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Full Length Article

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

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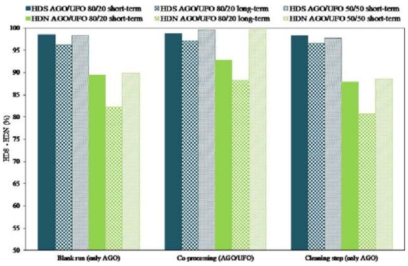
GRAPHICAL ABSTRACT



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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

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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 ($n\mathrm{C}_{16}$ and $n\mathrm{C}_{18}$) and water, or HDC, leading to paraffins with an odd number of carbons in the chain ($n\mathrm{C}_{15}$ and $n\mathrm{C}_{17}$) 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 ($n\mathrm{C}_{15}$ and $n\mathrm{C}_{17}$) 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 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.

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, mm^2/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

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

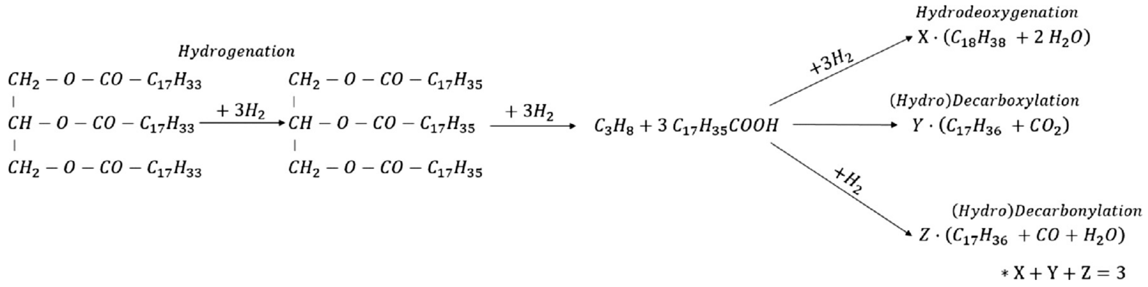

Fig. 1. Reaction pathways in the hydrotreating of a triglyceride (triolein) [2].