

Characterization of Hydroprocessed Used Cooking Oils in Blend with Low Quality Gasoil Samples

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ABSTRACT

The scope of this work is to examine the use of hydroprocessed used cooking oils as substitute for automotive diesel fuel. Hydroprocessing is an alternative method for the transformation of vegetable oils into high quality transport fuels, even if the quality of the oils is low, such as used cooking oils. In the present work, the utilization of hydroprocessed used cooking oil (HUCO) as neat fuel was proved to be very difficult, due to its very poor cold flow properties; therefore, mixtures of the HUCO with low quality middle distillates (a low cetane number gasoil and a light cycle oil) were prepared and evaluated. Throughout the process the formed blends were evaluated according to the european standard EN 590. The following points were mainly recorded: The lower density of HUCO was beneficial, permitting the use of poor quality distillates, in specific concentrations, and the high cetane number of HUCO was appreciable, improving the worse behavior of the other components. On the other hand, some downsides of HUCO have been enhanced by blending, with the low quality middle distillates. The cold flow properties of HUCO were inferior for direct use in diesel engines even in temperate climates. The blends with low cetane number gasoil (LCN) and light cycle oil (LCO) allowed the addition of HUCO in a specific content, leading to a "summer grade" fuel, appropriate for utilization in Greece and the warm Mediterranean region. The conformance with EN 590 requirements is easier for the low cetane number gasoil, compared to the very high density LCO. Therefore, the utilization of HUCO as a biocomponent should further be investigated, since it may be valuable as blending component for the upgrade of low quality middle distillates.

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INTRODUCTION

At present the world energy needs are mainly satisfied from petroleum; worldwide many countries are heavily dependent on petroleum for the production of electricity and transport fuels. Taking into consideration that the fossil resources are being restricted, along with the increase of their use, their elimination in the future is unavoidable. The increasing concern of greenhouse emissions has prompted the replacement of petroleum fuels with alternative fuels as produced by renewable sources. An alternative solution is the "traditional" biodiesel, coming mainly from domestic resources. It is defined as mono-alkyl esters of vegetable oils and animal fats and it is produced by transesterifying the oil or fat with an alcohol, having usually a low chain length, such as methanol under mild conditions in the presence of a catalyst, basic or acidic. Nowadays, the use is economically limited since a satisfactory quality of biodiesel mainly demands refined oils, facing complementary issues such as the conversion of forest lands and pastures to crop lands, exclusively for biodiesel production, raising the food prices and resulting in food scarcity in producing biodiesel areas. [1] These statements have prompted the investigation of renewable feedstocks utilization as an alternative solution, coming from sustainable

and economically feasible sources. The target of transesterification process is the commercial use of a product that by total complies with the specifications of the european standard EN 14214. The costless feedstocks suffer from inferior quality, being reflected in final product assessment, due to a higher viscosity value or a less triglycerides conversion compared to the set limits in european standard. Moreover, the low quality raw products such as frying oils for biodiesel production require pretreatment stage for reducing the acidity of used oils, increasing thus the process cost. [2,3,4,5,6,7]

Another alternative way to process vegetable oils, by removing oxygen compounds and hydrogenating the existing double bonds in triglycerides molecule is hydroprocessing. The initial stages included are hydrogenation and scissoring into intermediates such as diglycerides, monoglycerides and free fatty carboxylic acids. Afterwards, the intermediates are converted into alkanes through three different pathways as hydrodeoxygenation, decarboxylation and decarbonylation. The by-products of the process are propane, water, carbon monoxide, carbon dioxide. Additionally, the partial pressure of hydrogen should be rather high for achieving efficient conversion and for hindering the aromatic formation. However,

an excessive pressure of hydrogen may lead to methanized carbon oxides, increasing the number of by-products, consuming as a result more hydrogen than the required for complete conversion, and, decreasing simultaneously the partial pressure of hydrogen. The test parameters and the type of catalyst may seriously affect the required products, such as an increased temperature in a high rate and increased hydrogen pressure may lead to catalyst deactivation, producing more iso-alkanes than n-alkanes, accelerating on the other hand the conversion along with the minor remained triglycerides. Thus, the hydroprocessed vegetable oils have composition that simulates the diesel profile, including mainly n-C₁₇ and n-C₁₈, also the heteroatoms compounds of mainly O, and as well as, S, and N have been eliminated during hydroprocessing, surpassing the downsides of fatty acid methyl esters (FAME). The traditional biodiesel (FAME) consists of large hydrocarbon chains including oxygen surrogates (~10%), which oxygen compounds on the one side are advantageous since they attribute to diesel lubricity and ignition quality, but on the other side their presence results in a lower heating value, having at the same time the issue of poor cold flow properties. Also, the presence of intermediates (mono, di, tri- glycerides) as impurities in biodiesel composition may accelerate the sedimentation (separation) of biodiesel from regular diesel, especially in cold climates.

Hydroprocessing is promising because is a process that can be easily incorporated in refineries, in contrast to biodiesel where extra units are demanded for processing, and the final product while has many properties in the same range with conventional petroleum diesel, it remains a product of different nature as it contains esters and not hydrocarbons. [8, 9] Furthermore, the advantages should be highlighted; the benefit of high cetane number indicates an easy autoignition improving the pollutant emissions as regulated and unregulated THC, NO_x, PM, CO emissions, and also, taking advantage of its superior oxidation stability [2, 10, 11].

On the other hand there are some bottlenecks, related to the nature of product. It has reduced lubricity compared to diesel as a result of sulfur, nitrogen, and oxygen compounds elimination, and the paraffinic nature undoubtedly leads to a lower energy density of the hydroprocessed vegetable oils (HVOs), which have similar composition and properties with Hydroprocessed Used Cooking Oils (HUCO). A bottleneck of HVOs is without question the cold flow properties values if the product isn't isomerized, compared with the values of commercial diesel. Under these circumstances, the idea of using neat HVOs in refinery is limited; only blends of HVOs and commercial diesel could be carried out, either in a coprocessing mode or in blends of HVOs, thus being a special "cetane improver" for diesel.

According to the published works, the co-processing mode is recommended. Particularly, a mixture of vegetable oils up to 10% with petroleum-derived feedstock was intentionally examined. In such case, a 10% mixture of cottonseed oil in diesel under specific conditions enhanced the cetane number

of diesel, a raise of 3 units. [12] Additionally, the co-processing prompted the dilution of the free fatty acids in oil composition, hindering in turn polymerization and cracking reactions, providing a better triglycerides conversion to straight chain alkanes C₁₅ - C₁₈. [13] Furthermore, as the literature revealed the addition of sunflower oil even in a fraction of 5% (V/V) in heavy gasoil, conversely led to the maximum theoretical straight chain C₁₅ - C₁₈ yield of (87%), whereas the hydrotreating process of pure sunflower oil yielded a lower conversion of n-alkanes of 75%; the improvement of conversion was justified by the less concentration of free fatty acids in oil, rendering more n-alkanes. In addition to the mentioned advantages, hydroprocessing of blends didn't affect the rate of desulfurization, prompting sunflower oil added in low fraction (~15%) in heavy vacuum gasoil blends. [13]

The further investigation of HVOs use is mandatory, since the refinery should take advantage from their physicochemical properties. If the hydroprocessed product includes mainly n-alkanes the enhancement of HVOs cold flow properties could be achieved by a step of isomerization, adjusting the conditions of hydroprocessing, such as a higher temperature may be needed [14] or different catalysts with a more acidic nature [15, 16, 17], improving the cold flow properties.

In the present work a HUCO sample produced in Greece was used as base fuel for the preparation of blends with two different low quality gasoil samples. Particularly, one low cetane number gasoil (LCN) sample, and one light cycle oil (LCO) sample were used for the preparation of binary blends of each of these two fuels with the hydroprocessed used cooking oil (HUCO) sample. The blends were analyzed for the determination of their main the physicochemical properties. The goal of those blends was an attempt to use low grade fuels, even partially, facilitating the refinery processing, by taking advantage of the very good ignition quality of the HUCO, in order to facilitate the utilization of lower quality gasoil samples in the diesel fuel pool. Thus, mixing rules and derived relations were evaluated as a function of the volume fraction of HUCO in the blends. Specifically, the mixtures prepared by a step of 10% addition of HUCO and they covered all the range from neat (LCN) and LCO to pure HUCO. The evaluation of mixtures prepared, was with respect to European Standard EN 590: 2013.

EXPERIMENTAL - DISCUSSION

Test Methods

All base fuels and fuel blends that were prepared in this series of experiments were analyzed according to EN 590:2013 standard for automotive diesel in the European Union. [18] All experimental procedure was carried out by using the official test methods (mainly EN and ISO) that are described in the EN 590 standard.

It is mentioned that CEN has issued the technical specification TS 15940 for paraffinic diesel form synthesis or hydrotreatment, which is valid for the analysis of the HUCO sample. [19] This technical standard (which supersedes CWA 15940:2009) was not used in this series of experiments because the main idea was to use the HUCO as high cetane number blending component in order to produce fuel within the automotive diesel fuel range. Therefore, for comparison, the properties of the base fuels are compared with the specifications of EN 590 standard.

Characterization of Base Fuels

HUCO Characterization

The catalytic hydrotreatment of used cooking oil (UCO) technology was developed and demonstrated in the hydrotreating pilot plants of the Chemical Processes and Energy Resources Institute (CPERI) of the Centre for Research and Technology Hellas (CERTH), via the financial contribution of the BIOFUELS-2G LIFE+ project. [20] A total of 2 tons of the new fuel was produced from UCO collected from local restaurants.

A commercial NiMo/Al₂O₃ hydrotreating catalyst was employed for an efficient conversion of triglycerides of the used cooking oils. The selection of the catalyst and the operating conditions were based on research work of CERTH, dealing with the optimization of the UCO conversion. [21, 22, 23] The optimum operating parameters were: temperature 350 °C, pressure 1200 psig, LHSV 1 h⁻¹ and H₂/oil ratio equal to 4000 scfb. Under these conditions the diesel fuel yield was maximized. [22, 23] These conditions were optimum for conversion to fuel in the diesel fuel range, especially, as revealed a higher than the aforementioned temperature at 390°C led to undesirable cracking reactions, producing lighter products. Moreover, it was observed that the yield of aromatics enhanced with the increasing temperature, as a result of enhanced rate of cyclization reactions (from 0.1% m/m at 360°C to 5.2% m/m at 390°C). [14] The liquid hourly space velocity (LHSV) defines the conversion and the catalyst life. A higher tested LHSV than 1.5 h⁻¹ enhanced the conversion to diesel, but a long-lasting presence (Days on Stream: 37) may result in cracking and further catalyst poisoning, thus the optimum LHSV was designated at 1 h⁻¹ [23]. Concluding moderate temperature and LHSV are attractive for diesel production, since higher values of temperature, LHSV and not many days on stream, result in lighter products such as gasoline. [24] After the reaction and the flash for gas phase separation, the liquid organic product was fractionated in order to remove any lighter components that have boiling points below the diesel fuel range, and any heavier fractions from the fuel. [20, 24] The HUCO sample was the main product derived from this fractionation.

The composition of HUCO obtained from chromatography is shown in Table 1. [15] Table 1 also depicts the percentage of iso-alkanes and n-alkanes, dependent on reaction conditions used. Their ratio reveals which process precedes,

decarbonylation or decarboxylation towards hydrodeoxygenation. The composition of oil has carboxylic acids with an even number of carbon atoms, such as C₁₈, the presence of C₁₇ expresses the prevalence of decarbonylation and decarboxylation. For the HUCO used in the present work, the ratio of C₁₇/C₁₈ is accounted to 1.48 showing the dominance of decarbonylation and decarboxylation. The high concentration of normal paraffins in the HUCO explains the excellent cetane number of the fuel, and the very poor cold flow properties at the same time.

Table 1. Hydroprocessed used cooking oils composition [15]

Carbon Number	Normal Paraffins	Iso Paraffins
C ₁₅	7.8	0.0
C ₁₆	7.0	5.9
C ₁₇	41.8	5.0
C ₁₈	30.6	1.0

LCN and LCO Characterization

Apart from the HUCO, the other two base fuels used was one LCN gasoil sample and one LCO sample. These two base fuels used were supplied by Hellenic Petroleum SA, Aspropirgos Refinery. Hellenic Petroleum is the biggest petroleum refining industry in Greece, operating two high complexity refineries in South Greece (Aspropirgos and Elefsis), and one hydroskimming refinery with petrochemicals facilities in North Greece (Thessaloniki). The low cetane number gasoil (LCN) is a high aromatic content gasoil sample, produced from hydroprocessing of various low quality streams of the refinery. The light cycle oil sample (LCO) is the middle distillate cut produced in the fluid catalytic cracking (FCC) unit of the refinery. The physicochemical properties of the two fuels, along with the properties of the HUCO sample are depicted in Table 2. Moreover the test methods with which the properties of fuels reviewed are recorded separately.

As seen from Table 2, the properties of all the three base fuels were out of limits based on the established specifications in EN 590, for different properties in each case, but, for this reason the fuels could not be used in standalone mode. HUCO for example has excellent cetane number, but suffers from very poor cold flow properties. LCN has excellent cold flow properties, but critical properties like density, cetane index and cetane number fail to meet EN 590 specifications. LCO is, as expected, the fuel with the worst properties. The high aromatics (and especially polyaromatics) content result into very high density and very low cetane index and cetane number. Regarding the aromatics content shown in Table 2, they are measured by HPLC according EN 12916 test method. This technique separates the aromatic hydrocarbons of the test sample into mono- (one aromatic ring), di- (two aromatic rings) and tri+ (three or more aromatic rings). From these aromatic

hydrocarbon groups the sum of di- and tri+ is the polyaromatics which according to EN 590 must be below 8.0% (m/m) in order to be accepted as automotive diesel fuel.

Table 2. Base fuels properties

Property	Unit	HUCO	LCN	LCO	Limits		Test Method
					min	max	
Density at 15 °C	kg/m ³	790.8	862.2	911.0	820.0	845.0	EN ISO 12185
Viscosity at 40 °C	mm ² /s	3.78	2.82	3.53	2.00	4.50	EN ISO 3104
Sulfur Content	mg/kg	2.6	140	1250	—	10.0	EN ISO 20846
Aromatic Hydrocarbons	% m/m						EN 12916
Mono	% m/m	0.6	39.6	23.1			
Di	% m/m	—	6.2	25.5			
Tri+	% m/m	—	0.3	7.3			
Poly	% m/m	—	6.5	32.8	—	8.0	EN 12916
Distillation							EN ISO 3405
Recovered at 250 °C	% V/V	—	31.4	29.2	—	65	
Recovered at 350 °C	% V/V	96.3	98.1	80.2	85	—	
95% (V/V) Recovered at	°C	321.5	328.2	382.1	—	360	
Residue	% V/V	3.2	1.6	2.0			
IBP	°C	254.7	200.2	184.5			
10%	°C	291.5	228.1	228.9			
50%	°C	297.7	266.4	288.4			
90%	°C	311.1	310.7	370.2			
95%	°C	321.5	328.2	382.1			
FBP	°C	345.2	347.1	389.3			
Derived Cetane Number		102.7	37.5	27.7	51.0	—	EN 16144
Cetane Index		96.0	42.6	33.2	46.0	—	EN ISO 4264
Flash Point	°C	>100.0	84.0	73.0	55.0	—	EN ISO 2719
Copper Corrosion (3h at 50 °C)		1A	1A	1A	Class 1A		EN ISO 2160
Cloud Point	°C	24	-17	3	—		EN 23015
Pour Point	°C	19	-18	-2	—		ISO 3016
CFPP	°C	21	-16	4	—	+5 -5	EN116
Lubricity corrected wear scar diameter (wsd 1,4) at 60 °C	µm	518	370	315	—	460	EN ISO 12156-1

Another critical parameter is the sulfur content of the two gasoil samples employed in this study. Both fuels exceed the maximum allowable of 10 mg/kg according to EN 590. Hydrodesulfurization of LCO is one of the most difficult tasks in petroleum industry due to the high amount of substituted dibenzothiophenes in the LCO, but recent developments have achieved high desulfurization efficiencies. [25, 26] Apart their high sulfur content as blending components for automotive diesel, these two gasoil samples were evaluated as blending components since they are low quality samples in terms of ignition quality, and the addition of the very good ignition quality HUCO is expected to produce fuel with ignition quality in the diesel fuel range.

As seen from Table 2, both low quality gasoil samples have very good lubricity values, expressed as low wear scar diameters (370 µm for LCN and 315 µm for LCO), well below the EN 590 limit of 460 µm. HUCO on the other hand has poor lubricity with wear scar diameter measured at 518 µm. As referred in the literature, severe hydrotreated fuels with few or no polar groups have poor lubricity compared to fuels that have not been hydrotreated under severe conditions. [27, 28]

Characterization of HUCO / Gasoil Blends

As above mentioned, the properties of the base fuels are not satisfactory in order to can be used as diesel fuel according to EN 590. For this reason, the two refinery gasoil samples (LCN and LCO) were blended with HUCO, in a step of 10% addition of HUCO. The blends were tested according to the test methods described in EN 590, in an attempt to evaluate the ability to produce fuel complying with the european standard.

Distillation Characteristics

A significant property for the definition of a commercial fuel is the volatility interpreted well by the distillation curve. The distillation curve gives the amount of a fuel sample evaporated in atmospheric pressure at each temperature, while the temperature is being increased gradually. Distillation temperature includes the determination of the range of boiling points for the fuels and it is used to characterize the fuel in terms of the boiling temperatures of its component. Moreover, the distillation range of the fuel affects other fuel properties such as viscosity, density, flash point. So, the volatility demonstrates how heavy or light a product is; some fractions, boiling at low temperatures are needed for engine start-up, while fractions boiling at too high temperatures may not burn completely, forming engine deposits and increasing tailpipe emissions and simultaneously diluting the engine oil. Figure 1 depicts the distillation profiles of the three base fuels.