Biodiesel Produced by Two Step Hydroprocessing of Waste Cooking Oil

II. Hydrocracking of hydrotreated waste cooking oil and straight run gasoil mixture

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The aim of this study is to evaluate the potential production of biodiesel from waste cooking oil (WCO). The feedstock are hydrotreated mixtures of straight run gas oil (SRGO) with 5, 7,5, 10% WCO. The hydrotreated mixture was hydrocracked at 350°C and 370°C temperatures, 100 bar pressure, liquid hourly space velocity (LHSV) of 1h^{-1} *in the presence of industrial catalyst* $Co/Mo/Ni/gAl_2O_3$*. The research has focused on the influence of temperature and the WCO/SRGO ratio on the yields and the physicochemical properties of the biofuel obtained. The research findings highlighted a good characteristics of biofuel that fit with the requirements of EN 590.*

Keywords: waste cooking oil, biofuel, green diesel, hydrocracking, pour point

The usage of energy is a fundamental requirement for human existence for either industrial necessities, agricultural or transportation or even for social needs. Currently, fossil fuels cover the biggest part of the energetic necessity on a global scale, but in the future their usage will become unsustainable due to depletion of reserves and their negative consequences over the environment. Because of this, the interest for alternative sources of energy has increased, especially for biofuels obtained from biological renewable sources. The usage of biofuels as an alternative source of energy for the transportation industry is promoted through legislation and through supportive measurements; the production is sustainable and leads to economic growth.

The FAME (fatty acid methyl esters) type Biodiesel is a replacement for diesel fuel, which is obtained mostly through trans-esterification of triglyceride out of raw vegetable oil with methanol and it is the most used biofuel in Europe.

The biodiesel has a significant influence on the emission reduction generated by Diesel engines with 68% for unburned hydrocarbon, 40% for material particles, 44% for carbon monoxide, 100% for sulfur and 80-90% for polycyclic aromatic hydrocarbons [1, 2].

On the other hand, the production of biodiesel from natural sources used for human needs as obtaining food can generate a food crisis. Because of this, most of researchers have focus on using waste cooking oil (WCO) as a source for biodiesel [3, 4].

Recent studies regarding the biodiesel production have reported WCO as a viable alternative over edible vegetable oils because it is 2-3 times cheaper over the virgin vegetable oil and friendly with the environment. Therefore, the total costs of biofuels can be reduced significantly. Revaluation of WCO and animal fats as raw materials for biofuels can avoid the pollution problems or storage generated by used oils [5-7].

The resulted waste from fraying, together with cooking oil, are eliminated through the drainage system, causing the pollution of water which require treatment and energy consumption. Better way is to be transformed into biodiesel [8- 10], avoiding the necessity of wasting agricultural lands for crops and producing vegetable oils for biodiesel production. WCO has different properties over refined and raw oils [11].

The main problem in processing wasted oils unlike fresh vegetable oils, consists of the fact that they are collected randomly as different types of oils, everyone having a significant different quality. This characteristic is unfavorable for a satisfactory conversion to biodiesel [12].

Cooking oil is frequent subject to high temperatures and because of this process there an increase in Free Faty Acids (FFA) content, changing colour in dark, brown, increase of viscosity, specific heat and increase fats foaming tendency [13].

For economic reasons generated by the impossibility to value large quantities of glycerol obtained as a byproduct in the trans-esterification reaction, there have been new endeavors regarding new technologies in obtaining biofuels.

An alternative process to conversion of vegetable oils into biofuels is catalytic hydroprocessing. Catalytic hydroprocessing constitutes a modern technology to produce high quality biofuel named Green Diesel (GD). Hydrotreated vegetable oils are produced by Ecofining technology from Universal Oil Products (UOP) [14], and by Next Generation Bio to-Liquid from NesteOil Corporation [15]. The two technologies are an integrated two-stage hydrorefining process. The first step includes catalytic hydrodeoxygenation process producing a normal paraffin-rich product with poor flow properties that is then submitted to a second step of catalytic hydroisomerization resulting to a high quality renewable diesel fuel with sufficiently low cold flow properties.

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Several research activities have focused to conversion via catalytic hydroprocessing of virgin oil and WCO on the first hydrotreatment step and in second hydroizomerisation or hydrocraking step [16 - 21]

The hydrotreated WCO fuel resulting is a mixture of paraffinic hydrocarbons, free of sulfur and oxygen compatible with fossil gas oil fuels characteristics. The hydrotreatment has increased cold flow properties due to the paraffinic content of the product, which requires isomerization or hydrocraking step.

This research is focused on obtaining biofuels through a 2 step process consisting of hydrotreating and hydrocracking of a mixture of SRGO and WCO. The study regarding hydrotreating has been described in article [22]. The hydrotreated product presents good physical and chemical properties with the exception of the pour point and sulfur content. The hydrotreated mixture from the first stage are hydrocracked at temperatures of 350 and 370°C at 100 bar pressure. By hydrocracking is intended to obtain the conversion of normal paraffines obtained in the hydrotreated process, into isoparaffines with lower molecular weight which reduces the freezing point of biofuel. Also following the deep hydrogenation reactions, an important quantity of sulfur will be eliminated and the obtained biofuel will meet the requirements of EN590 standard "diesel fuel types".

Experimental part

The feedstock used in the middle hydrocraking (MHC) is hydrotreated mixtures of 5, 7,5 and 10% WCO and SRGO. Hydrotreating was performed at 360°C and 380°C, 60 bar pressure, LHSV of $1h^{-1}$, H_2 flow rate of 1L/min. in the presence of an industrial catalyst type $CoMo/Al_2O_3$ according to the method presented in [22].

From the products obtained by the hydrotreating mixtures with the same composition were formed three feedstocks with the characteristics as show in table 1, which have been subject to hydrocracking. Hydrocracking was conducted on a commercial catalyst Axens type Mo-Ni-Co, on activated alumina support used for middle pressure hydrocracking of heavy oil fractions. The catalyst was activated by sulfurization with di-methyl-di-sulfide (DMDS) according to the catalyst provider's recommended procedure. For hydrocracking was used a micropilot plant with 60 cm^3 fixed bed reactor as described in [22]. Experiments of hydrocracking were performed at of 350 and 370°C temperatures, 100 bar pressure and LHSV $1h^{-1}$, and H_2 flow rate of 0.5 L/min.

Results and discussions

The hydrocracking products are cooled and separated into two phases: gas and liquid. Liquid phase is separated by distillation PRF into a light distillate with 185°C final boiling point associated with a gasoline, a middle distillate with final boiling point lower than 360°C with diesel specific characteristics, associated with biofuel type Green Diesel and heavy product with the initial boiling point greater than 360°C.

The separate liquid products were weighed and the gases were determined by the difference between the amount of hydrocracked feedstock and liquid quantity obtained. Material balance for each experience is presented in table 2. Characteristics of green diesel were determined by standard methods as follows: density (EN ISO 12185), distillation curve (ASTM- D86), pour point (SR 13552), flash point (SR 5489), viscosity (SR EN ISO 3104), sulfur content (EN ISO 2084-2004) and cetane index ASTM-D4737. The green diesel characteristics obtained are presented in table 2.

In the hydrocracking process occurring cracking reactions of paraffins with 15-20 carbon atoms obtained from WCO hydrotreating and cracking, dealkylation, hydrodecyclization of paraffins, naphthenes and aromatics from gas oil. Also, on the presence of a metal function catalyst in hydrogen atmosphere at high pressure occur partial saturation reactions of aromatics from gas oil and hydrogenolysis reactions of heteroaromatic compounds with sulfur and oxygen mainly unchanged in the hydrotreating step.

Product yields (table 2) are influenced by the hydrocracking temperature and WCO content of the mixture. The yield in Green Diesel decreases with

Table 1
PROPERTIES OF WCO AND SRGO HYDROTREATED MIXTURES

WCO in mixture [% wt.]		5	7.5	10
Density at 15°C [g/cm³]		0.8420	0.8426	0.8430
Flash point [°C]		71.8	74.5	78
Viscosity at 40°C [mm²/s]		4,25	4,33	4,40
Pour point [°C]		-5	-5	-3
Lubricity [μm]		412	389	358
Cetane index		59.4	60.5	61
Sulfur content [ppm]		186	124	87
Distillation curve ASTM	ti [°C]	223	226	236
	10 % [°C]	254	257	260
	30 % [°C]	287	288	291
	50 % [°C]	304	308	308
	70 % [°C]	329	334	337
	90 % [°C]	366	370	374

Table 2
THE YIELDS FROM HYDROCRACKING OF WCO AND SRGO HYDROTREATED MIXTURES

Temperature, [°C]	350			370		
WCO in mixture [% wt]	5	7,5	10	5	7,5	10
Yields [% wt]						
Gases	8.12	9.04	11.06	11.23	13.42	15.62
Gasoline (<185°C)	10.14	11.85	15.48	15.52	16.76	20.46
Green diesel (185-360°C)	80.12	77.31	71.50	71.32	67.46	61.34
Residue (>360°C)	1.62	1.80	1.96	1.93	2.36	2.58

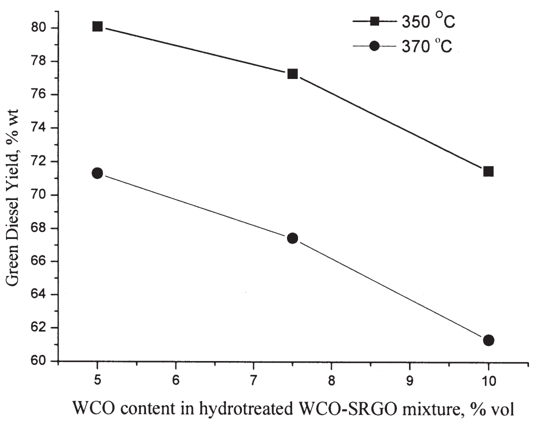

Fig.1 Influence of temperature and WCO content on green diesel yields obtained by hydrocracking of WCO and SRGO hydrotreated mixtures

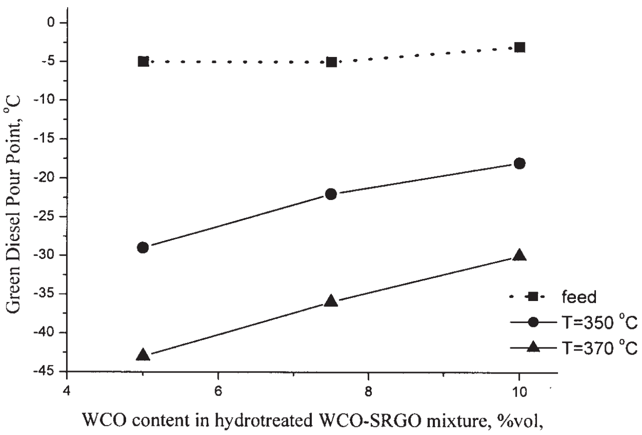

Fig.2 Influence of temperature and WCO content on the green diesel pour point obtained by hydrocracking of WCO and SRGO hydrotreated mixtures

Table 3
PROPERTIES OF GREEN DIESEL

Temperature [°C]		350			370		
WCO in mixture [% wt.]		5	7.5	10	5	7.5	10
Characteristics							
Density at 15°C [g/cm³]		0.8348	0.8384	0.8402	0.8204	0.8317	0.8343
Viscosity at 40°C [mm²/s]		4.01	4.10	4.24	3.97	4.08	4.16
Pour point [°C]		-29	-22	-18	-43	-38	-30
Lubricity [µm]		434	417	410	462	431	422
Cetane index		62.1	62.4	63.1	64.7	64.8	64.9
Sulfur content [ppm]		17	12	9	13	10	8
Distillation curve ASTM	ti [°C]	190	194	195	190	193	193
	10 % [°C]	243	250	259	242	247	250
	30 % [°C]	280	288	290	277	284	281
	50 % [°C]	312	310	313	305	306	306
	70 % [°C]	338	342	345	323	325	328
	90 % [°C]	356	357	357	353	355	356

increasing added ratio of WCO mixed with SRGO and with reaction temperature increase (fig. 1). At a higher content of WCO in the mixture under hydrocracking, the n-paraffinic structures increase, easily hydrocrack and turns into paraffin with a small number of carbon atoms that are found in lighter fractions of gas type, gasoline or light gas oil. The table 2 data confirm obtaining higher yields of gasoline and gas as the WCO added ratio increase. The temperature increase will lead to an intensification of CC bonds breaking reactions associated with decreasing in Green Diesel yield (fig.1) and increase in gasoline and gas yields (table 2).

Successive processing of WCO and SRGO mixtures by hydrotreating followed by hydrocracking aims to achieve a biofuel with physicochemical characteristics within the requirements of EN590 standard. The Green Diesel properties obtained by hydrocracking mixtures of WCO and hydrotreated SRGO are shown in table 3.

Density of the Green diesel obtained by hydrocracking decreases compared with WCO and hydrotreated SRGO mixture density, used as feedstock due to the cracking reactions which generate structures with fewer carbon atoms and partial saturation of aromatic hydrocarbons with a high density from SRGO. With increasing of WCO/SRGO ratio, the density of biodiesel obtained, slowly increase, as WCO contains paraffinic hydrocarbons with large numbers of carbon atoms (C15-C20) compared with SRGO which have also lighter compounds with lower carbon atoms (C11-C14). By enhancing the cracking reaction velocity and aromatics saturation, at the temperature increase a density decrease of the Green-diesel occurs (table 3). For all experimental conditions, hydrocracked product density, assimilated as diesel, meets the quality requirements of EN 590 standard.

After hydrocracking of WCO and SRGO hydrotreated mixtures the viscosity of obtained green diesel decrease slightly by about 0.16 to 0.28 mm²/s for all experimental conditions due to modifications in its composition cause of cracking and hydrogenation reactions. Increasing in temperature which intensifying the cracking reactions, do not conduct to a significant decrease in viscosity because the hydrocracked product was stabilized by eliminating light components with low viscosity. In terms of viscosity the EN 590 quality standard is meet.

Inadequate flow properties of the biofuel obtained by hydrotreating of WCO- SRGO mixtures in first stage were successfully corrected for the green diesel obtained with the second stage of hydrocracking. Pour point was reduced from (-3 to -5)°C after hydrotreating to (-18 to -43)°C after successive hydrotreating-hydrocracking process.

After hydrocracking reactions in the presence of an acid acting catalyst, cracking and isomerization reactions of paraffins from the hydrofined mixture of WCO and SRGO occur, which lead to the formation of isoparaffinic hydrocarbons with small number of carbon atoms and high branching that have very low pour point.

As result of these reactions intensification,with temperature increase, pour point of the Green diesel decreased significantly (fig. 2). Due to the high content of

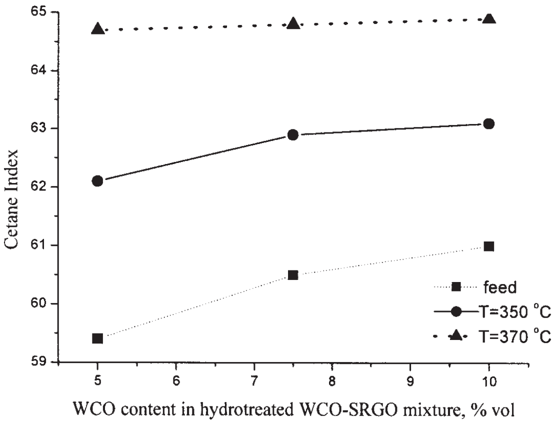

Fig.3 Influence of temperature and WCO content on the cetan index of green diesel obtained by hydrocracking of WCO and SRGO hydrotreated mixtures

paraffins with 16-20 carbon atoms in the WCO molecule, biodiesel pour point obtained by hydrocracking slightly increase with WCO added ratio (fig 2). Analysis of the data presented in figures 1 and 2, show that a very good flow properties of the green diesel are obtained in the reaction conditions when the lowest yields are obtained.

After sequential processing hydrotreating-hydrocracking the cetane index of obtained green diesel substantially exceeds the lower limit (CI > 46) required by EN 590 standad (fig. 3).

By the cracking, isomerization and saturation reactions, occurring in the hydrocracking process, the chemical composition of green diesel changes significantly by increasing of the isoparaffins content obtained from the triglycerides conversion of WCO and naphthenes resulting from aromatics hydrogenation of SRGO. Cetane index increases with the WCO adding ratio to the hydrocracking of mixture, due to increased content of paraffins (fig. 3). Also slightly increase with rising of the hydrocracking temperature cause of the reactions intensification which generate components with high cetan index (paraffins and naphthenes).

Lubricity as measured by the size of wear scar diameter (WSD) determined by the HFRR method is an important characteristic for diesel fuel. Sulfur compounds from SRGO and ester groups from vegetable oil have good lubrication properties. Because by successive hydrotreating-hydrocracking process these compounds are eliminated almost entirely, the green diesel obtained has lower lubrication properties, the WSD is close to the standard imposed limit of 460 μm.

Structural changes due hydrocracking reactions and especially advanced removal of sulfur compounds from (87-186 ppm) to (8-18ppm) justify the influence of the adding ratio and temperature on lubricity of obtained Green diesel (table 3). After hydrotreating–hydrocracking sulfur content decreases significantly compared to fossil diesel (7215 ppm) [22], the obtained green diesel fits in the maximum 10 ppm limit imposed by EN590 standard with one exception (table 3). The decrease is justified on the one hand by the cumulative effect in desulfurization due to the two – stages hydroprocessing and on the other hand as the trimetallic Co-Mo-Ni great catalyst activity used in hydrocracking. Also, a significant contribution to the deep desulfurization has the high pressure of hydrocracking (100 bar).

Conclusions

Sequential co-processing by HDT - HC of SRGO and WCO mixtures is a promising method for biofuels fabrication. The researches presented in this paper highlights influence of the main parameters to the yield and quality of green diesel.

The green diesel obtained after hydrocracking has moderate yields (60-80% wt) and properties that meet or even exceed the requirements of EN 590.

Lower yields are compensated on the one hand by the high quality of the green diesel and on the other hand by recovered gasoline obtained as feedstock in catalytic reforming or pyrolysis.

As a result of cracking and isomerization reactions isoparaffins with 14 to 20 carbon atoms are obtained which significantly reduce the biofuel pour point. Decreasing pour point is associated with significant decreases of green diesel yield.

At the 100 bar pressure and in the presence of a Co-Mo-Ni catalyst with high desulfurization activity a significant removal of sulfur at low levels of 8-18 ppm occurs.

Based on a sustainable valorization of a waste vegetable oil the two step hydrotreated-hydrocracking processing is one of the most attractive option to produce a high quality green diesel.

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