Full Length Article

Suitability of used frying oil for co-processing with atmospheric gas oil

Héctor De Paz Carmona[a,*], Jan Horáček[b], Andrea Brito Alayón[a], José Juan Macías Hernández[a]

[a] *University of La Laguna (ULL), Faculty of Chemical, Chemical Engineering Department, Cno. San Frco. de Paula, s/n, 38206 San Cristóbal de La Laguna, Spain*
[b] *Unipetrol Centre of Research and Education (UniCRE), Block 2838, 436 70 Litvínov-Záluží 1, Czech Republic*

GRAPHICAL ABSTRACT
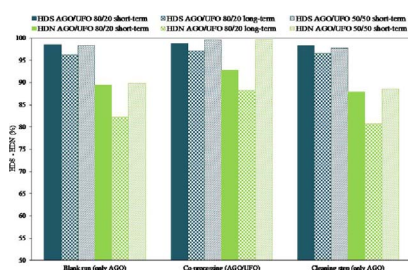
ARTICLE INFO

ABSTRACT

This work study the catalytic co-hydroprocessing of used frying oil (UFO) with atmospheric gas oil (AGO), paying particular attention to the effect of UFO on the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) efficiency, the products selectivities and its influence on fuel properties. Hydrotreating experiments were performed in a pilot plant for diesel hydrodesulphurization using a commercial catalyst of $NiMo/Al_2O_3$, temperature 320–350 °C, pressure 5.5 MPa, WHSV 2 h-1, UFO content 20–50 wt% and H_2/feed ratio 500–1200 NL/L. At the operating conditions used, a total conversion of the triglycerides of UFO was obtained with a 96–99% sulfur elimination. This produced a slightly increase of the HDS/HDN rates during the co-processing, without irreversible effects over its activity and important variation in some properties such as cetane index, density 15 °C or kinematic viscosity 40 °C. The main products obtained were paraffins with 15 and 17 atoms of carbons and light gases such as CO_2 and CH_4, which imply that the catalyst used stimulates decarboxylation reactions in detriment of hydrodeoxygenation reactions.

1. Introduction

Triglycerides are easy-to-convert feedstocks for first- and second-generation biofuels. The first-generation biofuels (typically fatty acids methyl esters (FAME) and ethanol) are becoming unviable because of the implementation of the Indirect Land Use Change (ILUC) legislation, which could start on 1st January 2021 in the European Union (European directives 2009/28/EC and 2009/30/EC). Together with higher CO_2 emissions savings requirement, second- and third-generation biofuels are becoming promising alternatives. The most important parameter for the qualification of fuels as second generation is to be produced from feedstocks with no possible use in the food industry. The third-generation biofuels are typically based on algae or lignocellulose feedstock origin and usually require more sophisticated processing technologies, which are not usually available on a commercial scale. In the case of triglycerides, only waste materials and inedible oils can be used as feedstocks for second-generation biofuels. The most commonly investigated materials are waste materials, such as used cooking oil (UCO), used frying oil (UFO), and waste fat produced by rendering plants and energy crops. While food quality oils and fats do not

normally need special handling before transesterification or hydrotreatment, waste materials must be purified before use, especially those for conversion by hydrotreatment.

Food residues and mechanical impurities, in general, represent problems in flow systems, where they can plug pipelines or damage pumps. In the case of hydrotreatment, the heterogeneous catalyst bed might become plugged quite quickly by mechanical impurities. Another problem might be caused by inorganic impurities, such as salts, which can be precipitated inside the catalyst bed at some unknown degree of conversion. The formation of inorganic solid deposits in the catalyst bed might have the same effect as mechanical impurities, plugging the bed and possibly changing the active phase composition and the activity.

Although both transesterification and hydrotreating processes can be used for UCO/UFO conversion, product quality makes hydrotreating more lucrative. In the case of building a new conversion unit, the disadvantages of high hydrogen consumption and the need for medium pressures make transesterification plants cheaper. Hydrotreating is very attractive for refineries, where these materials can be co-processed in hydrotreating or hydrocracking plants with standard fossil feedstocks. Based on the parallel reaction mechanisms of (hydro)deoxygenation (HDO) and hydrodecarboxylation (HDC) [1] and on the fatty acid distribution, C_{15}–C_{18} alkanes are the main expected products. The ratio of alkanes formed by HDO (even carbon number) and HDC (odd carbon number) is highly dependent on catalyst selection and the reaction temperature and pressure.

The catalytic deoxygenation of the triglycerides of UFO during the co-processing stage could occur following the reaction pathways shown in Fig. 1.

The first step is the hydrogenation of the double bonds of the alkyl chains followed by hydrogenolysis of the triglyceride structure, producing free fatty acids and one molecule of propane. Based on the operating conditions and catalyst selection, the reaction continues via the following reaction pathways: HDO, producing paraffins with an even number of carbons (nC_{16} and nC_{18}) and water, or HDC, leading to paraffins with an odd number of carbons in the chain (nC_{15} and nC_{17}) and CO_2 [3]. Together with these reaction mechanisms, a third mechanism frequently mentioned in publications is (hydro)decarbonylation, which is included in Fig. 1. The products of this reaction are identical to the HDC mechanism (nC_{15} and nC_{17}) together with propane and CO. For simpler data processing and identification, the decarboxylation and decarbonylation reaction paths and their products are marked with the HDC prefix.

In this work, used frying oil was investigated to identify its role in determining the quality of diesel from co-processing with atmospheric gas oil.

2. Materials and methods

2.1. Feedstocks

Two different types of feedstock were used for catalytic tests: used frying oil (UFO) and atmospheric gas oil (AGO). The UFO used was gathered from local restaurants in the Czech Republic. Before use, the

Table 1
Characterisation of the two UFO batches.

Physical characterisation	UFO batch 1	UFO batch 2	Chemical characterisation	UFO batch 1	UFO batch 2
Density 15 °C, kg/L	0.9205	0.9203	Acid number, mg KOH/g	1.15	0.58
Refractive Index 20 °C	1.4701	1.4729	Sulfur content, wt. ppm	4.2	4.4
Kin. viscosity 40 °C, mm²/s	43.0	35.7	Nitrogen content, wt. ppm	33.1	25.4
SimDis, wt%	–	–	Carbon, wt%	77.8	79.7
10	581	596	Hydrogen, wt%	12.0	12.0
20	592	602	Oxygen, wt%	10.2	8.3
30	598	605	Ca, mg/kg	0.2	0.2
50	601	608	P, mg/kg	0.5	0.7
70	608	610	Fe, mg/kg	0.1	0.2
80	609	611	Mg, mg/kg	0.05	0.1
90	610	612	K, mg/kg	0.5	0.7
—	—	—	Na, mg/kg	0.3	0.8

UFO was purified to remove solid food residues and water by filtration and decantation, respectively. Two batches of UFO were used to prepare the feedstocks for the hydrotreating experiments. Table 1 shows the main characterisation of these two batches.

The characterisation of both UFO batches indicated their very similar properties (such as density and metal content). Based on this characterisation, the same behaviour of these materials in hydrotreating, as well as similar products properties, can be expected. A low concentration of metals was determined in both oils. This indicates zero or very low contamination with inorganic materials and a low risk of poisoning of the active sites. The other characterisation methods indicate typical values for vegetable oils.

The fatty acid distribution in both materials was used as an additional parameter for hydrotreatment product characterisation. This analysis was performed using an ISO 12966 standard method, which consists of three main steps: dissolving the vegetable oil sample with *n*-hexane, complete transesterification with methanol and potassium hydroxide (2 M), and finally, analysis by gas chromatography. Table 2 shows the results of this analysis.

The fatty acid distribution showed that rapeseed oil is the main components of both UFO batches. High concentrations of oleic ($C_{18:1}$) and linoleic ($C_{18:2}$) acids, which are specific for this plant oil [4] were determined in both batches. The high concentration of palmitic acid ($C_{16:0}$, ca 22 wt%) in the 1st UFO batch points to traces of some other vegetable oil(s), probably palm oil.

Both UFO batches can be assumed to be approximately identical, based on the 98 wt% sum of fatty acids in their composition having carbons number between 16 and 18.

The AGO used in the experiments was obtained by the industrial atmospheric distillation of 'Russian export blend' (REB) crude oil, which is the most common crude oil for fuel production in the Czech Republic. Two different model mixes with a high percentage of used frying oil (UFO) content (20 and 50 wt%) were used for hydrotreatment experiments. A high blending degree was selected to identify the effects
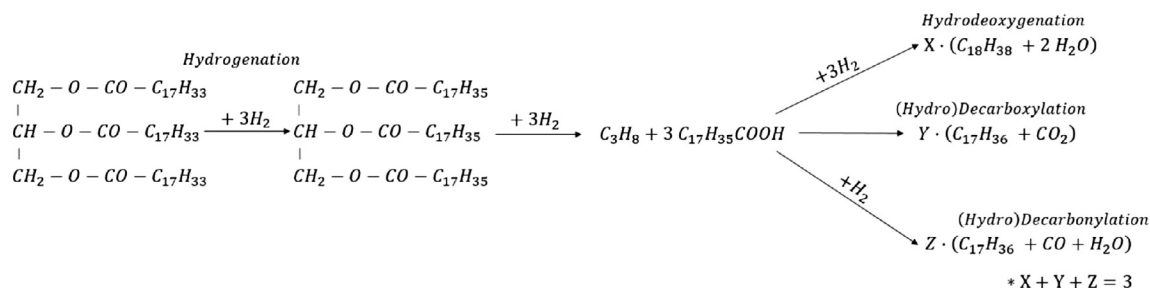

Fig. 1. Reaction pathways in the hydrotreating of a triglyceride (triolein) [2].

Table 2
Fatty acid composition UFO batches.

Fatty acid, wt%	UFO batch 1	UFO batch 2	Fatty acid, wt%	UFO batch 1	UFO batch 2
Myristic $C_{14:0}$	0.64	0.07	Arachidic $C_{20:0}$	0.46	0.57
Palmitic $C_{16:0}$	21.81	4.81	Eicosenoic $C_{20:1}$	0.70	1.35
Palmitoleic $C_{16:1}$	0.25	0.23	Behenic $C_{22:0}$	0.00	0.31
Stearic $C_{18:0}$	2.91	1.79	Erucic $C_{22:1}$	0.00	0.25
Oleic $C_{18:1}$	54.87	61.27	Lignoceric $C_{24:0}$	0.00	0.11
Linoleic $C_{18:2}$	15.70	19.60	Nervonic $C_{24:1}$	0.00	0.15
Linolenic $C_{18:3}$	2.66	9.49	—	—	—

of UFO co-processing on product quality and catalyst activity. A higher UFO blending degree represents a greater possibility of UFO impurities passing through the catalyst. In this way, some positive or negative effects of co-processing on the catalyst activity could be identified in a short on-stream time. Table 3 shows the main characterisation of AGO and the mixes used in these co-processing experiments.

The AGO density, sulfur concentration, and boiling point distribution are typical for middle distillates. This material is commonly used for automotive diesel. These were the reasons for its selection as a reference material for co-processing. As expected, the addition of UFO to AGO reduced the sulfur and nitrogen content. The feedstock density increased a little after UFO addition. The determination of metals in AGO was not carried out because it is a standard feedstock for hydrotreatment with a stable metal content, which was used as a background in this case.

To maintain the activity of the catalyst, 0.5 wt% of dimethyl disulfide (DMDS) was added to promote the catalyst activity when co-processing with 20 wt% or more UFO.

2.2. Experimental setup

Experiments were carried out in a bench-scale stainless-steel fixed-bed reactor equipped with electric heating designed for an isothermal operating regime. A reactor with an inner diameter of 17 mm and an integrated thermowell having an outer diameter of 5 mm was used. The maximal catalyst bed length available for this reactor is 300 mm, allowing a maximal catalyst bed volume of 62.2 cm^3. Inside the thermowell, thermocouples were placed accurately to control the reaction temperatures in the catalyst bed. The gas–liquid separator and product lines were heated to 45 °C by a thermostat (filled with deionised water) to avoid the sedimentation of paraffins in the pipelines. The separator was operated under reaction pressure. To avoid pressure changes inside catalyst bed during sample collection, the separator inlet was closed for around 60 s, and the pressure drop in the separator after sampling was

Table 3
Parameters of standard and model feedstocks for hydrotreatment and co-processing.

| Analysis	AGO	AGO/UFO 80/20 (batch 1) wt%	AGO/UFO 80/20 (batch 2) wt%	AGO/UFO 50/50 (batch 2) wt%
Density 15 °C, kg/L	0.8616	0.8728	0.8727	0.8735
Refractive index 20 °C	1.4790	1.4772	1.4778	1.4760
Sulfur content, wt%	1.30	1.07	1.14	0.94
Nitrogen content, wt. ppm	270	218	236	156
SimDis, wt%	T, °C			
10	247	249	254	276
20	282	283	287	307
30	302	302	305	329
50	326	328	334	390
70	352	355	369	604
80	367	369	402	606
90	386	391	603	608
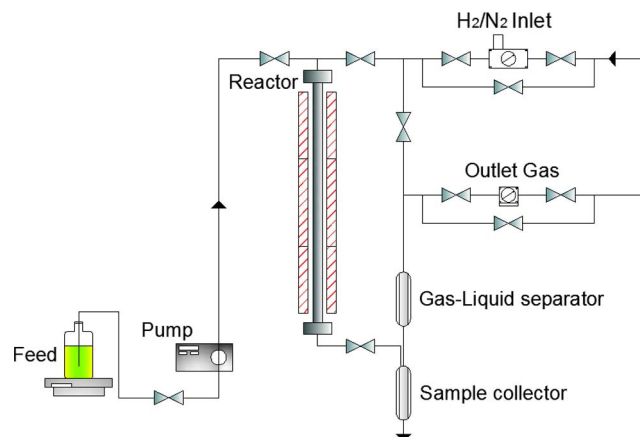
Fig. 2. Simplified schematic of the experimental unit.

compensated by the addition of fresh hydrogen via a by-pass to a level around 0.05 bar lower than the pressure in the reactor. Then, the reactor and separator were connected again. The experimental unit is located in an experimental facility of the Unipetrol Centre for Research and Education (UniCRE) in the Czech Republic. Fig. 2 shows a simplified schematic of the experimental unit.

The liquid feedstock was stored in a glass bottle placed on a weighing scale and pumped into the top of the reactor by a high-performance liquid chromatography (HPLC) pump. Standard quality refinery hydrogen was used as hydrogen source (H_2 > 99 v/v%, CH_4 < 1 v/v%) and the products were separated in a gas/liquid separator. The liquid product was periodically collected from a separator vessel. The off-gas was measured by a mechanical gas flow meter.

A commercial $NiMo/Al_2O_3$ catalyst was used for the experiments. The catalyst was delivered as extrudates with an approximate diameter of 1.3 mm. This catalyst is commonly used in the industrial middle distillates of hydrodesulfurisation units for the production of ultra-low sulfur diesel (ULSD), which is based on European legislation (maximum of 10 ppm of sulfur in diesel fuels). The suitability of the commercial catalyst for co-processing is the subject of this study.

The catalyst was crushed and sieved to obtain a particle size of 0.25–0.50 mm. Then, 15 g of fresh catalyst was used to prepare the catalyst bed in each experiment. To minimise the wall-flow effect and to improve the heat transfer inside the reactor, the catalyst was diluted with SiC (particle size 0.1 mm) as an inert material. Because of the highly exothermic nature of UFO hydrotreatment, a higher SiC:catalyst = 1:2 ratio was used in the top of the catalyst bed (middle and bottom of catalyst layer SiC:catalyst = 1:1).

The experimental co-processing procedure included four steps: sulfiding, stabilisation, co-processing, and cleaning. Catalyst sulfiding was performed according to the method recommended by the catalyst manufacturer: drying under H_2 flow at 150 °C, followed by pumping the middle distillate with 1.3–3.0 wt% dimethyl disulfide, which was added with a slowly increasing temperature until the reaction temperature was reached. After the sulfiding procedure had finished, the feedstock was changed to pure AGO, which was fed in until a steady reactor state was reached. If necessary, a feedstock change was performed after reaching a steady state. When the AGO/UFO co-processing was finished, the feedstock was changed to pure AGO. This last part, the so-called 'cleaning step', lasted 48 h to compare the hydrodesulfurisation (HDS) and hydrodenitrogenation (HDN) catalyst activities before and after the co-processing step.

2.3. Experiments

Three co-processing experiments were performed to describe the effect of the addition of UFO on the hydrotreatment process. To

Table 4
Operating conditions used in co-processing tests.

Parameter/Experiment No.	1	2	3	4
Temperature, °C	350	350	350	320
Pressure, MPa	5.5	5.5	5.5	5.5
WHSV, h^{-1}	2	2	2	2
H_2 to feed, NL/L	500	500	1200	500
UFO, wt%	20	20	50	20
Time of co-processing (AGO/UFO) step, h	144	252	168	24
Overall time on stream, h	360	388	304	72
Catalyst amount, g	15	15	15	30
UFO batch	1	2	2	2

Fig. 3. ATR Spectrum of UFO.

complement this study and evaluate the effect of temperature on the HDS and HDN conversion and product distribution, one further co-processing experiment with 30 g of catalyst at 320 °C was performed. A higher amount of catalyst was used because of the change of the H_2S washer instrumentation to a larger one that required larger sample volumes to operate correctly. Based on previous experience, a higher catalyst amount does not affect product quality or the reaction mechanism preferences. Table 4 shows the operating conditions of each test, similar to those found in previous publications [5] and used in our previous experiments [6].

In this table, the 'overall time on stream' refers to the total time for all the experiment steps (stabilisation, co-processing, and cleaning steps). The 'time of co-processing (AGO/UFO) step' is the time on stream of the AGO/UFO co-processing step of the experiment.

A high H_2 to feed ratio was used in all the experiments, especially during experiment 3, in which an increase of the feed ratio was required because of the increase of UFO content to 50 wt%, which is accompanied by increased hydrogen consumption.

2.4. Analytical methods

During the experiments, liquid and gaseous products were obtained. The liquid consisted of organic and aqueous phases, especially in the case of co-processing. After quantitative separation of the aqueous phase, the organic layer was analysed to determine its density at 15 °C (ASTM D 4052) and the refractive index at 20 °C (ASTM D 1218) as a routine measurement to identify when a steady state had been reached. Then, the organic layer was washed with nitrogen to remove the H_2S. This step is necessary to avoid the formation of elemental sulfur in the product.

After sulfur removal, more detailed characterisation was performed: sulfur content (ASTM D 1552), nitrogen content (ASTM D 5291), elemental analysis (ISO 29541), SimDis (ASTM D 2887), cloud point (ASTM D 2500), cold filter plugging point (ASTM D 6371), viscosity at 40 °C (ASTM D 445), water content by Karl Fischer titration (ASTM D 4928), aromatic compounds content (IP 391), and metal content (ISO 11885). The analysis of the gaseous products was performed offline using Tedlar sampling bags to collect the off-gas and GC (refinery gas analysis (RGA)) to determine its composition (such as H_2, CO, CO_2, CH_4, and C_3H_8).

The total conversion of the triglycerides of the vegetable oil was verified using IR-attenuated total reflectance (ATR) analysis of the desulfurised diesel oil product. Fig. 3 shows the characteristic peaks for vegetable oils.

The peaks at 1745 and 1710 cm^{-1} are typical of carbonyl functional groups, the peaks at 1350–1500 cm^{-1} represent the angular deformations of CH_2 and CH_3, and, finally, the peak at 1159 cm^{-1} can be assigned to saturated acyl groups [7].

The absence of these peaks in the spectra of the liquid products confirms the total deoxygenation [8]. Incomplete deoxygenation requires changing the reaction parameters to increase the UFO conversion by modifying the reaction temperature, pressure, H_2:feed ratio, or feed
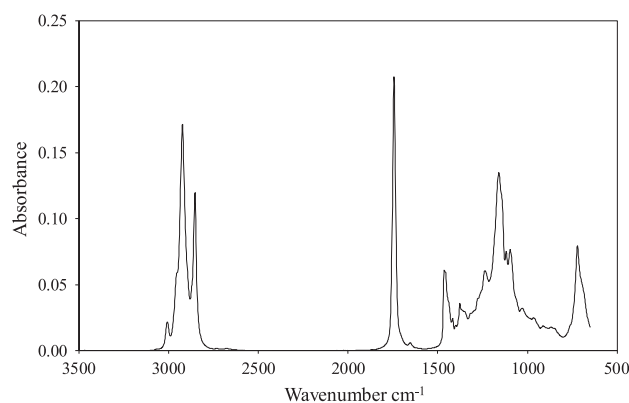
rate. The paraffin content (nC_8 to nC_{28}) was quantified by a gas chromatograph with a flame ionisation detector (GC-FID).

After completing each experiment, the spent catalyst was collected and sieved to separate the inert SiC from the catalyst. The reactants residues were extracted with toluene in a Soxhlet extractor. The washed catalyst sample was then characterised by analytical methods (X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma (ICP) mass spectrometry, nitrogen physisorption (BET), mercury porosimetry, and elemental analysis).

3. Results and discussion

The co-processing of the UFO with AGO was performed to study its effect on the HDS and HDN reactions, the products formed, and their influence on fuel properties and the catalyst.

3.1. Effect on the HDS and HDN performance

The process yield, η, was defined as the relationship between the mass of desulfurised gas oil obtained and the feedstock used. Taking into account the sulfur content in the feedstock, and the sulfur content in the product, as well as the yield of the process, the HDS efficiency was determined according to the following equation:

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

(1)

where S_0 and S_p represent the sulfur content of the feedstock and liquid product respectively (wt. ppm). In the same way, the HDN efficiency can be determined using the nitrogen content, according to the following equation:

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

(2)

where N_0 and N_p represent the nitrogen content of the feedstock and liquid product respectively.

To study the effect of the UFO on the catalyst activity, the HDS and HDN efficiencies were determined in each experiment with three different reaction setups: a stabilisation or blank run, a co-processing step, and a cleaning step. Fig. 4 shows the variation of the HDS and HDN efficiencies for these stages during co-processing experiments 1, 2, and 3.

In all cases, the addition of UFO to the feedstock did not reduce the degree of HDS. In fact, a slight increase in the HDS efficiency was detected, 0.4%, 0.9%, and 1.3% for experiments 1, 2, and 3 respectively, as shown in Fig. 4. This HDS efficiency increase is in good agreement with the published results concerning the co-processing of waste cooking oil with fossil fuel streams, such as refinery gas oil, heavy gas oil (HGO), or heavy atmospheric gas oil (HAGO) [9–11]. This behaviour indicates an adequate number of active sites in the catalyst for the HDS
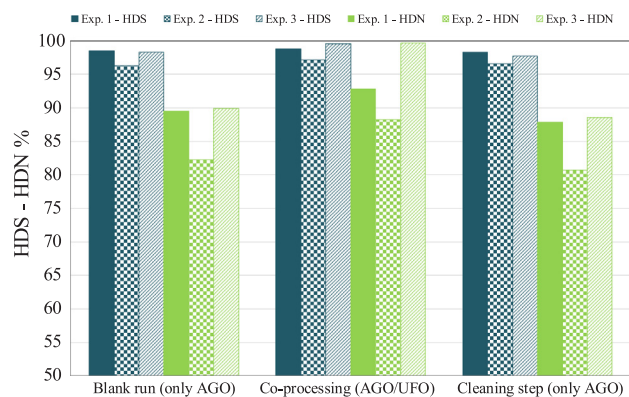
Fig. 4. HDS and HDN performance during co-processing experiments.

Fig. 5. HDS and HDN performance at different temperatures and feedstocks.

and deoxygenations reactions to occur simultaneously without mutual inhibition by competitive adsorption to anionic vacancies in the active phase [12,13]. This behaviour cannot be caused just by the dilution of the sulfur in the feedstock because the differences in yields, in that case, would be lower.

The cleaning stage allowed the return of the initial HDS activity to approximately the same efficiency as determined in the initial stage (pure AGO fed). The biggest difference (0.6%) was obtained in the experiment with the highest concentration of UFO. This indicates that, for the operating conditions used (such as time on stream of co-processing, temperature, and weight hourly space velocity (WHSV)), the addition of UFO did not have an irreversible effect on the HDS activity of the catalyst. This conclusion was also confirmed in the cases of extended co-processing (108 h) or increased UFO content (from 20 to 50 wt%).

The HDN efficiency was not reduced by the addition of UFO to the feedstock. UFO increased HDN efficiency during the co-processing stage more significantly than in the case of the HDS reactions. The HDN efficiency increases of 3.5%, 6.1%, and 9.7% for experiments 1, 2, and 3 showed that the HDN activity increased with increasing co-processing time on stream and with increasing UFO addition to the feedstock. This behaviour has also been reported by Bezergianni et al. during the co-processing of UFO and HAGO [10,11]. As in the case of HDS, the dilution effect from UFO addition favours the HDN reactions because the concentration of nitrogen compounds in the feed is reduced.

After the co-processing stage, no irreversible effects on HDS efficiency were observed, while the HDN activity was slightly reduced, having a maximum difference of 1.5%.

The reaction temperature also plays an important role in AGO-UFO co-processing and, thus, has an effect on the HDS and HDN activities. Fig. 5 shows the HDS and HDN efficiencies at two different temperatures during the AGO and co-processing hydrotreatment. Clearly, the reaction temperature plays an important role in AGO-UFO co-processing and, thus, in the HDS and HDN activities, and this parameter modification can be used to optimise the catalyst activity and product quality.

The importance of the reaction temperature on HDS and HDN activity is shown in both reaction regimes: conventional AGO hydrotreatment and co-processing with UFO. This confirms the behaviour observed during experiments 1, 2, and 3, in which the UFO addition did not produce a change in the catalyst HDS activity after the co-processing stage, regardless of the temperature. A slight increase in HDN activity during co-processing was observed at both reaction temperatures, and this is in good agreement with some results reported for co-processing with HGO and UFO at various temperatures [14].

Therefore, if there is any competitiveness between the HDS/HDN with deoxygenation reactions during co-processing, it is not significant because of the dilution of the feedstock.
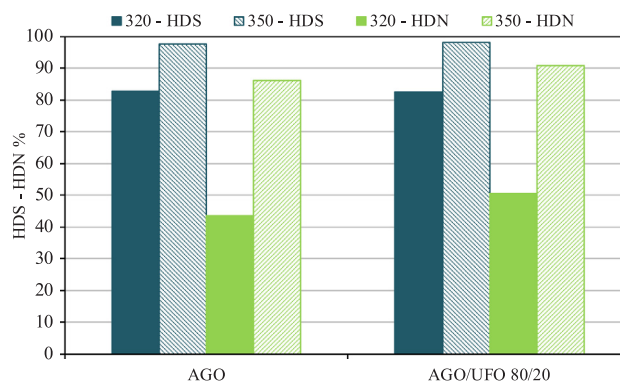
3.2. Reaction product analysis

GC data were used to identify and quantify the products and by-products in the off-gas, and Table 5 shows the composition of the off-gas after AGO hydrotreatment and the co-processing of AGO/UFO mixtures.

In all the off-gas samples, the main compound detected was H_2 (AGO: 97.0–98.8 mol.%; AGO/UFO: 95.0–96.7 mol.%). In the case of AGO hydrotreatment, lower concentrations of other gases were detected. The higher content of methane during experiments 2 and 3 was caused by changing the hydrogen source from pure hydrogen from flasks to standard refinery gas, which was used as the hydrogen source and contains traces of methane ($H_2 > 99$ v/v%, $CH_4 < 1$ v/v%). The off-gas sampled during the co-processing stages was specific in having a higher content of CO_2, CH_4, and C_3H_8 in comparison with the off-gas from AGO hydrotreatment. This is in good agreement with available data from the literature [6,14]. Propane formation is directly related to the feedstock structure (triacylglycerols), as is the CO_2 formed by the HDC reaction pathways from intermediates (carboxylic acids), as shown in Fig. 1. The increased CH_4 content is related to CO_2 methanation in the presence of H_2 and the catalyst.

The C_3H_8 produced could be positive from an industrial point of view because of its high added value as liquid petroleum gas (LPG), while the CO_2 could decrease the HDS and HDN rates during co-processing [15], which could be solved in industrial units by introducing an extra gas cleaning step before re-use or carrying out the co-processing alternately.

To study the overall products formed because of the addition of UFO during the co-processing, the mass balance was calculated for each experimental stage, and Table 6 shows the results obtained for the yields of the main reaction products.

As expected, the main products of UFO hydrotreatment were paraffins (80–85 wt%). The other products (by-products) were typically water (6.5–7.5 wt%) and gases in the range (8.2–13.1 wt%). The distribution of the by-products depended on the reaction pathways because HDC reactions produce more gaseous products, while the hydrodeoxygenation reaction produces water instead of CO_x.

Table 5
Off-gas composition.

Component, mol%	Experiment 1		Experiment 2		Experiment 3	
	AGO	AGO/UFO 80/20 wt%	AGO	AGO/UFO 80/20 wt%	AGO	AGO/UFO 50/50 wt%
H_2	98.80	96.67	97.01	94.99	97.93	95.87
CO_2	0.00	0.76	0.00	0.82	0.00	0.77
CH_4	0.05	0.53	1.11	1.69	1.10	1.37
C_3H_8	0.03	0.65	0.02	0.62	0.01	0.85
Other gases	1.12	1.40	1.86	1.88	0.97	1.14

Table 6
Product yields.

Product wt%	Experiment 1	Experiment 2	Experiment 3
Paraffins	79.42	81.45	84.86
Water	7.53	6.44	6.94
Gases	13.05	12.11	8.21

Nevertheless, carbon oxides can be reduced to methane and water as a by-product. This means that lower hydrogen consumption by the HDC reactions is not the key parameter for the overall hydrogen consumption. In fact, HDO produces higher yields of hydrocarbons and requires lower amounts of hydrogen compared to HDC reactions, followed by total CO_x deoxygenation of identical feedstock.

The deoxygenation reaction pathway preferences and product distributions are affected by changes in the operating conditions. Table 7 shows the yields of products during the co-processing of AGO/UFO 80/20 at two reaction temperatures, 320 and 350 °C.

A temperature increase resulted in the greater formation of gaseous products (9.45–12.11 wt%) and lower yields of water (8.40–6.44 wt%). This can be explained by the promoting effect of the temperature on the HDC of the UFO intermediates and the higher sensitivity of HDC to the operating temperature when compared to the temperature sensitivity of the hydrodeoxygenation reactions.

GC-FID analysis was used for the quantitative analysis of the liquid deoxygenation products of UFO hydrotreating. Fig. 6 shows the distribution of paraffins (nC_{15} to nC_{18}) in the liquid product during the three co-processing experiments at 350 °C.

The n-heptadecane (nC_{17}) yields were higher than those of n-octadecane (nC_{18}) in all the experiments. The same trend was found for nC_{15} and nC_{16} in the case of experiment 1, where UFO with a higher palmitic acid content was used (Table 2). Taking into account the paraffins with 15–18 carbons, the percentage of paraffins formed by HDO and HDC pathways was calculated using the following equations previously published by our group [6]:

$$HDO[\%] = \frac{nC_{16} + nC_{18}}{nC_{15} + nC_{16} + nC_{17} + nC_{18}} \cdot 100, \tag{3}$$

$$HDC[\%] = \frac{nC_{15} + nC_{17}}{nC_{15} + nC_{16} + nC_{17} + nC_{18}} \cdot 100, \tag{4}$$

where $nC_{16} + nC_{18}$ and $nC_{15} + nC_{17}$ represent the paraffins formed following HDO and HDC pathways (wt%) respectively, and $nC_{15} + nC_{16} + nC_{17} + nC_{18}$ represent the paraffins formed by the hydrotreatment of UFO (wt%). The results obtained are shown in Table 8 for each co-processing experiment.

As suggested by Fig. 6, the HDC pathway was preferred rather than HDO in all experiments (co-processing with AGO/UFO 80/20 and 50/50 at 350 °C; NiMo/Al$_2$O$_3$). In the case that no CO_x reduction occurs, lower H$_2$ consumption can be expected together with an increase in gas formation (mainly CO, CO_2, and CH_4). These results are in good agreement with the published results [6], where co-processing with straight run gas oil (SRGO) and UFO 80/20 at 385 °C and 5.5 MPa formed approximately 23% paraffins by the HDO mechanism and ca. 77% by the HDC mechanism. An example of calculated hydrogen consumption is given in Table 9 as the hydrogen consumption per 100 grams of UFO and per 100 grams of total feed during the

Table 7
Product yields at different temperatures.

Product, wt%	320 °C	350 °C
Paraffins	82.14	81.45
Water	8.40	6.44
Gases	9.45	12.11
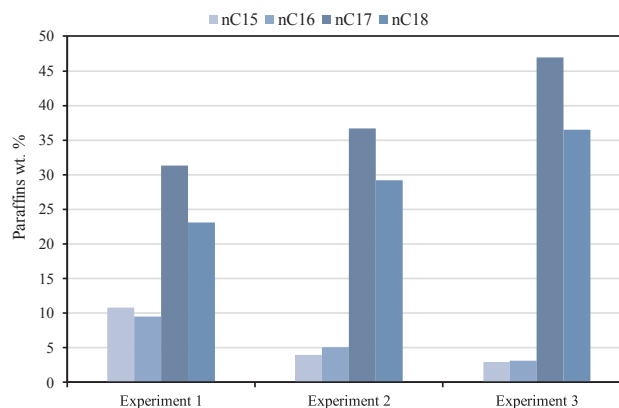
Fig. 6. Distribution of paraffins during co-processing experiments at 350 °C.

Table 8
Paraffin distribution by reaction mechanism.

Parameter	Experiment 1	Experiment 2	Experiment 3
HDO%	43.7	45.7	44.3
HDC%	56.3	54.3	55.7

experiment stage carried out at 350 °C.

Approximately the same value of H$_2$ consumption per 100 g of UFO processed was obtained in case of different UFO addition levels, showing good reproducibility in the experiments. A higher amount of UFO added into the feed resulted in an increase in hydrogen consumption of the hydrotreatment process. This increase would rise from 8% to 16% on the industrial scale for 5–10% UFO in the feedstock. It is necessary to consider the process efficiency regarding higher hydrogen consumption accompanied by lower gas oil yields with the LPG produced and its possible use in the specific conditions of each refinery. The main benefit is the elimination of waste material in conventional hydrotreatment plants producing second-generation biofuel (green diesel).

As mentioned, the reaction temperature affects the reaction mechanisms significantly. This can be observed in the paraffin distribution. Fig. 7 shows that, in the case of AGO/UFO 80/20 at 320 °C (experiment 4), the HDO mechanism was preferred. Increasing the reaction temperature to 350 °C promoted the HDC reactions so much that they become the main reaction pathway.

The distribution of paraffins in the liquid product changed in agreement with Table 7 (from a higher concentration of paraffins with even carbon numbers at 320 °C to an increased concentration of those with odd carbon numbers). Thus, the percentage of paraffins that follows the HDO pathway goes from 55.3% at 320 °C to 45.7% at 350 °C, while 44.7% of paraffins follows the HDC pathway at 320 °C and 54.3% at 350 °C.

The temperature effect on the deoxygenation mechanism significantly affects the process mass balance during the co-processing of AGO with UFO. Increasing the operational temperature (e.g., 320 → 350 °C) reduced the H$_2$ consumption from UFO hydrotreatment (in the case of low CO_x deoxygenation) and increased the CO_x production because of changes in the selectivity to favour HDC reactions to the detriment of HDO reactions. This result is in good agreement with the

Table 9
Hydrogen consumption of hydrotreatment at 350 °C.

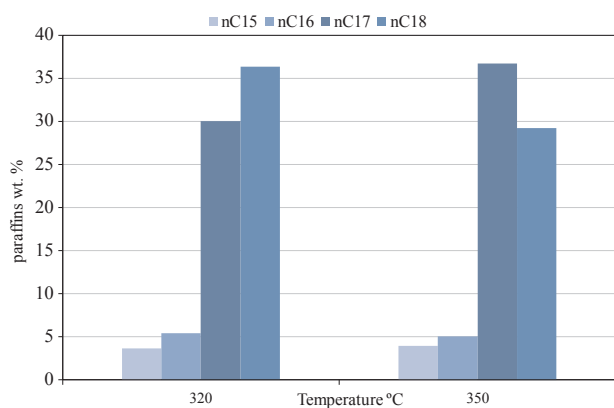| Parameter	AGO	AGO/UFO 80/20	AGO/UFO 50/50
H$_2$ consumption, g/100 g of UFO	—	3.52	3.63
H$_2$ consumption, g/100 g of feed	1.37	1.61	2.74

Fig. 7. Distribution of paraffins at 320 and 350 °C.

published results of Horáček et al. [1], in which nickel promoted C−C bond cleavage in carboxylic acids, particularly the loss of carboxylic acid groups and the release of CO_2 (i.e., decarboxylation).

3.3. Effect of the products on fuel properties

The nature of hydrotreated UFO is almost strictly paraffinic with traces of olefins and isoparaffins. This fact strongly affects the characterisation of products from co-processing related to AGO hydrotreatment products.

3.3.1. Density and kinematic viscosity

Density (ρ) measurements were used as a fast method to check the product quality. The kinematic viscosity (ν) was also used. Table 10 shows density at 15 °C and the kinematic viscosity at 40 °C for samples collected at a steady state of each experimental period.

The addition of UFO to the feedstock resulted in a decrease in the product density because of the lower density of the paraffins in comparison with other diesel fraction compounds [10,16].

The hydrotreatment product density decreased with increasing percentage of UFO in the feedstock going from a 1.4% decrease for 20% UFO content to 3.7% for 50% UFO content in the feedstock. This density reduction resulted in a higher quality of the desulfurised product by lowering the need for additives or kerosene during the industrial process, thus fulfilling the density requirements of the EN 590 standard (0.820–0.845 kg/L).

The kinematic viscosity of UFO (35–45 mm^2/s) is significantly higher than that of AGO (5.13 mm^2/s). This difference typically changes the co-processing product parameters because of the decrease in the viscosity and density related to the feedstock. The decrease in the kinematic viscosity was more significant in products from the hydrotreatment of blends with higher UFO contents (Table 10 experiments 1–3). The density decrease was caused by the relatively lower density of UFO-derived *n*-paraffins compared to the typical density of AGO-derived compounds [16,17].

Table 10
Product densities and kinematic viscosities.

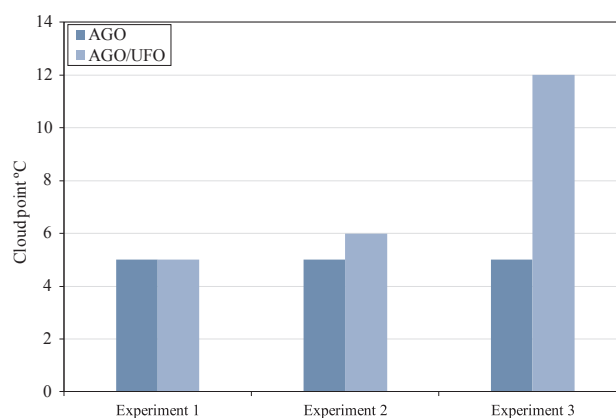| Run	Feedstock	ρ 15 °C, kg/L	ν, 40 °C, mm^2/s	t, h
Experiment 1	AGO	0.8451	4.79	168
	AGO/UFO	0.8327	4.35	144
Experiment 2	AGO	0.8464	5.07	60
	AGO/UFO	0.8343	4.52	252
Experiment 3	AGO	0.8457	5.00	60
	AGO/UFO	0.8143	4.16	168

Fig. 8. Cloud point during AGO and AGO/UFO co-processing (Exp. 1 and 2: 20 wt% UFO, Exp. 3: 50 wt% UFO) at 350 °C and 5.5 MPa.

3.3.2. Cold flow properties

The increase in paraffin content in the diesel affected its low-temperature properties negatively, as shown by the cloud point (CP) and cold filter plugging point (CFPP). This is a result of the high melting point of paraffins [16]. The CP and CFPP of desulfurised gas oil (Figs. 8 and 9) were not significantly different for the products of the co-processing of AGO/UFO 80/20 (experiments 1 and 2). A much stronger effect was observed after the increase in the UFO content in the feedstock from 20 to 50 wt%. This change significantly increased both parameters (CP: 4.5 °C and CFPP: 6.0 °C). For commercial use, these values are not acceptable, and it would be necessary to optimise them, for example, by blending and the use of additives [18].

3.3.3. Distillation and cetane index

The distillation curve and boiling point distribution are also part of the EN 590 standard, and any diesel fuel in Europe must fulfil these requirements. Table 11 and Fig. 10 summarise the boiling point distribution and the distillation curves for liquid products from co-processing experiments after reaching reactor steady state.

The UFO co-processing resulted in a 'lightening', giving rise to an increase of the relative content of compounds with boiling points between 250 and 380 °C, from 78.2 (AGO) to 81.3 and 87.6 wt% for AGO/UFO 80/20 and AGO/UFO 50/50, respectively. This can be explained by the increase in the C_{15}–C_{18} paraffin content without significant AGO hydrocracking. The changes in the distillation curve typically reflect the increase in the paraffin content.

The derivative boiling point distribution (Fig. 11) showed a significant increase in the C_{15}–C_{18} paraffins in the co-processing products, as expected based on the proposed reaction scheme (Fig. 1).
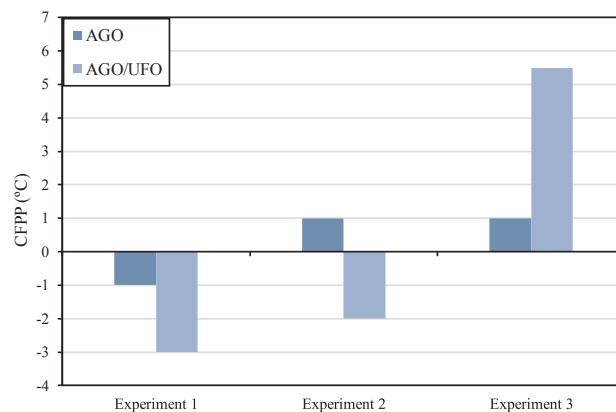

Fig. 9. CFPP during AGO and AGO/UFO co-processing (Exp. 1 and 2: 20 wt% UFO, Exp. 3: 50 wt% UFO) at 350 °C and 5.5 MPa.

Table 11
Boiling point distribution (initial boiling point (IBP) and final boiling point (FBP)).

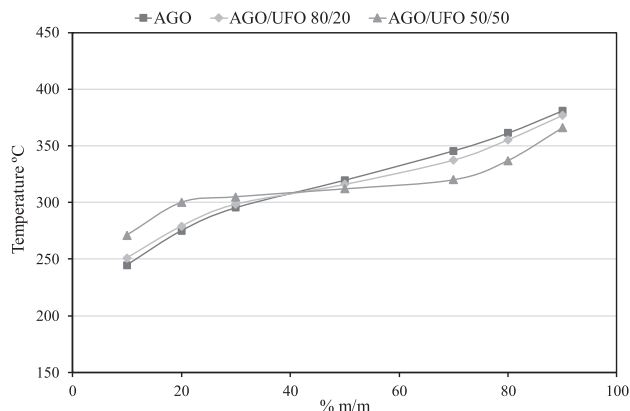|	AGO	AGO/UFO 80/20	AGO/UFO 50/50
IBP–250 °C, wt%	11.3	9.9	6.1
250–380 °C, wt%	78.2	81.3	87.6
380 °C–FBP, wt%	10.5	8.8	6.3

Fig. 10. Distillation curve of liquid products.

The cetane index (the quality index) increased (calculated from the density and distillation data; Fig. 12) as an effect of UFO co-processing with increasing AGO and UFO content.

In all the experiments, the cetane indexes of AGO-derived hydrotreatment products were nearly identical, showing good reproducibility of catalytic experiments. In general, it is possible to say that the presence of UFO or triglycerides in the feedstock resulted in a rapid increase in the cetane index. A comparison of the cetane indexes of products from experiments 1 and 2 points to near zero sensitivity of this parameter to the fatty acid distribution in UFO. This is an important result concerning the blending of co-processing products with other materials.

3.3.4. Refractive index at 20 °C and metal content

In a similar way to the density and kinematic viscosity, the increase in paraffin content resulted in a decrease in the refractive index (RI). This parameter is a bulk property, allowing the estimation of the aromaticity of the hydrotreated product. A lower RI indicates a low aromatic component and a high paraffinic component. Fig. 13 shows the RI differences for the products of co-processing stages and pure AGO processing.

The refractive index decreased in the co-processing product with increasing UFO content in the feedstock. No significant catalyst
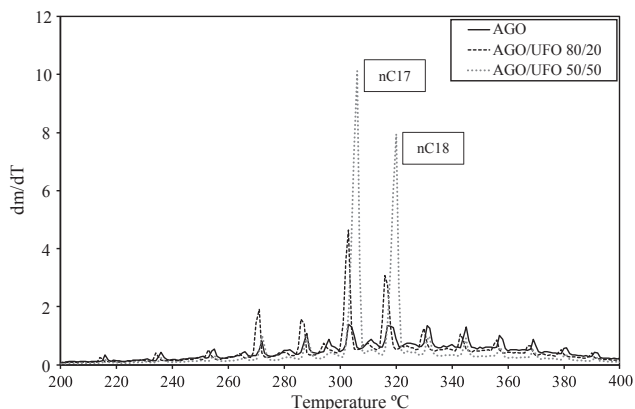

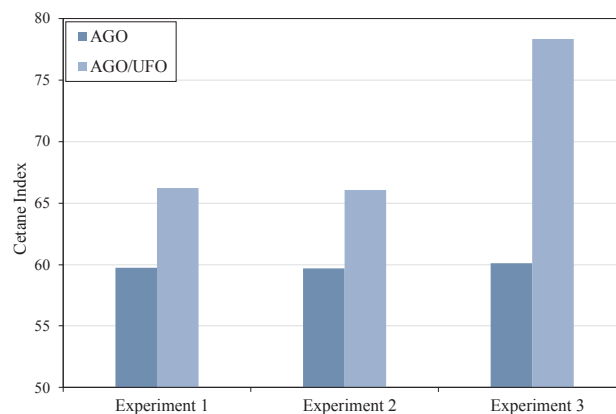**Fig. 11.** Qualitative distribution of paraffins during AGO and AGO/UFO hydrotreatment.

Fig. 12. Cetane index during AGO and AGO/UFO co-processing (Exp. 1 and 2: 20 wt% UFO, Exp. 3: 50 wt% UFO) at 350 °C and 5.5 MPa.
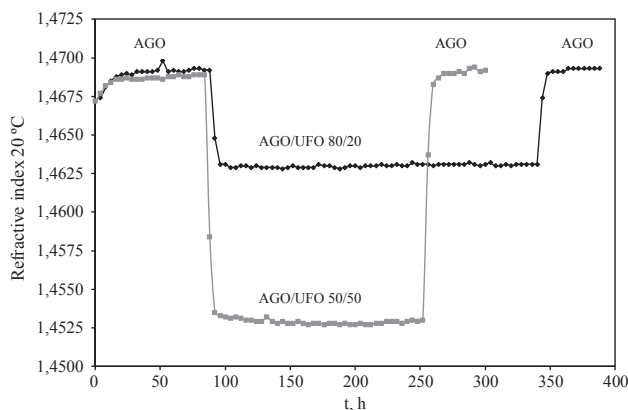

Fig. 13. Refractive index changes during AGO and AGO/UFO co-processing.

deactivation was observed with changes in the product RI at 20 °C, reaching almost identical values during the blank run and the cleaning step (before and after the co-processing stage).

3.3.5. The role of UFO impurities

The inorganic impurities, namely alkali metals and alkaline earth metals together with phosphorus, play a fundamental role in the deactivation of hydrotreatment catalysts [19]. In this study, the concentrations of metals in both batches of UFO used were very low (Table 1). The insignificant catalyst deactivation indicates that metal deposition had no effect on the catalyst surface and active sites. Table 12 shows the ICP-metal analysis for the co-processing experiment products, where almost no changes were observed in the quality of the products when AGO or AGO/UFO was processed.

4. Conclusions

UFO co-processing with AGO over a commercial NiMo hydrotreatment catalyst at constant reaction conditions with switching feedstocks, showed no irreversible HDS and HDN catalytic activity loss with UFO addition to the standard feedstock in amounts of 20–50 wt% at reaction temperatures between 320 and 350 °C. A temperature increase of 30 °C from 320 to 350 °C resulted in a selectivity change, preferring the HDC reaction mechanisms instead of the HDO reaction pathway. Paraffins were identified as the main UFO hydrotreatment products and affected the chemical and physical properties of the organic liquid product by increasing the yield of the fraction with a boiling point 250–380 °C and increasing the cetane number of the product. As additional effects, the density decreased and the low-temperature properties became poorer for the main products of co-processing.

Table 12
Metal content in the liquid products.

Metal, ppm	AGO	AGO/UFO 80/20	AGO/UFO 50/50
Al	0.10	0.10	0.10
Ca	0.10	0.10	0.10
Fe	0.16	0.21	0.72
K	0.50	0.50	0.50
Mg	0.05	0.05	0.05
Na	0.17	0.47	0.50
Ni	0.10	0.10	0.10
P	0.10	0.10	0.10
t, h	168	252	168

References

[1] Horáček J, Tišler Z, Rubáš V, Kubička D. HDO catalysts for triglycerides conversion into pyrolysis and isomerization feedstock. Fuel 2014;121:57–64.

[2] Kubička D. Future refining catalysis-introduction of biomass feedstocks. Collect Czech Chem Commun 2008;73:1015–44.

[3] Ki Kim S, Young Han J, 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.

[4] Meng X, Chen G, Wand Y. Biodiesel production from waste cooking oil via alkali catalyst and its engine test. Fuel Process Technol 2008;89:851–7.

[5] 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.

[6] 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.

[7] Liu C, Liu J, Zhou G, Tian W, Rong L. A cleaner process for hydrocracking of jatropha oil into green diesel. J Taiwan Inst Chem Eng 2013;44:221–7.

[8] Pinto F, Martins S, Gonçalves M, Costa P, Gulyurtlu I, Alves A, et al. Hydrogenation of rapeseed oil for production of liquid bio-chemicals. Appl Energy 2013;102:272–82.

[9] Rana BS, Kumar R, Tiwari R, Kumar R, Joshi RK, Garg MO, Sinha AK. Transportation fuels from co-processing of waste vegetable oil and gas oil mixtures. Biomass Bioenergy 2013;56:43–52.

[10] Bezergianni S, Dimitriadis A, Karonis D. Diesel decarbonization via effective catalytic co-hydroprocessing of residual lipids with gas-oil. Fuel 2014;136:366–73.

[11] Bezergianni S, Dimitriadis A, Meletidis G. Effectiveness of CoMo and NiMo catalysts on co-hydroprocessing of heavy atmospheric gas oil-waste cooking mixtures. Fuel 2014;125:129–36.

[12] Tiwari R, Rana BS, Kumar R, Verma D, Kumar R, Joshi Garg RK, Garg MO, Sinha AK. Hydrotreating and hydrocracking catalysts for processing of waste soya-oil and refinery-oil mixtures. Catal Commun 2011;12:559–62.

[13] Furimsky E, Massoth FE. Deactivation of hydroprocessing catalysts. Catal Today 1993;17:537–660.

[14] 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.

[15] Bezergianni S, Dagonikou V. Effect of CO_2 on catalytic hydrotreatment of gas-oil. Can J Chem Eng 2015;93:1017–23.

[16] Walendziewski J, Stolarski M, Łużny R, Klimek B. Hydroprocessing of light gas oil – rape oil mixtures. Fuel Process Technol 2009;90:686–91.

[17] Dragomir RE, Rosca P. Biodiesel by hydroprocessing of gas oil-vegetable oil mixtures. Rev Chim 2014;65:485–8.

[18] Bezergianni S, Dimitriadis A, Chrysikou LP. Quality and sustainability comparison of one-vs. two-step catalytic hydroprocessing of waste cooking oil. Fuel 2014;118:300–7.

[19] Kubička D, Horáček J. Deactivation of HDS catalysts in deoxygenation of vegetable oils. Appl Catal A 2011;394:9–17.