

Renewable Diesel Production by Co-processing of Rapeseed Oil Mixed with Straight Run Gas Oil

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The research study presents the sequential co-processing of rapeseed oil and straight run gas oil mixtures by hydrotreating (HDT) and hydroisomerization (HYD) as source of hydrocarbon-based biodiesel. The feedstocks are the mixtures of straight run gas oil with 5%, 10% and 15% rapeseed oil. The hydrotreating experiments were performed in a micropilot laboratory flow reactor over a commercial NiMo/-Al₂O₃ catalyst at 350°C, 50 bar pressure, space velocity (LHSV) of 1h⁻¹ and H₂/feedstock ratio of 1000 cm³/cm³. The hydrotreated products was subject to the HYD process in the same micropilot plant, over Pt- ZrO₂ sulphated/Al₂O₃ catalyst at 250, 280°C, 30 bar pressure, LHSV of 1h⁻¹ and H₂/feedstock ratio of 800 cm³/cm³. The co-processing by HDT and HYD of straight run gas oil and rapeseed oil mixtures produce biodiesel with physico-chemical properties which respect EN 590 quality standard.

Keywords: hydroisomerization, hydrotreating, rapeseed oil, pour point, viscosity

About 50% of global oil production is converted into transportation fuels component of the fastest growing energy sector. The growing demand for energy in conjunction with decreasing of oil reserves and environmental pollution is a challenge at scientific and industrial level for the use of renewable energy resources. Between these resources, biofuels are the most appropriate alternative in replacing traditional fuels. Literature classifies 4 generations of biofuels by the manufacturing technologies, marketing and obvious sources of feedstock [1,2].

The most important biofuels, ethanol and biodiesel, ranked in the first generation are produced from conventional crops of cereals, oilseeds, sugarcane which is used primarily for human food.

EU Directive set benchmarks for biofuels content in fuels, proposing a value up to 10% for 2020 [3], provided rational use of agricultural land, to increase its productivity by an efficient crop fertilization and production, based on quality genetic material. The first generation biodiesel associated with the generic name FAME (fatty acid methyl esters) is obtained by transesterification of triglycerides from vegetable oils, animal fats or used cooking oils [4,5]. Second generation biofuels are obtained from ligno-cellulosic biomass, plants or waste by enzymatic conversion processes in ethanol or thermo-chemical processes that convert biomass directly into hydrocarbons, similar to those present in the classical fuels [6-8]. Thermochemical conversion of biomass is done at much higher temperatures and pressures than the specific bioconversion by liquefaction processes [9,10], pyrolysis [11,12] and gasification followed by refining processes of liquid fraction or Fischer Tropsch synthesis for the gas fraction rich in CO and H₂ [13]. Third generation biofuels are obtained from algae, and the fourth generation is obtained by GTL technologies, from synthesis gas obtained by biomass gasification or pyrolysis. Although are attractive in terms of feedstock, by winning the competition with agricultural land used for food production, this generation of biofuels must overcome many obstacles from

investment, manufacturing costs, increasing the efficiency of transformation, new conversion processes up to use on an industrial scale. This is the main reason why biodiesel production currently is based on feedstocks materials such as vegetable oils.

FAME-type biodiesel has a low heating value due to the high oxygen content (11%), low stability to oxidation caused by the presence of double bonds in esters structure and lead to large amounts of glycerol by the transesterification reaction. These disadvantages for which were not found economic valuable solutions, require finding the new technologies to convert vegetable oils into biofuels. Vegetable oils can not be used directly as fuel due to high viscosity, low oxidation stability, volatility and material particles emissions [14,15].

Many research studies highlight hydrotreating, hydrocracking and catalytic cracking as efficient processes to direct conversion of vegetable oils, into high quality biodiesel, compatible with diesel fuel. The triglycerides and fatty acids from vegetable oils are converted by hydrodeoxygenation, decarboxylation, saturation, hydrocracking, and hydroisomerisation reactions [16, 17] in a biofuel known as "green diesel". "Green diesel" has similar properties to conventional diesel fuel and superior to FAME type biodiesel [8].

Hydrotreating of vegetable oils are industrially made by Neste and Ecofining processes proposed by Neste Oil Corporation [18] and UOP companies [19]. Also, vegetable oils can be co-processed with petroleum fractions by refining process such as hydrotreating, hydrocracking or catalytic cracking [5, 20].

The research study shows the influence of sequential co-processing of rapeseed oil and straight run gas oil mixture by HDT and HYD on the main fuel properties obtained. There are analyzed the influence of added ratio of vegetable oil mixed with petroleum diesel, co-processing sequence and reaction conditions for HYD and HDT processes on the principal properties with particular reference to pour point and sulphur content.

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Characteristics	Density at 20°C	Sulphur Content	Viscosity at 40°C	Pour point	Flash point	Diesel Index	Acidity Index	Saturated fatty acids	Unsaturated fatty acids
UM	[g/cm ³]	[ppm]	[mm ² /s]	[°C]	[°C]		[mg KOH/g]	[%]	[%]
Gas oil	0.8464	2316	4.2	-16	58	49.20	-	-	-
Rapeseed oil	0.912	-	36	-14.8	220	40	161	16	93

Table 1
CHARACTERISTICS OF STRAIGHT RUN GAS OIL AND RAPESEED 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

Table 2
ASTM DISTILLATION CURVE FOR STRAIGHT RUN GAS OIL

Experimental part

Feedstock and catalysts

The feedstocks are the mixtures of straight run gas oil with 5%, 10% and 15% rapeseed oil. Rapeseed oil used is a commercial product manufactured in Italy. Fatty acids C18 series (stearic acid, oleic acid, linoleic acid, linolenic acid) are about 92.3% weight and palmitic acid C16 series is about 4.5 % weight.

The physico-chemical characteristics of straight run gas oil and rapeseed oil are presented in tables 1 and 2.

An industrial-type catalyst NiMo/Al₂O₃ was used for HDT. The catalyst was activated by sulphurization with thiophene dissolved in gas oil at a concentration of 1000 ppm in hydrogen atmosphere, at 280°C and at a space velocity of 2h⁻¹. The activation is considered completed after H₂S formation in the reaction gases indicated by the yellow colour of cadmium acetate used as indicator.

Micro-pilot plant

HDT experiments were carried out in a continuous regime into a micropilot plant (fig.1) with fixed bed catalytic reactor. The total volume of the reactor is 80cm³, from which 30 cm³ is volume filled by the catalyst, which is distributed between two layers of an inert ceramic material.

The experiments have been carried out at 350°C and 50bar pressure. Mixture of straight run gas oil with vegetable oil was fed with LHSV of 1h⁻¹. Hydrogen is introduced together with the feedstock at a H₂/feedstock ratio of 1000 cm³/cm³. The water resulting from deoxygenation reaction of fatty acid from vegetable oil is separated from liquid phase, then hydrofined product was subject to the HYD process. The HYD was carried out in the same micropilot plant as HDT with the same volume of catalyst. The isomerization catalyst was Pt- ZrO₂

sulphated /Al₂O₃. The HYD experiments have been carried out at two temperatures 250, 280°C and at a 30 bar pressure, LHSV of 1h⁻¹, H₂/feedstock ratio of 800 cm³/cm³. After HYD reaction product was cooled and the liquid phase that contain hydroisomerization product used as biodiesel has been recovered.

Products resulted from HDT and HYD were characterized by standardised methods to establish 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 HDT and HYD results of experiments of straight run gas oil and rapeseed oil mixture are summarized in tables 3-6.

The products yields on each experiment have been calculated by material balance taking into account the feedstock quantity and weighting the hydrotreated and

Table 3
THE YIELDS FROM HDT STRAIGHT RUN GAS OIL AND RAPESEED OIL MIXTURES

Temperature, [°C]	360		
Vegetable oil in mixture, [% wt]	5	10	15
Yields, [% wt]			
Hydrotreated product	95.65	94.57	93.98
Gas +water	4.35	5.43	6.02

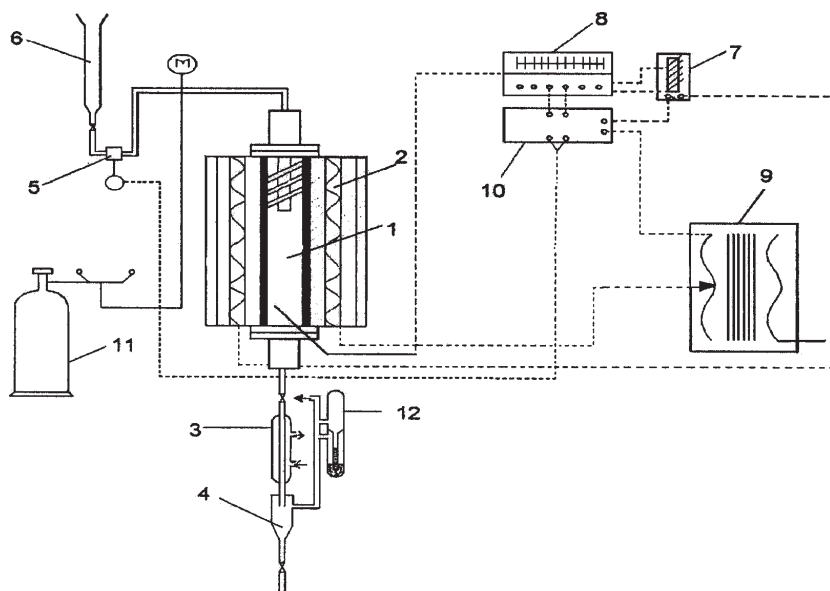


Fig. 1. HDT Micro-pilot Plant
(1-reactor, 2-electrical heater, 3-water cooler, 4- liquid-gas separator, 5-metering pump, 6- feedstock burette 7-relay, 8- temperature register, 9-autotransformer, 10-temperature controller, 11-hydrogen tank, 12- flow meter)

Temperature, [°C]	250			280		
	5	10	15	5	10	15
Vegetable oil in mixture, [% wt]	5	10	15	5	10	15
	Yields, [% wt]					
Hydroisomerization product	88.64	83.74	79.86	84.54	80.32	72.40
Gas	11.36	16.26	20.14	15.46	19.68	27.60

Table 4
THE YIELDS FROM HYD
HYDROTREATED STRAIGHT RUN GAS
OIL AND RAPESEED OIL MIXTURES

Temperature, [°C]	360 °C		
Vegetable oil in mixture, [% wt]	5	10	15
Characteristics			
Density at 15°C, [g/cm ³]	0.8336	0.8352	0.8410
Viscosity at 40°C, [mm ² /s]	3.77	4.08	4.82
Flash Point, [°C]	46	46	48
Pour Point, [°C]	-16	-13	-9
Sulphure content, [ppm]	10	8	8

Table 5
CHARACTERISTICS OF THE
HYDROTREATED PRODUCT

Temperature, [°C]	250			280		
Vegetable oil in mixture, [% wt]	5	10	15	5	10	15
Characteristics						
Density at 15°C, [g/cm ³]	0.8212	0.8308	0.8344	0.8154	0.8221	0.8320
Viscosity at 40°C, [mm ² /s]	2.98	3.12	3.88	2.27	2.64	3.16
Flash Point, [°C]	48	48	47	46	47	47
Pour Point, [°C]	-28	-23	-20	-36	-32	-28

Table 6
CHARACTERISTICS OF THE
HYDROISOMERIZATION PRODUCT

hydroisomerization product. The other products have been determined by difference.

Sequential co-processing of rapeseeds oil and straight run gas oil mixtures by HDT and HYD, significantly improves the physico-chemical properties of biodiesel obtained by conversion of triglyceride from vegetable oil through the following successive and parallel reactions: saturation, cracking, decarboxylation, deoxygenation and isomerization (fig 2) carried out using the two catalyst Ni-Mo/Al₂O₃ respectively Pt-ZrO₂ sulphated /Al₂O₃. In parallel with the triglycerides conversion, take place the reactions of

partial aromatics saturation, desulphurization and hydrocracking of the components from the straight run gas oil.

Hydrotreating of the straight run gas oil and rapeseed oil mixtures achieves obtaining of a hydrotreated product, with yields of over 93% and characteristics that fit to diesel fuel. The yields in hydrotreated product decreases with the increasing of vegetable oil ratio as a consequence of removal of oxygen present in the structure of the vegetable oil in the process of deoxygenation. By HYD process the liquid products yields decrease due the cracking reactions of paraffins result from hydrotreated process, according to the reactions schema as shown in figure 2. The yields

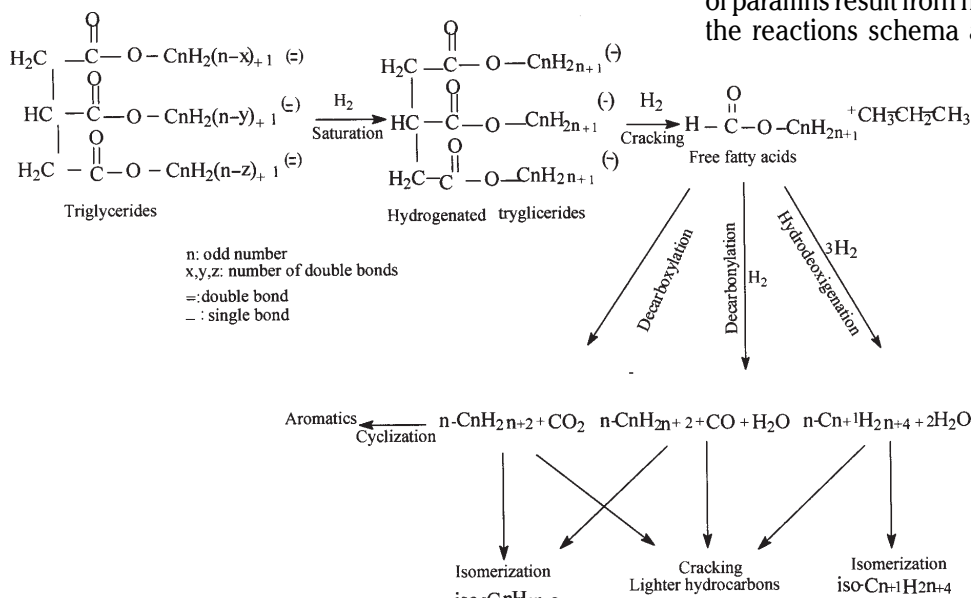


Fig. 2. Scheme of triglycerides
conversion in the HDT -HYD-
process

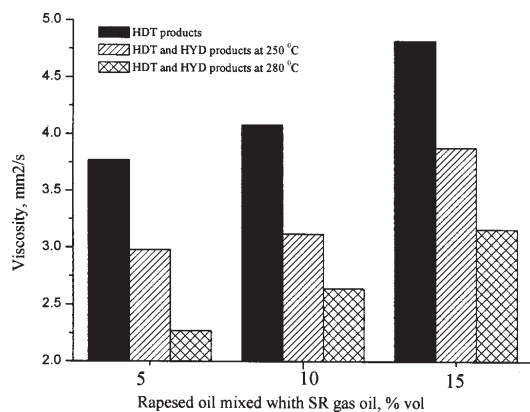


Fig. 3. Viscosity versus rapeseed oil/SR gas oil ratio and reaction temperature after HDT and HYD process

decrease with increasing of adding rapeseed oil ratio and temperature. This behaviour could be explained by intensifying cracking reactions of paraffins with 16-18 carbon atoms which results from tryglicerides conversion. By HDT and HYD of straight run gas oil and rapeseeds oil mixtures on different reactions conditions the global yields are between 68 -85% weight. The main physico-chemical properties of hydrotreated product (table 5) comply with the requirements of the quality standard EN 590. The density of the hydrotreated product is less than straight run gas oil and also less than rapeseed oil due to the chemical transformation of both components. This is due to the removal of the structure which contains oxygen from vegetal compounds and to partial saturation of aromatics with higher density from petroleum gas oil.

The vegetable oil hydrotreatment leads to significant decrease of viscosity due to the conversion of tryglicerides into smaller molecules and to the removal of the carboxyl groups. Thus the viscosity of HDT mixture of straight run gas oil with rapeseed oil was between 3.77 -4.82 mm²/s compared to 36 mm²/s of corresponding vegetable oil.

The lighter fractions which are formed by hydrocracking side reactions, resulted in lowering of flash point for hydrotreated product. The flash point can be corrected by removing the light hydrocarbons of hydrotreated product. The hydrotreated mixtures of straight run gas oil with rapeseed oil shows pour points slightly higher than gas oil (table 5) which increase with the ratio of rapeseed oil. The increase is explained by the structural changes produced by the hydrogenations of esters and double bonds in the fatty acids of the vegetable oil. After HDT the sulphur content significantly decrease to 8-10 ppm in accordance with standard requirements.

Co-processing by HDT and HYD of straight run gas oil and rapeseeds oil mixtures produces a considerable improvement of the main physico-chemical properties, viscosity (fig. 3) and pour point (fig. 4). The decrease of viscosity after HYD can be explained by conversion of normal paraffins with 16-18 carbon atoms resulting from hydrotreatment of fatty acids (fig. 2) of rapeseed oil into isoparaffinic structures (table 4).

Severe reduction of the pour point temperature with 20°C (fig.4) is the result of n-paraffins isomerizations reactions in accordance with the reactions scheme (fig. 2).

A significant contribution to lowering pour point is due to hydrocracking reactions that generate branched hydrocarbons with smaller number of carbons atoms. Increasing HYD temperature reaction that intensifying both hydroisomerization and hydrocracking reactions leads to pour point decrease. Increasing the ratio of vegetable oil/straight run gas oil, increases the pour point due to

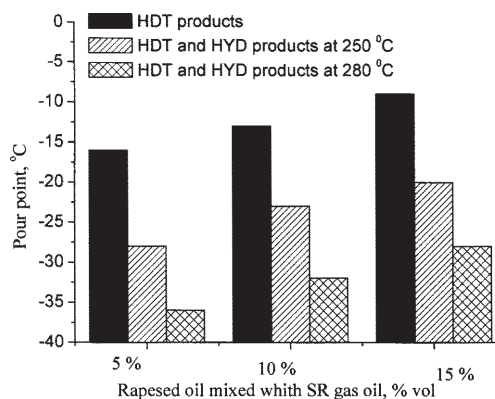


Fig. 4. Pour point versus rapeseed oil/SR gas oil ratio and reaction temperature after HDT and HYD process

enhanced paraffins/ isoparaffins ratio for co-processing product.

Conclusions

Sequential co-processing by HDT and HYD of straight run gas oil and rapeseeds oil mixtures produces biodiesel with physico-chemical properties which respect EN 590 quality standard.

The hydrocracking and hydroisomerization reaction occurring in HYD process form isoparaffins with less than 18 carbon atoms which improve the viscosity and pour point properties. Light hydrocarbons presence in the hydrotreated and hydroisomerization product lead to flash point decrease.

Cracking reactions promoted by acid sites of hydroisomerization catalyst generate gases that cause decreasing biodiesel yields.

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