (UCO), and category three animal fat were performed in a hydrotreatment pilot plant. Liquids and gaseous products obtained were analysed and quantified. The aim of the work was the study of the effect of the triglycerides feedstocks co-processing with the diesel fuel on the desulphurized gasoil properties, as well as their impact on the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalyst activities. These results were compared with the co-processing test of refined palm oil. Experiments were performed in a pilot plant that reproduced the hydrotreatment of diesel oil with a conventional NiMo/Al₂O₃ catalyst, under the following conditions: 350 °C 5.5 MPa, LHSV 2 h⁻¹ and a H₂ to feed oil ratio of 340 NL/L. The ratio SRGO/triglycerides feedstock was always 80/20 wt.%. At these operating conditions, linear paraffins (nC₁₅–nC₁₈) were the main reaction product (79–85 wt.%), followed by light gases (CO, CO₂ and C₃H₈) and water as by-products. The increment in paraffin content of the liquid product produced a significant variation of some of gasoil properties (density at 15 °C and cetane index). A decrease in the catalytic activity (HDS/HDN) was also observed in the co-processing stages, particularly when animal fat was co-processed.

1. Introduction

In order to decrease energy imports, to promote the use of energy from renewable sources and to reduce greenhouse gases, the European Parliament and the Council of European Union (EU) have developed a bioenergy sustainability policy that all countries must comply with. The current energy directive, the Directive 2009/28/EC, requires the EU to fulfill at least 20% of its total energy needs with renewables by 2020. All EU countries must also ensure that at least 10% of their transport fuels come from renewable sources by 2020. On the other hand, Directive 2015/1513 promotes the reduction of indirect land use change for biofuels and bioliquids, negating the greenhouse gas savings that result from increased biofuels because grasslands and forests absorb high levels of CO₂.

These EU energy requirements, as well as the increase in fuel consumption in the last few years, in particular the diesel oil, works as engine to develop new, more efficient and environmentally friendly biofuels, that allow complement or replace current fossil fuels, such as diesel oil or gasoline.

Depending on the feedstock and on the maturity and sustainability of the technology employed for their production, biofuels can be referred to as conventional (1st generation) and advanced (2nd and 3rd generation) [1,2]. Thus, conventional biofuels are based on commercial feedstocks and processes currently in use in many countries and are typically fatty acids methyl esters (FAME). They are obtained from an edible feedstock rich in triglycerides (e.g. sunflower oil) and methanol, always in presence of an acid (H₂SO₄) or basic catalyst (NaOH or KOH) [3]. The by-products obtained by this transesterification reaction, such as glycerine, could be used as cosmetic feedstock or catalytic reforming, in order to obtain other products such as hydrogen [4]. However, this generation of biofuels are becoming unviable because implementation of the Indirect Land Use Change (ILUC) legislation and the Food vs. Fuel debate [5].

The second-generation biofuels, uses raw materials not allowed for human or animal consumption, such as forest residues and non-edible vegetable oils or fats from frying processes. Some of the most relevant processes to obtain this biofuel generation are the catalytic hydro-treatment of vegetable oils to obtain hydrotreated vegetable oil (green

* Corresponding author.

E-mail addresses: hpazcarm@ull.es (H. De Paz Carmona), olalla.delatorre@cepsa.com (O. de la Torre Alfaro), andbrito@ull.es (A. Brito Alayón), mangeles.romero@cepsa.com (M.A. Romero Vázquez), josejuan.macias@cepsa.com (J.J. Macías Hernández).

<https://doi.org/10.1016/j.fuel.2019.05.166>

Received 26 June 2018; Received in revised form 24 February 2019; Accepted 30 May 2019

0016-2361/ © 2019 Elsevier Ltd. All rights reserved.

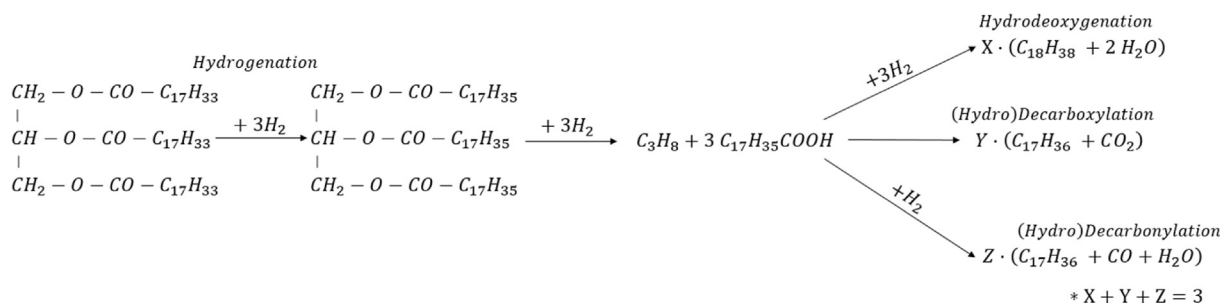


Fig. 1. Reaction pathways in the hydrotreating of a triglyceride model.

Table 1
Characterization of the triglycerides feedstocks used.

Analysis	Used cooking oil	Animal fat	Refined palm oil	Standard test method
Density 15 °C, kg/L	0.9236	0.9145	0.9159	ASTM D 4052
Acid number, mg KOH/g	5.44	6.17	0.08	ISO 660
Sulfur content, mg/kg	7.6	21.0	2.0	UNE-EN ISO 20486
Nitrogen content, mg/kg	50.2	183.0	2.0	ASTM D 4629
Karl Fischer Water, ppm	540	881	41	ASTM D 4928
Elemental analysis, wt. %	–	–	–	ASTM D 5291
Carbon, C	75.8	76.8	76.3	–
Hydrogen, H	11.5	12.0	11.0	–
Metals, mg/kg	–	–	–	IP 501 – AOCs Ca 17
Calcium, Ca	0.40	0.25	0.10	–
Phosphorus, P	2.40	5.20	1.00	–
Potassium, K	1.00	2.40	1.00	–
Sodium, Na	1.10	1.00	1.00	–

diesel) [6], the co-processing of bio-oils in catalytic cracking units [7] or the oxidation of lignocellulosic biomass from bimetallic catalysts [8]. Finally, third-generation biofuels are based on algae feedstock, requiring more sophisticated processing technologies [2].

Catalytic co-hydroprocessing of triglycerides feedstocks, such as used cooking oil (UCO) or animal fats (AF), in an industrial hydrodesulfurization unit, could be very attractive for refineries because existing installations can be employed [9]. On the other hand, it could be used the same conventional catalysts that in the hydroprocessing of diesel oil, such as CoMo/Al₂O₃ or NiMo/Al₂O₃ [10]. By hydrotreating, these triglycerides produce a paraffinic biofuel, called green diesel, which is integrated in the desulfurized product improving some of its critical properties, such as density at 15 °C and flammability. However, the increment of paraffins have to be carefully studied, because could get worse cold flow properties.

At these operating conditions, (350–370 °C and 70–80 bar), the triglycerides are hydrogenated according to the pathways shown in Fig. 1 [11].

First, the triglyceride molecule is saturated by hydrogenation and then it breaks, releasing a propane molecule and producing three molecules of carboxylic acids as intermediate products. The mechanism continues by three different chemical reactions or pathways: the hydrodeoxygenation step (HDO), producing two molecules of water and linear paraffins with even number of carbons (normally nC₁₆ and nC₁₈); the (hydro)decarboxylation (HDC) reaction, which produces one molecule of carbon dioxide and paraffins with an odd number of carbons (normally nC₁₅ and nC₁₇) and (hydro)decarbonylation (also HDC), releasing paraffins with an odd number of carbons (nC₁₅ and nC₁₇) and CO and H₂O molecules.

The selectivity of each pathway depends on the operating conditions or catalysts used, so the selection of these parameters is critical in an industrial process in order to minimize hydrogen consumption or light gases production [12]. In this way, it is necessary to carry out a detailed research about the co-processing of raw materials such as UCO, animal fats, etc., in order to study the possible impact on the catalysts activity and the desulfurized gas oil properties at industrial level. The aim of

this work is the study of the co-hydroprocessing of animal fats and UCO with straight run gas oil (SRGO) at typical industrial operating conditions (350 °C and 5.5 MPa). An edible oil (refined palm oil) has been used to compare the results with those obtained when a first-generation feedstock is used. In this study, special attention was taken in products and by-products formed, defined by HDO/HDC selectivity; their influence over the properties of desulfurized diesel oil and the effect of co-processing in HDS/HDN activities of the commercial catalyst used.

2. Materials and methods

2.1. Feedstocks

Two different triglycerides feedstock were used for these co-processing experiments: UCO, gathered from Spanish local household and restaurants and animal fat of category number three. Then, refined palm oil was used to compare results obtained with the use of first-generation edible vegetable oils. To remove food scraps and frying waste, the UCO was purified by filtration and decantation. On the other hand, animal fat was filtered to reduce metal content. Table 1 shows the main characterizations of the three feedstock processed.

As expected, refined palm oil showed a lower acid number and water content than residual lipids. A low concentration of metals was determined in all the products (UCO, filtered animal fat and refined palm oil), this indicates a very low contamination with inorganic materials and low risk of poisoning of the catalyst active sites. The fatty acid distribution was used as an additional parameter to complete the feedstock characterization. This analysis was performed using an ISO 12966 standard method and Table 2 shows the obtained results.

All feedstocks showed a similar fatty acid distribution, mainly in the range of C₁₆–C₁₈. The fatty acids distribution of UCO shows that it contains mainly olive and sunflower oil, and animal fat showed high concentrations of saturated fatty acids (C_{16:0}, 26 wt%; C_{18:0}, 17 wt%), which could be the reason of its solid state at room temperature. Fatty acids distribution of refined palm oil agrees with the reported in the literature [13].

Table 2
Fatty acid composition triglycerides feedstocks.

Fatty acid, wt.%	Used cooking oil	Animal fat	Refined palm oil
Myristic C _{14:0}	0.17	2.30	0.94
Palmitic C _{16:0}	9.89	26.06	42.72
Palmitoleic C _{16:1}	0.33	3.12	0.18
Stearic C _{18:0}	3.79	16.82	4.32
Oleic C _{18:1}	41.04	42.59	40.70
Linoleic C _{18:2}	42.84	6.24	9.92
Linolenic C _{18:3}	0.30	0.60	0.24
Arachidic C _{20:0}	0.30	0.15	0.38
Eicosenoic C _{20:1}	0.31	0.60	0.15
Behenic C _{22:0}	0.57	0.05	0.06
Erucic C _{22:1}	0.31	0.00	0.00
Lignoceric C _{24:0}	0.22	0.04	0.06

For the co-processing experiments, straight run gas oil (SRGO) was used as petroleum feedstock, which was supplied by one of the Spanish Cepsa refineries. This middle distillate was selected due to its good properties and high quality for gasoil production. In all the experiments, a mixture of triglycerides feedstock and SRGO of 20/80 wt% was used. A high blending degree was selected to identify the impact of biomass co-processing on product quality and catalyst activity. Table 3 shows the main characterisation of SRGO and the mixes used in these co-processing experiments.

The SRGO used showed common characteristics in this kind of middle distillates, especially low density and sulfur or nitrogen content. As expected, feedstock triglycerides addition produced an increase of density, as well as a decrease of sulfur and nitrogen content.

2.2. Experimental setup

Experiments were carried out in a hydrodesulfurization bench scale unit at Cepsa Research Center facility in Madrid, which is well equipped to perform simulations of industrial processes of diesel hydrodesulfurization. Fig. 2 shows a simplified diagram of the bench scale unit, which consists of three sections: reagents feed, reactor and gas-liquid separator/sampling.

Liquid feedstock was stored in a stainless steel tank placed on a weighing scale and pumped into the top of the reactor through a dosing pump. The storage system was provided of a heating system in order to keep warm the feedstock during the experiment. This fact allowed feedstock homogenization, particularly important during the co-processing steps. Standard commercial hydrogen gas was used as hydrogen

Table 3
Characterization of feedstocks used.

Analysis	SRGO 100	SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Palm oil 80/20	Standard test method
Density at 15 °C, kg/L	0.8474	0.8627	0.8603	0.8600	ASTM D 4052
Sulfur content, wt.%	1.191	0.956	0.953	0.952	UNE-EN ISO 20486
Nitrogen content, wt. ppm	104	98	117	86	ASTM D 4629
Karl Fischer Water, ppm	–	103.0	173.0	6.9	ASTM D 4928
Acid number, mg KOH/g	–	1.42	1.39	0.09	ISO 660
Aniline point, °C	70.4	–	–	–	ASTM D 1218
Aromatics content, wt.%	–	–	–	–	UNE-EN 12916
Mono-aromatic	18.3	–	–	–	–
Di-aromatic	11.8	–	–	–	–
Tri-aromatic	0.9	–	–	–	–
Elemental analysis, wt. %	–	–	–	–	ISO 29541
Carbon, C	85.06	83.45	83.16	83.28	–
Hydrogen, H	13.88	13.20	13.73	13.32	–
SimDis, wt.%	T, °C	–	–	–	ASTM D 2887
10	226	–	–	–	–
30	270	–	–	–	–
50	301	–	–	–	–
70	335	–	–	–	–
90	381	–	–	–	–

source (H₂ > 99 vol%). The reaction system consists of a stainless steel fixed bed reactor with a concentric furnace with four heating sections to reach the reaction temperature inside the reactor. Heating was controlled by two sets of four thermocouples, one of them inside a thermowell and the other outside the reactor.

Catalytic bed was inside the tubular reactor, which consisted of a mixture of a conventional NiMo/Al₂O₃ catalyst (121–122 mL) and carborundum (SiC) in volume relation (1):1, in order to minimize the wall-flow effects and improve the heat transfer inside the reactor. After hydrotreatment, reaction product continues to reach the gas-liquid separator, obtaining a product with two phases. When separated, liquid products were accumulated in a storage tank and gaseous products were quantified by a wet gas flow meter.

The experimental procedure of co-processing experiments included four steps: sulfiding, blank run or stabilization, co-processing, and catalyst activity evaluation. Catalyst sulfiding were performed according to the method established by the catalysts manufacturer: first the catalyst is dried under H₂ flow at 150 °C, secondly the spiked SRGO within 3.0 wt% total sulfur (using Sulfrzol-54) is fed to the reactor, followed by a slow increasing of temperature until the breakthrough is reached (hydrogen sulfide formation). After the sulfiding step, the feedstock was changed to pure SRGO, which was fed in until the steady state was reached. This step was called blank run or stabilization and it was used as reference during the experiment.

The steady state of the reaction was determined by a routine analysis of density at 15 °C, sulfur and nitrogen content of the organic product produced. After 96 h of operation, these parameters keep stable, which indicates that the steady state has been reached in the reactor. The experiments continued with the co-processing step, where the feedstock was changed to the mixture of SRGO/triglycerides feedstock. When co-processing was finished, the feedstock was changed again to pure SRGO. This last step was used to compare the HDS/HDN catalytic activity before and after the triglycerides feedstock co-processing.

2.3. Experiments

Three co-processing experiments were performed to describe the effect of the addition of triglycerides on the catalytic activity and product characteristics. Table 4 shows the operating conditions of each experiment, similar to those found in the literature [6] and used in authors previous experiments [14].

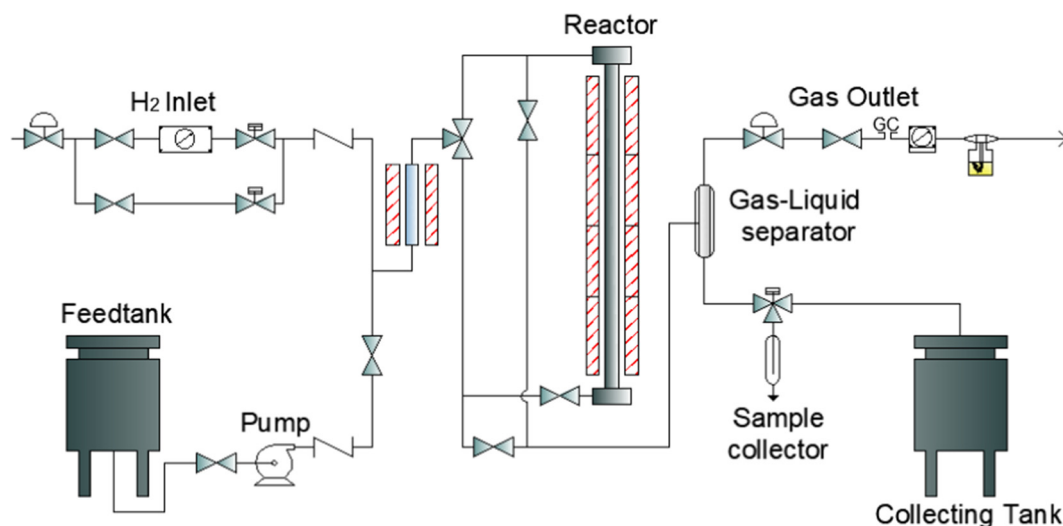


Fig. 2. Simplified scheme of the bench scale unit.

Table 4
Operating conditions used in co-processing experiments.

Parameter\Experiment	SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Refined palm oil 80/20
Temperature, °C	350	350	350
Pressure, MPa	5.5	5.5	5.5
LHSV, h ⁻¹	2.0	2.0	2.0
H ₂ to feed, NL/L	340	340	340
Biomass, wt.%	20	20	20

2.4. Product analysis

When the steady state was reached in each step (stabilization, co-processing and catalyst activity evaluation), samples of liquid and gaseous products were collected every eight hours. Liquid samples consisted of organic phase during diesel oil processing or organic and aqueous phases during co-processing steps. H₂S was removed from liquid samples using stripped with nitrogen. The density at 15 °C (ASTM D 4052), sulfur and nitrogen content (UNE-EN ISO 20486/ASTM 4629) analysis were performed. After sulfur removal, a more detailed characterisation was performed: SimDis (ASTM D 2887), cloud point (ASTM D 2500), cold filter plugging point – CFPP (UNE-EN ISO 116) and cetane index (ASTM D 4737). The analysis of the gaseous products was performed online using a gas chromatograph (GC) Agilent Micro GC 490 composed by four channels: Channel Molecular sieve 5A plot (MS5A) to measure H₂ (Argon gas is used as carried gas), Channel Molecular sieve 5A plot (MS5A) to measure N₂, O₂ and CO (Helium gas is used as carrier gas), Channel ParaPlot Q PPQ to measure CO₂ and CH₄ (Helium gas is used as carrier gas) and Channel Aluminium oxide PLOT column (Al₂O₃/KCl) to measure C1-C5 hydrocarbons (Helium gas is used as carrier gas). A three-way valve situated at the outlet of reaction gases allowed divert part of the outlet flow to the chromatograph. A set of 20–30 gas samples were analysed in each step of the experiment, particularly during the blank run and the co-processing.

Complete hydrotreatment of triglycerides was verified by fourier-transform Infrared spectroscopy (FTIR) analysis, as has been described in previous articles by the authors [14,15]. Fig. 3 shows the FTIR spectrum of the SRGO/UCO 80/20 wt% feedstock (black colour) and the same feedstock after the hydrotreatment (red colour).

The absence of peaks in 1745 cm⁻¹ (carbonyl functional group) and 1350 cm⁻¹ (angular deformation of CH₂ and CH₃) of the desulfurized product shows the complete conversion of the triglycerides of the feedstock.

In order to study the reaction products formed due to the triglycerides hydrotreatment, i.e. green diesel (mainly linear paraffins), water and light gases (mainly C₃H₈ and CO_x), it has been calculated the mass balance of the experiment during the blank run (i.e. pure SRGO processing) and the co-processing (SRGO and UCO, animal fat or refined palm oil 80/20 wt%) steps. Thus, taking into account the amount of SRGO processed during the co-processing (80 wt% of the feed), it is possible to estimate the amount of organic phase (paraffins), water and light gases that come just from the triglycerides hydrotreatment, assuming that there is not interaction between SRGO and UCO. These results have been expressed as a yield, according to the next equation:

$$\text{Product yield (\%)} = \frac{\text{Product formed [paraffins, water or gases] (g)}}{\text{Vegetable oil or animal fat in the feed (g)}} \cdot 100, \quad (1)$$

where, the ‘product formed’ would be only refer to the amount (in grams) of that reaction product (green diesel – paraffins, water or gases) that come from the triglycerides feedstock hydrotreated, and the ‘vegetable oil or animal fat in feedstock’ is referred to the amount (in grams) of UCO, animal fat or refined palm oil co-processed (20 wt% of the feed). These values are just a mathematic estimation, to determine accurately the paraffins that proceed from the SRGO and/or triglycerides feedstocks, a detailed analysis of the desulfurized gasoil compounds would be necessary. This procedure was not possible to carry out during these co-processing experiments. Light gases were quantified by flow measurements and analysis of its composition.

Gas Chromatography with Flame Ionization Detector (FID) was used for the quantitative determination of linear paraffins in the desulfurized gasoil produced during the blank run and the triglycerides feedstock co-processing. Taking into account the linear paraffins formed during the blank run and the amount of triglycerides feedstock used during co-processing (20 wt% of feed), it is possible to estimate the amount of paraffins due to the vegetable oil or animal fat addition. Thus, according with the number of carbons in its chain, it was possible estimate the percentage of paraffins formed by HDO and HDC pathways, according with the following equations previously published by the authors [14]:

$$\text{HDO [\%]} = \frac{\Delta(\text{even paraffins})}{\Delta(\text{total paraffins [even + odd]})} \cdot 100, \quad (2)$$

$$\text{HDC [\%]} = \frac{\Delta(\text{odd paraffins})}{\Delta(\text{total paraffins [even + odd]})} \cdot 100, \quad (3)$$

where $\Delta(\text{even paraffins})$ and $\Delta(\text{odd paraffins})$ represent the paraffins

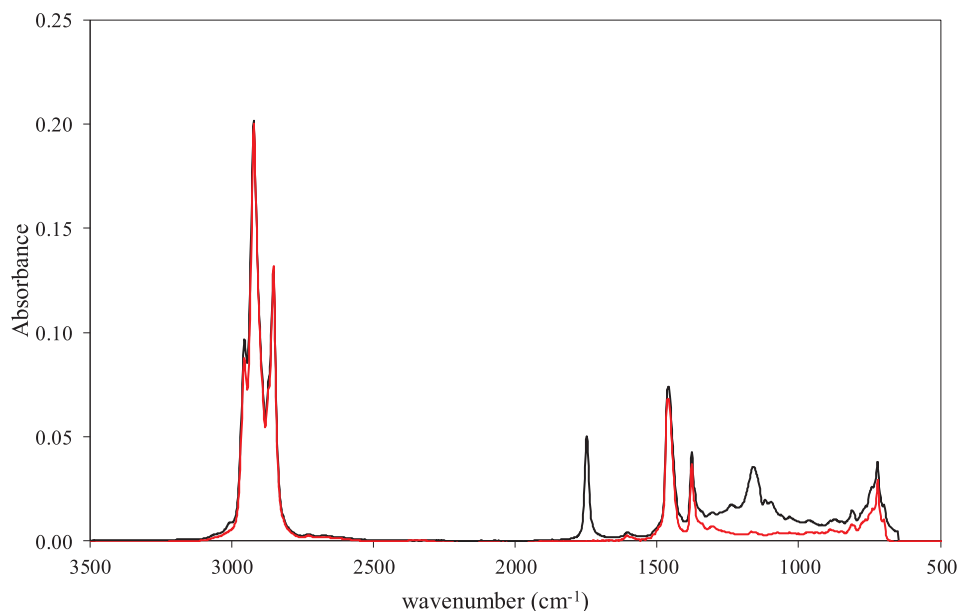


Fig. 3. FTIR Spectrum of SRGO/UCO feedstock and the corresponding desulfurized diesel.

proceed from triglycerides hydrotreatment formed following the HDO (mainly nC_{14} , nC_{16} , nC_{18} and nC_{20}) and HDC (mainly nC_{13} , nC_{15} , nC_{17} and nC_{19}) pathways (wt. %) respectively, and $\Delta(\text{total paraffins [even + odd]})$ represent the total paraffins formed only by the hydrotreatment of vegetable oil/animal fat (wt.%).

Taking into account the sulfur content in the feedstock the sulfur content in the product, as well as the yield of the process, the HDS activity was determined according to the following equation:

$$\text{HDS [\%]} = \frac{(S_0 - (S_p \cdot \eta))}{S_0} \cdot 100, \quad (4)$$

where S_0 , S_p and η represent the sulfur content of the feedstock and liquid product (wt. ppm) and the process yield (%), respectively. The yield of the process was defined as the ratio between the mass of desulfurized diesel oil obtained and the feedstock (SRGO or corresponding mix) used. In the same way, the HDN activity could be determined using the nitrogen content, in accordance to the following equation:

$$\text{HDN [\%]} = \frac{(N_0 - (N_p \cdot \eta))}{N_0} \cdot 100, \quad (5)$$

where N_0 , N_p and η represent the nitrogen content of the feedstock and liquid product (wt. ppm) and the process yield (%), respectively.

3. Results and discussion

Different experiments of co-processing with SRGO and vegetable oil/animal fats were carried out to study the products formed, its influence on fuel properties and its effect on the HDS and HDN activities.

3.1. Products formed

To study the products formed due to the addition of vegetable oil/animal fat during co-processing (i.e. paraffins, water and gases), the mass balance was calculated during the blank run and the co-processing step. In this way, assuming that SRGO hydrotreatment provide a similar product distribution during the blank run and the co-processing, it was possible the estimation of the products yield derived from the triglycerides hydrotreatment during the co-processing step. Table 5 shows the results obtained for triglyceride hydrotreatment products yields using Eq. (1).

The sum of products yields (i.e. “Total”) estimated shows a high

Table 5

Product yields.

Product yield, wt.%	SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Refined palm oil 80/20
Green diesel – Paraffins	84.99	78.64	80.51
Water	2.89	3.08	3.27
Gases	10.55	12.58	9.96
Total	98.4	94.3	93.7

value (93–98%), which is indicative of a good results reproducibility. The apparent loss of mass shown in the mass balance (“Total”), for the co-processing of SRGO/Animal fat 80/20 and SRGO/Refined palm oil, are within the order of accuracy of the wet gas meter used in the experiments, which means that could be considered that the mass balance is fulfill.

In general, similar results were obtained for all the experiments, independently of the feedstock co-processed. A slightly decreased of green diesel yield has taken place during animal fat or refined palm oil hydrotreatment, producing more light gases. In all cases, the main product was the green diesel (78.6–85.0 wt%), followed by light gases (9.9–12.6 wt%) and water (2.9–3.3 wt%). These results are according with the previous ones of the same authors for the co-processing of used frying oil (UFO) and atmospheric gas oil (AGO), where an 80–85 wt% were paraffins, 8.2–13.1 wt% gases and 6.5–7.5 wt% water. The differences in water production could be due to hydrodeoxygenation (HDO) pathway promotion, slightly higher during that set of co-processing experiments with UFO and AGO [14].

In this sense, the distribution of the by-products depends on the reaction pathways occurred during the co-processing. These results (Table 5) could mean a higher contribution of (hydro)decarboxylation/ (hydro)decarbonylation (HDC) reactions instead of HDO reactions for all the experiments, which means more gaseous products, particularly CO and CO₂.

Fig. 4 shows the distribution of paraffins (nC_{10} to nC_{22}) in the organic phase of the liquid product obtained during the blank run and the co-processing of each triglycerides feedstock, determined by GC-FID.

As expected, a significant increase of linear paraffins content (nC_{15} to nC_{18}) was produced during co-processing steps, which is due to the HDC/HDO reactions of triglycerides. The selectivity of each pathway

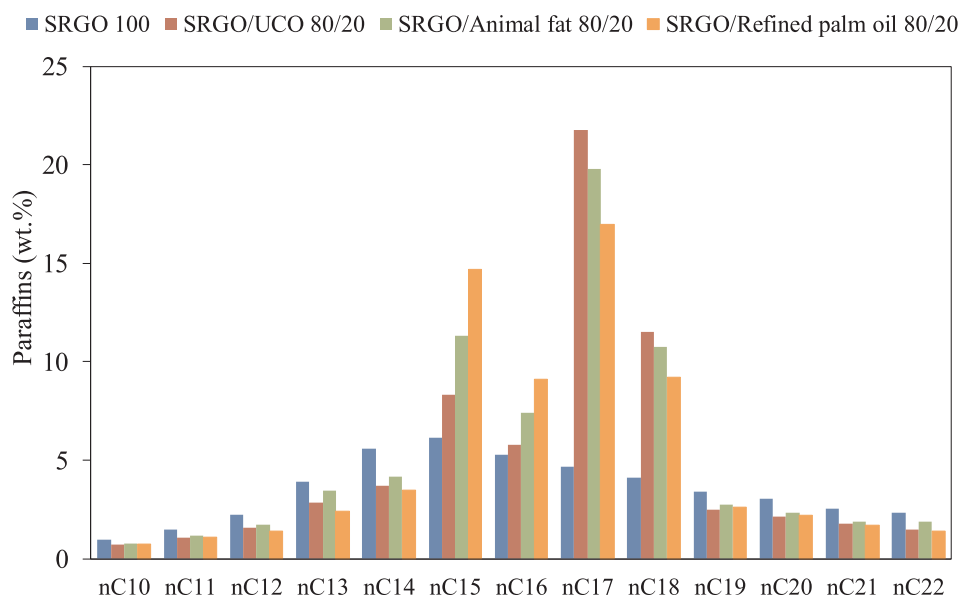


Fig. 4. Distribution of paraffins during co-processing experiments.

Table 6
Paraffin distribution by reaction pathway.

Parameter	SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Refined palm oil 80/20
HDO %	36.5	36.4	36.7
HDC %	63.5	63.6	63.3

can be calculated from Eqs. (2) and (3) and Table 6 shows the results obtained for each experiment.

The HDC pathway was preferred rather than HDO in all the experiments, independently of the feedstock used during the co-processing. This result is close to the relation 65/35 expected for this kind of conventional catalyst, as well as it is in good agreement with results in bibliography [16]. This fact indicates the possibility that nickel, in NiMo/Al₂O₃ catalysts and at these operating conditions could promote C–C bond cleavage in carboxylic acids, i.e. HDC pathway. According to previous experiments [14], operating temperature plays a significant role in this deoxygenation pathway promotion, increasing the HDO dominance at lower temperatures (320 instead of 350 °C). This paraffins distribution results are in accordance with mass balances (Table 5), in which a high percentage of light gases (9.9–12.6 wt%) were obtained during all the co-processing experiments.

A GC-TCD instrument was used to identify and quantify the gaseous products formed. Table 7 shows the composition of the gas samples during SRGO hydrotreatment and the co-processing experiments, once reached the steady state.

As expected, the main component in the output-gas samples was H₂, with a percentage of 97 mol% during SRGO 100 hydrotreatment and 91.60–93.40 mol% during co-processing steps. This decrease in

Table 7
Output-gas composition.

Component, mol %	SRGO 100	SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Refined palm oil 80/20
H ₂	97.33	92.21	91.64	93.36
CO ₂	0.07	1.07	1.34	1.01
CO	0.00	2.24	2.84	2.04
CH ₄	0.21	0.41	0.42	0.25
C ₃ H ₈	0.09	1.14	1.16	1.09
Other gases	2.40	2.95	2.60	2.25

hydrogen composition (4–6 mol%) goes parallel to the significant production of other light gases as C₃H₈, CO, CO₂ and CH₄, in the same range for all the feedstocks; as well as to the increment of H₂ consumption. In this way, propane formation is related to the hydrotreatment of triglycerides, which is interesting from industrial point of view as LPG; CO and CO₂ are a by-product of HDC reactions or reverse water gas shift (RWGS) and methane could be due to other secondary reactions like CO₂ methanation or hydrocarbon cracking reactions. Similar distribution of light gases has been obtained in bibliography during co-processing experiments of UCO and heavy atmospheric gas oil (HAGO) [17,18], as well as in AGO/UFO co-processing [14], in which the small differences in some light hydrocarbons (CH₄ and C₃H₈), could be due to the use of standard refinery gas instead of standard commercial hydrogen gas (H₂ > 99 vol%) as hydrogen source.

As described in experimental set up, at the end of each co-processing step, the feedstock was changed to pure SRGO, so light gases concentration decreased. Fig. 5 shows light gases production before, during and after the co-processing of SRGO with UCO 80/20 wt%. Similar behaviour was registered for the other co-processing experiments.

The hydrogen consumption and light gases production can be calculated from the output-gas composition and mass balances. Following the reaction scheme given in Fig. 1, a theoretical estimation of the products obtained from triglycerides hydrogenation has been carried out [19]. As it is generally used in the literature, a 35:65 relation has been assumed between the hydrodeoxygenation reactions and the joint contribution of the (hydro)decarboxylation and (hydro)decarbonylation reactions, i.e. HDO/HDC. In addition, an equal proportion of the (hydro)decarboxylation and (hydro)decarbonylation reactions to the system has been considered. Table 8 shows the theoretical and the calculated results for hydrogen consumption and light gases production (CO_x, CH₄ and C₃H₈) per 100 g of the triglycerides feedstock co-processed.

Both results (theoretical and calculated) are approximately in the same order and the small differences observed can be due to several reasons. Firstly, the assumptions on which the theoretical estimate was based could not be fully met, mainly with regard to the relationship between the (hydro)decarboxylation and (hydro)decarbonylation reactions. Secondly, it is likely that there are secondary reactions that have not been taken into account such as the methanation of CO₂, RWGS or cracking of hydrocarbons.

The co-processing of vegetable oils/animal fats produced an increase of hydrogen consumption (1.60–2.10 g/100 g of triglycerides

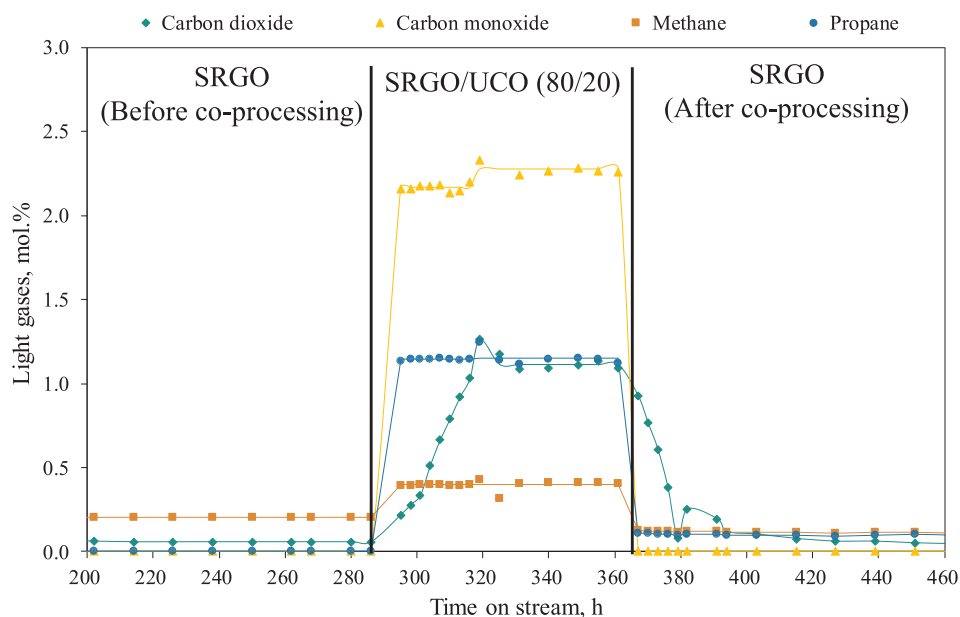


Fig. 5. Light gases changes during SRGO/UCO 80/20 wt% co-processing.

feedstock), as well as a light gases production (C_3H_8 : 2.90–3.40; CO: 3.90–7.10; CO_2 2.45–5.10 g/100 g of triglycerides feedstock), particularly during animal fat and UCO co-processing experiments. Therefore, quality or nature of biomass used plays a significant role in gases production and H_2 consumption. In particular, during animal fat co-processing cracking reactions could also be taking place, which would result in a higher increment of light gases production. This fact would be in concordance with its less green diesel yield.

3.2. Effect of co-processing on fuel properties

The nature of green diesel is almost strictly paraffinic with certain amount of isoparaffins. This fact affects the characterisation of co-processing products related to SRGO hydrotreatment products, particularly to density at 15 °C, cold flow properties and cetane index. To study this effect, the hydrotreated products obtained during the SRGO pure processing (blank run) and the SRGO/triglycerides feedstocks 80/20 wt% co-processing were compared. Palm oil is a first-generation feedstock, which has been widely studied and described in bibliography when co-processing with middle distillates [20–22]. Thus, the properties of the desulfurized gasoil produced during the co-processing of waste triglycerides feedstocks (animal fat and UCO) were compared with the product produced during the refined palm oil co-processing. Table 9 shows the characterization of the hydrotreated product obtained during the SRGO processing and the SRGO/triglycerides feedstock 80/20 co-processing.

Table 8

Increase of hydrogen consumption and light gas production.

Parameter		SRGO/UCO 80/20	SRGO/Animal fat 80/20	SRGO/Refined palm oil 80/20
H_2 consumption, g/100 g of triglycerides feedstock	Experimental	2.08	2.11	1.64
	Theoretical	2.50	2.20	2.10
C_3H_8 production, g/100 g of triglycerides feedstock	Experimental	3.29	3.36	2.88
	Theoretical	4.90	5.20	5.10
CO production, g/100 g of triglycerides feedstock	Experimental	5.65	7.14	3.82
	Theoretical	4.80	5.10	5.00
CO_2 production, g/100 g of triglycerides feedstock	Experimental	4.06	5.12	2.46
	Theoretical	4.80	5.10	5.00
CH_4 production, g/100 g of triglycerides feedstock	Experimental	0.49	0.51	0.11

Table 9

Characterization of SRGO and SRGO/triglycerides feedstocks 80/20 wt hydro-treatment.

Analysis	Product from SRGO 100	Product from SRGO/Refined palm oil 80/20 wt%	Product from SRGO/UCO 80/20 wt%	Product from SRGO/Animal fat 80/20 wt%
Density 15 °C, kg/L	0.8257	0.8196	0.8208	0.8206
CFPP, °C	−2	−4	−4	−4
CP, °C	0	−1	0	−1
<i>SimDis</i> , wt.%	Temperature, °C			
10	230	241	242	243
30	260	270	274	273
50	283	286	293	290
70	310	306	310	309
90	348	343	345	344
Cetane Index	61.5	66.5	67.0	67.0

As expected, the increase of linear paraffins in the desulfurized product produced during the refined palm oil co-processing, resulted in a decrease in the product density, due to the lower density of the paraffins when compared with other diesel fractions compounds [23,24]. In the same way, this increment of paraffins produced an important increase of diesel range compounds [25], resulting in an alteration of distillation curve during co-processing [18], as well as in a significant increase of cetane index. These results are in agreement with those

reported in the literature [20].

On the other hand, there were not significant negatively effects over the cold flow properties (CP and CFPP), remaining with no changes or within the analysis error. This behaviour is according to previous works of the authors [14], where it was necessary an increment up to 50 wt% of UCO in the feedstock to appreciate a significant deterioration of the cold flow properties of up to 6 °C. This behaviour could be justified in case of *iso*-paraffins conversion, which has been reported with isomerization catalyst [26].

Although numerous works have been reported in the literature about the co-processing of palm oil, it is not the same case for waste feedstocks as animal fats or used cooking oil. The co-processing of these waste materials produced a lower decrease in density and a desulfurized diesel more paraffinic, which results in an increment of the cetane index as well as the diesel compounds fraction of up to 6 units, analogous to the effect observed during AGO/UFO 80/20 wt% co-processing [14]. On the other hand, no significant changes were observed in the cold flow properties, staying in the range of values under 0 °C.

These results indicate a light dependence between the characteristics of the desulfurized gasoil produced during the co-processing, and the corresponding triglycerides feedstock used [27]. In this way, the use of waste materials allows the production of a more paraffinic fuel with a higher cetane index which, from the environmental point of view, it would have the added value of reducing the amount of accumulated waste.

3.3. Effect on the HDS and HDN activities

To study the effect of triglycerides feedstock co-processing on the catalysts activity, the HDS and HDN activities were determined (Eqs. (4) and (5)) in each step of the experiments: blank run, co-processing and the catalyst activity evaluation. Fig. 6 shows the variation of the HDS and HDN activities for these steps during co-processing experiments, as well as the middle value obtained during SRGO 100 wt% hydrotreatment.

At the operations conditions used (20 wt% of vegetable oils or animal fat, 350 °C and 55 bar) triglycerides feedstock addition did not produced an important decrease of HDS activity, always lower than 0.60 wt%, according with results published in bibliography [28,29]. When comparing waste feedstocks with refined palm oil, a decrease of the HDS efficiency obtained during the co-processing was observed,

with worst result for animal fat, 0.42 wt% less than for palm oil.

These results mean that the addition of UCO or animal fat produced a slight reduction of the HDS activity of the catalyst, higher than for first-generation feedstocks, but still no significant at the operating conditions used, as well as in the range described in previous experiments during AGO/UFO co-processing (0.4–0.9 wt%) [14]. Thus, the behaviour observed indicates an adequate number of active sites in the catalyst, for the HDS and vegetable oil/animal fat hydrotreatment reactions to occur simultaneously, without mutual inhibition by competitive adsorption to anionic vacancies in the active phase [30–32].

As in the case of HDS activity, a slight decrease in HDN activity was observed during co-processing experiments, always less than 1.20 wt%. When comparing waste feedstocks with refined palm oil the HDN efficiency decreases, with worst result for animal fat, 0.49 wt% less than for palm oil. Again, this fact could mean a possible dependence of the feedstock co-processed on the catalyst activity (HDS and HDN), but not with very significant influence.

As commented, after finish each co-processing step, a catalyst activity evaluation with only SRGO was performed. This procedure was carrying out to study the possible remaining effects over HDS/HDN activity. Fig. 7 shows the HDS and HDN activities before, during and after the UCO co-processing.

After the co-processing step with UCO no irreversible effects on HDS/HDN activities were observed at the described operating conditions. Similar behaviours were registered during animal fat or refined palm oil co-processing.

Therefore, at the operating conditions used, there is a slightly competitiveness between the HDS/HDN and triglycerides deoxygenation (HDO and HDC). However, a rigorous kinetic study has to be done to make a clear conclusion about the behaviour observed.

4. Conclusions

According to the results, the main product of the triglycerides feedstocks co-processing was the green diesel (estimated in a range of 78.6–85.0 wt%) composed mainly by linear paraffins, particularly in the range of 15 to 18 carbon atoms. By-products include light gases (9.9–12.6 wt%) and water (2.9–3.3 wt%). At the operating conditions employed, the catalyst always promoted the HDC pathway instead of HDO one, independently of the feedstock used during the co-processing (first-generation or waste materials). However, the results obtained

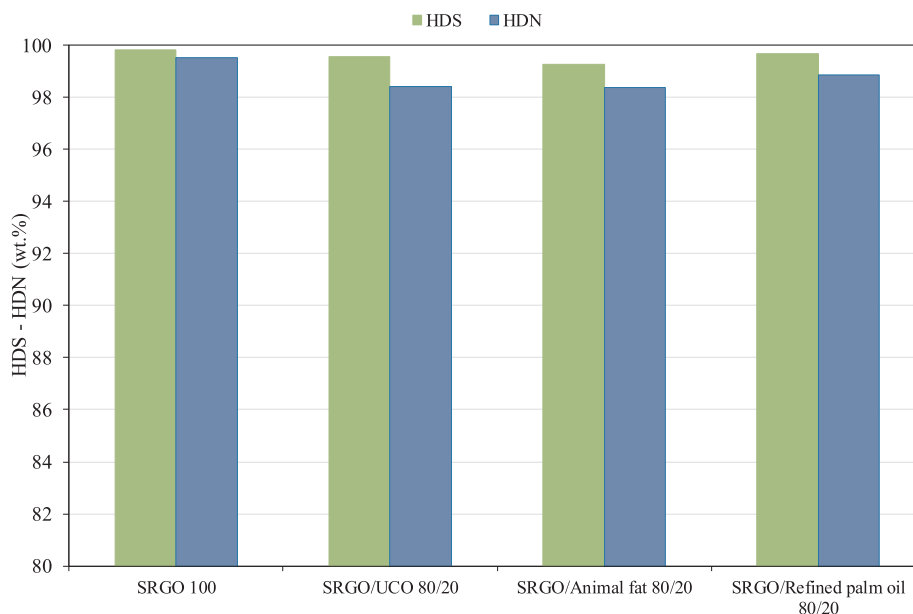


Fig. 6. HDS/HDN activities during co-processing experiments.

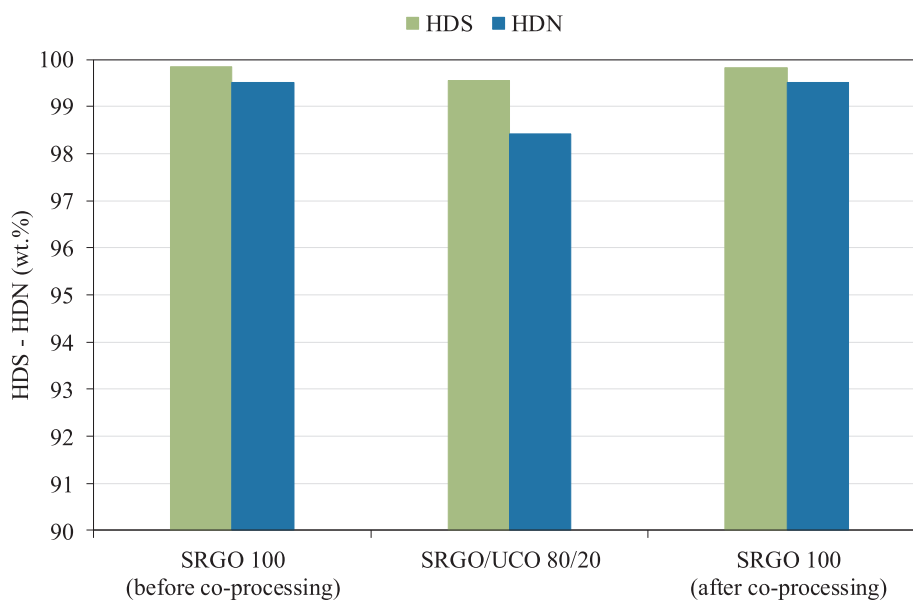


Fig. 7. UCO remains effect over HDS/HDN activities.

during the desulfurized gasoil characterization, as well as the HDS/HDN catalysts activities, showed a light dependence with the quality or nature of the triglycerides used in the co-processing. In this sense, waste materials, as UCO or animal fats, promoted the formation of a fuel with higher density and cetane index, in comparison with the fuel produced during the refined palm oil co-processing. In the same way, it was observed a higher decrement of catalyst activity during the UCO or animal fat co-processing. Along the described operating conditions, this effect was not significant and it should be confirmed by a rigorous kinetic study.

Acknowledgements

This research has been financed by The Ministry of Education, Culture, and Sports of the Government of Spain (FPU grant AP2012-4532) and the Centre for Industrial Technological Development (IDI-20151249).

References

- Naik SN, Goud VV, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. *Renew Sustain Energy Rev* 2010;14:578–97.
- Maity JP, Bundschuh J, Chen C, Bhattacharya P. Microalgae for third generation biofuel production, mitigation of greenhouse gas emissions and wastewater treatment: present and future perspectives – a mini review. *Energy* 2014;78:104–13.
- Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chem Rev* 2006;106:4044–98.
- Dou B, Song Y, Wang C, Chen H, Xu Y. Hydrogen production from catalytic steam reforming of biodiesel byproduct glycerol: issues and challenges. *Renew Sustain Energy Rev* 2014;30:950–60.
- Pimentel D, Marklein A, Toth MA, Karpoff MN, Paul GS, McCormack R, et al. Food versus biofuels: environmental and economic costs. *Hum Ecol* 2009;37:1–12.
- Al-Sabawi M, Chen J, Ng S. Fluid catalytic cracking of biomass-derived oils and their blends with petroleum feedstocks: a review. *Energy Fuels* 2012;26:5355–72.
- Bertero M, Sadrán U. Coprocessing of bio-oil in fluid catalytic cracking. *Elsevier*; 2015. p. 355–81. DOI: 10.1016/B978-0-444-63289-0.00013-2.
- Alonso DM, Wettstein SG, Dumesic JA. Bimetallic catalysts for upgrading of biomass to fuels and chemicals. *Chem Soc Rev* 2012;41(24):8075–98.
- Sotelo-Boyd R, Trejo-Zárrega F, Hernández-Loyo F. Hydroconversion of triglycerides into green liquid fuels DOI: 10.5772/48710. Available from: (accessed November, 2017). InTech; 2012. p. 187–216 <https://www.intechopen.com/books/howtoreference/hydrogenation/hydroconversion-of-triglycerides-into-green-liquid-fuels>.
- Veriansyah B, Han JY, Kim SK, Hong S, Kim YJ, Lim JS, et al. Production of renewable diesel by hydroprocessing of soybean oil: effect of catalysts. *Fuel* 2012;94:578–85.
- Kim SK, Han JY, Lee H, Yum T, Kim Y, Kim J. Production of renewable diesel via catalytic deoxygenation of natural triglycerides: comprehensive understanding of reaction intermediates and hydrocarbons. *Appl Energy* 2014;116:199–205.
- Bezergianni S, Dagonikou V, Sklari S. The suspending role of H₂O and CO on catalytic hydrotreatment of gas-oil; myth or reality? *Fuel Process Technol* 2016;144:20–6.
- Pinzi S, Mata-Granados JM, Lopez-Gimenez FJ, Luque de Castro MD, Dorado MP. Influence of vegetable oils fatty-acid composition on biodiesel optimization. *Bioresour Technol* 2011;102:1059–65.
- De Paz Carmona H, Horáček J, Brito Alayón A, Macías Herández JJ. Suitability of used frying oil for co-processing with atmospheric gas oil. *Fuel* 2018;214:165–73.
- De Paz Carmona H, Romero Vázquez MA, Frontela Delgado J, Macías Hernández JJ, Brito Alayón A. Catalytic co-processing of used cooking oil with straight run gas oil in a hydrotreatment pilot plant. *Hydrocarb Process* 2016;95:59–66.
- Donnis B, Egeberg RG, Blom P, Knudsen KG. Hydroprocessing of bio-oils and oxygenates to hydrocarbons. Understanding the reaction routes. *Top Catal* 2009;52:229–40.
- Bezergianni S, Dimitriadis A. Temperature effect on co-hydroprocessing of heavy gas oil-waste cooking oil mixtures for hybrid diesel production. *Fuel* 2013;103:579–84.
- Bezergianni S, Dimitriadis A, Karonis D. Diesel decarbonization via effective catalytic co-hydroprocessing of residual lipids with gas-oil. *Fuel* 2014;136:366–73.
- Jeczmiónek Ł, Porzycka-Semczuk K. Hydrodeoxygenation, decarboxylation and decarbonylation reactions while co-processing vegetable oils over a NiMo hydro-treatment catalytic. Part I: thermal effects – theoretical considerations. *Fuel* 2014;131:1–5.
- Boonyasuwat S, Tscheikuna J. Co-processing of palm fatty acid distillate and light gas oil in pilot-scale hydrodesulfurization unit over commercial CoMo/Al₂O₃. *Fuel* 2017;199:115–24.
- Guzman A, Torres JE, Prada LP, Nunez ML. Hydroprocessing of crude palm oil at pilot plant scale. *Catal Today* 2010;156:38–43.
- Kiatkittipong W, Phimsen S, Kiatkittipong K, Wongakulphasatch S, Laosiripojana N, Assabumrungrat S. Diesel-like hydrocarbon production from hydroprocessing of relevant refining palm oil. *Fuel Process Technol* 2013;116:16–26.
- Walendziewski J, Stolarski M, Łuźny R, Klimek B. Hydroprocessing of light gas oil – rape oil mixtures. *Fuel Process Technol* 2009;90:686–91.
- Sági D, Baladincz P, Varga Z, Hancsók J. Co-processing of FCC light cycle oil and waste animal fats with straight run gas oil fraction. *J Cleaner Prod* 2016;111:34–41.
- Chen J, Farooqi H, Fairbridge C. Experimental study on co-hydroprocessing canola oil and heavy vacuum gas oil blends. *Energy Fuels* 2013;27:3306–15.
- Bezergianni S, Dimitriadis A, Chryssikou LP. Quality and sustainability comparison of one- vs. two-step catalytic hydroprocessing of waste cooking oil. *Fuel* 2014;118:300–7.
- Bezergianni S, Dimitriadis A, Kikhtyanin O, Kubička D. Refinery co-processing of renewable feeds. *Prog Energy Combust* 2018;68:29–64.
- Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Appl Catal A* 2007;329:120–9.
- Watkins B, Olsen C, Sutovich K, Deady J, Petti N, Wellach S. New opportunities for co-processing renewable feeds in refinery processes. *Hydrocarbon Eng* 2009;14(1):49–58.
- Furimsky E, Massoth FE. Deactivation of hydroprocessing catalysts. *Catal Today* 1999;52:381–495.
- Tiwari R, Rana BS, Kumar R, Verma D, Kumar R, Joshi RK, et al. Hydrotreating and hydrocracking catalysts for processing of waste soya-oil and refinery-oil mixtures. *Catal Commun* 2011;12:559–62.
- Rana BS, Kumar R, Tiwari R, Kumar R, Joshi RK, Garg MO, et al. Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures. *Biomass Bioenergy* 2013;56:43–52.