Biodiesel by Hydroprocessing of Gas Oil-vegetable Oil Mixtures

RALUCA ELENA DRAGOMIR, PAUL ROSCA*
Petroleum-Gas University of Ploiesti, Faculty of Petroleum Refinning and Petrochemistry, 39 Bucuresti Blvd., 100680 Ploiesti, Romania

This paper presents the results of hydrotreating straight run gas oil mixed with soybean oil in a proportion of 10%, 15%, 20%. Hydrotreating was performed at temperatures of 360°C and 380°C, 50 bar pressure, hydrogen/feedstock ratio of 800cm³/cm³, space velocity 1,5cm³/cm³h. The present research has focused on the influence of temperature and of the vegetable oil/gas oil ratio on the yields and the physicochemical properties of the hydrotreating products. By hydrotreating of straight run gas oil with soybean oil mixtures, result an improvement of flashpoint, sulfur content and density. The secondary hydrocracking reactions which occur during the process, determine the pour point and the flashpoint decreases. These characteristics can be corrected by stabilizing the hydrotreated product.

Keywords: gas oil, soybean oil, pour point, flash point, hydrotreating

Continuous reduction of oil reserves, associated with increased energy consumption and emissions of greenhouse gases (GHGs), require finding alternatives to oil fuels, that will simultaneously meet consumption increase and the requirement to limit environmental pollution [1-3].

The EU has adopted a series of measures, that have determined a reference value of 2% in terms of biofuels share in gasoline and diesel consumption for 2005; 5.75% in 2010 [4] and an increase up to 10% for the year 2020, provided that their production should be carried out in sustainable ways that will not affect the food needs of the population [5].

Although they are expensive, biofuels are currently the only form of renewable energy, which can meet the energetic demands of the transport industry, the necessary reduction of GHGs emissions imposed by the Kyoto Protocol [6] and the socio-economic development of the rural sector [7].

Due to high viscosity, low oxidation stability, low volatility and emissions of material particles, vegetable oils cannot be used directly as fuel [8, 9].

Transesterification is the most widely used method for the producing of biodiesel.

In reality the generic name "biodiesel" - fatty acid methyl ester (FAME)- is given to the esters obtained through the transesterification of vegetable oil triglycerides with lower alcohols using acid or alkaline type catalysts [10, 11].

The hydrotreating and the catalytic cracking of vegetable oils as such but mostly with petroleum fractions of straight run gas oil or vacuum distillate, have been the subject of many research and have been translated into industrial processes which are currently applied.

Hydroprocessing includes saturation reactions of double bonds, decarboxylation, decarbonylation, deoxigenation, cracking and izomerization reactions of carbon chains of the vegetable oil fatty acids.

Reactions occur at temperatures of 350-450°C, partial pressures of H_2 10-20 bar in the presence of typical hydrogenation catalysts Ni/Mo or Co/Mo type on neutral or acid support [12 -17]. Some research on vegetable oil hydrocracking signal the presence of cycloalkanes and aromatics as secondary products [18].

Hydrotreated vegetable oils have a high content of C_{15}-C_{18} izoparaffines, are part of the second generation of biofuels and are known as "green diesel". In terms of physiochemical properties these vegetable oils are comparable with standard diesel and are superior to those of FAME type biofuels.

For hydroprocessing of vegetable oils several commercial processes have been developed and proposed by Neste Oil Corporation companies [19] or UOP [20].

This paper presents the hydrotreating results of a mixture between straight run gas oil with 10, 15 and 20% soybean oil, and has focused on the influence of the vegetable component, adding ratio and temperature reaction on the yields and the quality of the hydrotreated product.

Experimental part

Feedstock and catalysts

The feedstock are the mixtures of straight run gas oil with 10%, 15% and 20% soybean oil. Physicochemical properties of gas oil and soybean oil are presented in tables 1 and 2.

An industrial-type catalyst $NiMo/Al_2O_3$ was used for hydrotreating. The catalyst was activated by sulphurization

Table 1
PROPERTIES OF STRAIGHT RUN GAS OIL AND SOYBEAN OIL

Characteristics	Density at 20 °C	Sulphur Content	Viscosity at 40°C	Pour point	Flash point	Diesel Index	Acidity Index	Unsaturated fatty acids	Saturated fatty acids
UM	[g/cm³]	[ppm]	[mm²/s]	[°C]	[°C]		[mg KOH/g]	[%]	[%]
Gas oil	0.8452	2290	4.18	-13	56	48.70	-	-	-
Soybean oil	0.9196	-	30.70	-14.2	66	-	204	84	16

* *email: prosca@upg-ploiesti.ro; Tel.: 0723699482*

Table 2
ASTM DISTILLATION CURVE FOR STRAIGHT RUN GAS OIL

% vaporized	t_i	10	20	30	40	50	60	70	80	90	99
Temperature [°C]	180	230	250	265	280	290	300	310	318	325	342

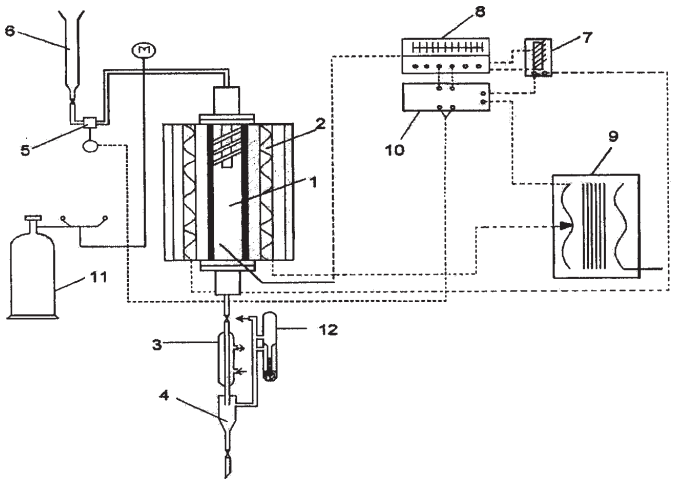

Fig.1 The Hydrotreating Micro-pilot Plant (1-reactor, 2-electrical heater, 3-water cooler, 4- liquid-gas separator, 5-metering pump, 6- feedstock burette 7-relay, 8-temperature register, 9-autrotransformer, 10-temperature controller, 11-hydrogen tank, 12- flow meter)

Temperature [°C]	360			380		
Vegetable oil (in mixture) [% wt]	10	15	20	10	15	20
	Yield, [% wt]					
Hydrotreated Product	95,32	94.64	94.01	93.65	93.12	92.86
Gas	3.16	3.31	3.16	4.75	4.81	4.39
Water	1.52	2.05	2.73	1.60	2.07	2.75

Table 3
YIELDS OBTAINED FROM HYDROTREATING GAS OIL & VEGETABLE OIL MIXTURES

The yields in products on each experiment have been calculated by material balance taking into account the feedstock quantity, weighting the hydrotreated organic product and the separated water. The gases have been determined by difference.

with thiophene dissolved in gas oil at a concentration of 1000ppm in hydrogen atmosphere, at a temperature of 280°C and at a space velocity of $2h^{-1}$. The activation is considered completed after H_2S formation in the reaction gases indicated by the yellow color of cadmium acetate used as indicator.

Micro-pilot plant

Hydrotreating experiments were carried out in a continuous regime into a micropilot plant (fig.1) with fixed bed catalytic reactor (1) mounted in an electrical heater (2). The total volume of the reactor is ($80cm^3$) of which $40cm^3$ is the volume occupied by the catalyst, which is distributed between two layers of an inert ceramic material.

The experiments have been carried out at two temperatures 360, 380 and at a 50bar pressure. The temperature in the reactor is controlled and recorded by an automatic temperature control system (10). The operating pressure of the reactor is set by means of the gas exit valve of the separator.

Micro-pilot plant feeding is done with a metering pump (5) from the burette (6) with a flow rate of 1 cm^3/min which corresponds to a space velocity of $1.5cm^3/h$. Hydrogen is introduced together with the feedstock at a flow-rate of 0.8l/min corresponding to a H_2/feedstock ratio of $800cm^3/cm^3$). Hydrogen flow-rate is controlled with a flow meter (12).

Each experiment lasted 1 hour. The reaction mixture is cooled in a water cooler (3) and it is then passed into the phase separator (4) which separates the un-reacted hydrogen, small amounts of light hydrocarbons (which are discharged into the atmosphere) and two liquid phases. The two liquid phases are formed from a mixture of hydrotreated gas oil-soybean oil and small quantities of water resulting from the deoxygenation reactions of the fatty acids from vegetable oil. After separation, the hydrotreated product is mixed with $CaCl_2$ to remove traces of water which remained as emulsion.

After each experiment the hydrotreated product has been characterised by standardised methods which have determined the main characteristics as: density (EN ISO 12185); flashpoint (SR 5489); pour point (SR 13552); viscosity (SR EN ISO 3104). Sulphur was determined by X-ray spectrometry on a PW4025MiniPal using the method EN ISO 2084-2004

Results and discussions

The hydrotreating experiments aimed to establish the influence of the reaction temperature and vegetable oil / gas oil ratio on the yields and on the main quality of the hydrotreated product.

Results are summarized in tables 3 and 4.

The yields in products on each experiment have been calculated by material balance taking into account the feedstock quantity, weighting the hydrotreated organic product and the separated water. The gases have been determined by difference.

By hydrotreating of straight run gas oil and vegetable oil mixtures are obtained more than 92% yields in hydrotreated

Temperature [°C]		360			380		
Vegetable oil in mixture, [% wt]		10	15	20	10	15	20
Characteristics							
Density at 15°C [g/cm3]		0.8322	0.8338	0.8421	0.8316	0.8331	0.8430
Viscosity at 40°C [mm2/s]		3.58	3.83	4.18	3.47	3.78	4.02
Flash Point [°C]		48	50	51	47	48	48
Pour Point [°C]		-9	-6	-4	-16	-12	-8
Sulphure Content [ppm]		45	34	26	15	12	11
Distillation Curve ASTM	t_i [°C]	172	178	182	156	158	158
	10 % [°C]	212	218	220	213	215	215
	30 % [°C]	264	268	275	265	270	272
	50 % [°C]	274	280	282	278	283	284
	70 % [°C]	304	4310	311	304	312	312
	90 % [°C]	332	340	343	335	341	243
	t_f % [°C]	352	358	360	351	356	357
	250°C [% vol.]	26	23	20	23	21	20
	350°C [% vol.]	99	98.5	98	99	98	98.5

Table 4
CHARACTERISTICS OF THE HYDROTREATED PRODUCT

product. Yields are higher than those obtained in the industrial plants because the hydrotreated reaction product obtained directly from the separator vessel is unstabilized and it contains small amounts of gasoline which result from secondary hydrocracking reactions.

Also, due to intensification of secondary hydrocracking reactions, the yields in the hydrotreated product decrease with increase of the reaction temperature. By hydrotreating the vegetable oil there are obtained small amounts of water resulted from the deoxygenation of the fatty acids. With the increase of vegetable oil / gas oil ratio the water yield increases. By increasing the temperature of hydrogenation the water yield does not change significantly, which demonstrates that all the oxygen present in the structure of the vegetable oil is removed as water constituent.

Physicochemical characteristics of the hydrotreated product presented in table 4, are influenced both by the reaction temperatures as well as by the gas oil/soybean oil mixture ratio.

The density of the hydrotreated product, compared to the feedstock, decreases as a result of the hydrogenation reaction due to the changes that are taking place in the chemical composition of the vegetable oil and of the gas oil. So, from the vegetable component, are removed the oxygen structures which are responsible for high density of soybean oil (0.9196g/cm^3) and from the gas oil the high-density aromatic hydrocarbons are partly hydrogenated into saturated hydrocarbons with lower density.

In addition, by hydrotreating there also occur secondary hydrocracking reactions which generate molecules with a low number of carbon atoms specific to kerosen which have lower densities than the diesel). These reactions, which are intensified by temperature, justify lowering the density of the hydrotreated product with temperature increasing from 360 to 380°C (fig. 2). The hydrotreated product fits in terms of density with requirements of the quality standards for Diesel fuel EN 590 (820-845kg/m^3 density).

The viscosity of the hydrotreated product increases with the added ratio of the vegetable oil (fig. 3), as a result of its much higher viscosity (30, 70mm^2/s) as compared to the diesel (4.18mm^2/s).

Hydroprocessing at higher temperature decreases the viscosity of the hydrotreated product due the hydrocracking reactions which transform the triglycerides into smaller molecules and the remove of carboxylic groups. As with the density, viscosities of all hydrotrated products were conformed to the EN 590 standard requirements, between 2-4,5mm^2/s.

The flash point of the hydrofined products increase creases as a result of hydrocarbons with a smaller number of carbon atoms produced by the secondary hydrocracking reactions. Also, the flash point decrease depends on the temperature of the separator vessel which determinate the stabilization conditions of the hydrofined product.

Product distillation curves confirm by the initial boiling points, lower than 180°C, the presence of light fractions with low flashing point in hydrofined product.

Increasing the vegetable oil added ratio determines a slight increase in the flash point of the hydrotrated mixture, and increasing the hydrotreating temperature generate a decrease of flash point due the enhanced of hydrocracking secondary reactions (table 4).

Pour point of hydrotreated mixtures increases as compared with pour point of gas oil and vegetable oil (table 4). The increase is explained by the structural modifications produced by the hydrogenation of ester and double bonds from the fatty acids present in the vegetable oil. For diesel fuel the hydrocracking secondary reactions generate isoparaffins of lower pour points temperatures that improve the flowing conditions. Pour point increase is the exclusive contribution of the vegetable oil hydrotreating and it is confirmed by the experimental data presented in table 4, which shows its growth with the added ratio of vegetable oil.

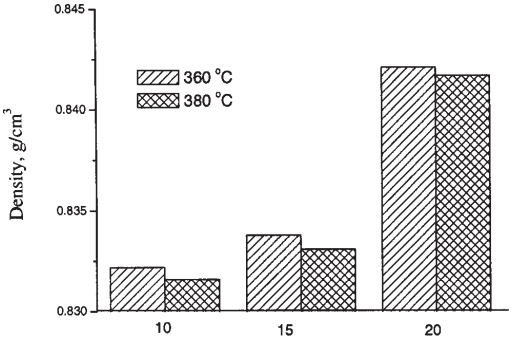

Fig.2. Influence of reaction temperature and soybean oil/gas oil ratio on density of hydrotreated product

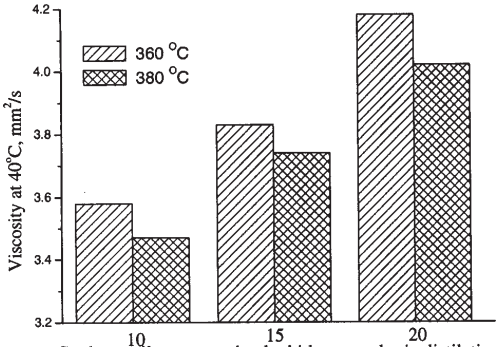

Fig. 3. Influence of reaction temperature and soybean oil/gas oil ratio on viscosity of hydrotreated product

At higher hydrotreating temperatures, due to hydrocracking reactions which generate hydrocarbons with smaller numbers of carbon and branched structure, pour point drops to -8 to -16°C.

The sulphur content in the hydrotreated mixture decreases with the increase of vegetable oil added ratio which does not contain sulphur as compared with gas oil (2290ppm sulphur). With the increase the hydrotreated temperature the sulphur content decreases as a result of hydrogenolysis reaction intensification of the sulfphur compounds from diesel fuel. Hydrotreated product does not fit into the imposed sulfur content condition required by the quality standard EN 590 for the diesel fuel (sulphur < 10 ppm). In order to fit in the standard requirements it is necessary to either increase the severity of the hydrotreating process (higher operating pressure, lower space velocity or a more advanced high-tech catalyst or use the hydrotreated product mixed with hydrofined diesel fuel with a sulphur content below 10ppm.

Conclusions

Hydroprocessing of the straight run gas oil and vegetable oil mixtures is an accessible process from the technological point of view and proves its efficiency in the production of the second generation biofuels.

By hydrotreating process of the mixtures of 10, 15 and 20% soybean oil with gas oil, at 50bar pressure and 360-380°C temperature, results hydrofined products with 92% or higher weight yields and physicochemical characteristics that fit to the quality standard for Diesel fuel EN 590.

Hydrogenation of the double bonds and of the carboxylic groups from fatty acids and sulfur compounds hydrogenolysis from gas oil conduct to pour point increase, density and sulfur content decrease in the hydrotreated product.

Hydrocracking reactions and hydroisomerization that accompany the saturation reactions produce lighter hydrocarbons with a branched structure that determine a decrease of the flash point and of the pour point. These two characteristics can be corrected through a stabilization process of the hydrotreated product which removes the light fractions resulted from hydrocracking.

Hydrotreating followed by hydroisomerization process can be a solution to improve certain characteristics of the biofuels obtained from the hydroprocessing of the gas oil and vegetable oils mixtures.

References

1. ESCOBAR, J.C., LORA, E.S., VENTURINI, O.J., YANEZ, E.E., CASTILLO, E.F., ALMAZAN, O., Biofuels: environment, technology and food security, Renew Sustain Energy Rev. 13, 2009, p.1275-1287
2. AGRAWAL, AK., Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Prog Energy Combustion Sci, 33, 2007, p.233-271;
3. NAIK, S.N., GOUD, V.V., ROUT, P.K., DALAI, A.K.. Production of first and second generation biofuels: a comprehensive review, Renew Sustain Energy Rev., 14, 2010;
4. *** Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 On the promotion of the use of biofuels or other renewable fuels for transport, Official Journal of the European Union L 123/42;
5. *** Presidency Conclusions. Council of the European Union. Brussels European Council; March 8/9, 2007;
6. *** Kyoto Protocol to the United Nations Framework Convention on Climate Change, 1998;
7. REIJNDERS, L., Conditions for the sustainability of biomass based fuel use. Energy Policy 34, 2006, p.863–876;
8. DEMIRBAS, A., Progress and recent trends in biodiesel fuels. Energy Conserv Manage, 50, 2009, p.14-34;
9. POONAM, N. S., ANOOP, S., Production of liquid biofuels from renewable resources, Prog. Energy Combustion Sci., 37, 2011, p.52-68;
10. BALA, B.K., Studies on biodiesels from transformation of vegetable oils for diesel engines. Energy Educ. Sci. Technol. 15, 2005, p.1–45;
11. DEMIRBAS, A., Biofuels sources, biofuel policy, biofuel economy and global biofuel projections, Energy Conserv. Manage. 49, 2008, p.2106–2116;
12. STUMBORG, M., WONG, A., HOGAN, E., Hydroprocessed vegetable oils for diesel fuel improvements. Bioresource Technology, 56, 1996, p.13;
13. WALENDZIEWSKI, J., STOLARSKI, M., ŁU NY, R., KLIMEK, B., Hydroprocesssing of light gas oil rape oil mixtures, Fuel Processing Technology, 90, 2009, p.686–691;
14. SCHERZER, J., GRUIA, A.J., Hydrocracking Science and Technology. Marcel Dekker Inc., New York. 1996
15. GUSMAO, J., BRODZKI, D., DJEGA-MARIADASSOU, G., FRETY, R., Utilization of vegetable oils as an alternative source for diesel-type fuel: hydrocracking on reduced Ni/SiO_2 and sulphided Ni-Mo/c-Al_2O_3. Catalysis Today, 5,1989, p.544–553;
16. KUBIC˙KOVA, I., SNARE, M., ERANEN, K., MAKI-ARVELA, P., MURZIN, D.Y., Hydrocarbons for diesel fuel via decarboxylation of vegetable oils. Catalysis Today 106, 2005, p.197–200;
17. BEZERGIANNI, S., KALOGIANNI, A., VASALOS, A.I., Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production, Bioresource Technology, 100, 2009, p.3036–3042;
18. da ROCH FILHO, G.N., BRODZKI, D., DJEGA-MARIADASSOU, G., Formation of alkanes, alkylcycloalkanes and alkylbenzenes during the catalytic hydrocracking of vegetable oils, Fuel 72 (4), 1993, p.543–549;
19. *** http://www.nesteoil.com/NExBTL renewable diesel
20. *** http://www.uop.com/hydroprocessing-ecofining/

Manuscript received: 12.11.2013