

Biofuel from Hydroprocessing Fish Oil

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This paper deals with the hydroprocessing of Fish Oil (FO) as a source to produce biofuel. The hydrotreating experiments were performed at 380°C and 50bar pressure over the CoMo/Al₂O₃ and CoMoRe/Al₂O₃ catalysts. Through hydrogenation of double bonds and carboxyl groups of Fatty Acids (FAs), accompanied by secondary hydrocracking and isomerization reactions, there results a mixture of normal & isoparaffin with 13-22 carbon atoms per molecule with physicochemical characteristics similar to diesel fuel. The hydrotreatment of Straight Run Gas Oil (SRGO) mixed with 5% and 10% (FO) was also studied. The research focuses on the influence of the SRGO-FO ratio and of the catalyst type on the yields and the physicochemical properties of the obtained biofuel. The results show that the hydrotreatment of FO and of SRGO-FO mixtures is an alternative for biofuel production with characteristics similar to diesel fuel.

Keywords: Fish oil; biofuel, hydroprocessing, hydrotreating, straight run gas oil, pour point

The largest part of world energy consumption is ensured by fossil fuels: coal, oil and natural gas which are non-renewable resources with a high rating of depletion in the following 50 to 100 years [1-3]. The increasing consumption of fossil fuels has a negative impact not only on remaining hydrocarbon reserves, but also on environmental pollution by high grade NO_x, CO₂ and SO_x emissions which result from fossil fuel combustion [4-7].

Fossil fuels replacement with Renewable Energy Sources (RES) has mainly gained in importance in recent years [1,8-10]. All the EU countries have decided to increase the biofuel content in commercial fuels for cars from 2% in 2005 to 5.75% in 2010 and 10% in 2020 without affecting food needs for the population [11,12]. In 2020 Romania advances its targets to 24% RES on gross energy consumption; respectively 10% as biofuels for transportation and from 2030 the target is 27% RES on total energy consumption, an increase of 27% in energy efficiency and a reduction of GHG emissions by 40% as compared to 1990 [13].

Vegetable oils, animal fats, waste cooking oil and waste of animal origin are the most important RES used to produce biofuels for diesel engines.

Due to high viscosity, lower oxidation stability, lower volatility and particle emissions, vegetable oils cannot be used directly as diesel fuels [14,15].

Numerous technologies based on physical phenomena (dilution and emulsification) or chemical transformations (transesterification, hydrotreating, hydrocracking, catalytic cracking and pyrolysis) can be used to produce biodiesel.

The classic biodiesel, named Fatty Acid Methyl Esther (FAME), is produced from triglycerides of raw vegetable oils, animal tallow and waste oil by conventional transesterification technologies, with basic, acidic, enzymatic or heterogeneous catalysts [16-22].

Biodiesel has: an adequate cetane number, biodegradability, lower toxicity, carbon neutral and eco-friendly fuel which produces: less sulphur, HC, PM, and CO emissions [23]. As compared with fossil diesel, biodiesel FAME type has: lower energy content, higher viscosity, augmented NO_x emissions, higher pour point and cloud point [24].

Together with FAME the transesterification reaction produces glycerol at a volumetric ratio of 10/1. Glycerol still remains a barrier in biodiesel production. Analysing an impressive number of scientific articles, databases and patents, Monteiro [25] identifies 4 major directions for glycerine capitalization:

- Manufacture of chemical product;
- Production of polymers;
- Production as biofuels and biogas;
- Purification and use as glycerol.

Despite FAME higher production costs compared with fossil fuels, it is estimated that biodiesel production will grow to 41 million m³ in 2022 [25]. This growth will be encouraged through government policies, constraints on environmental legislation and fiscal policies.

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Moreover, the efficient valorisations of glycerol can maintain the biodiesel type FAME in biofuels competition. At the same time, hydroconversion of triglycerides from vegetable oils and animal fats can be an alternative way to produce biodiesel named Renewable Diesel (RD) [26-32].

In comparison with FAME production by transesterification the hydroconversion process to produce RD has the following advantages:

- Compatibility of the RD with existing engines;
- Feedstock flexibility regarding the content of free FAs;
- Free of by-product (glycerol).

Also, the RD biofuel has superior characteristics such as: higher cetane number, higher oxidation stability, higher energy, 0% oxygen content than FAME, negligible sulphur and aromatics [33].

The main limitation in biofuel fabrication is the direct competition with the usage of biomass for food production.

A solution to this problem is to use the waste of: cooking oil, animal fats and industrial used oils as raw materials for the production of biofuel, reducing significantly the overall price [34-36], as well as the environmental pollution effects caused by storage. A significant resource of non-food oil can be the oil obtained from fish waste. For centuries, fish and secondary products out of fish, have been consumed as food for humans and animals.

Humans consume just a small amount of the total annual caught fish, while the rest is used as animal food or in industry in order to fabricate: fodder, soap, glycerine or other non-food products. Fish processing results in considerable waste quantities which is a major problem for the storage and for environmental protection.

A beneficial solution is processing the fish waste into different FO sorts: a) black-brown colour raw oil, very viscous with powerful odour or b) transparent refined oil resulting from the extraction of omega FAs, with a low viscosity and less odour. The most common FO obtaining method is the wet reduction in three steps: cooking at high temperature (85-95°C), pressing and centrifuging. Other alternative methods are: hydraulic pressing, vacuum distillation, urea crystallization, hexane solvent extraction and conventional crystallization [37]. The oil obtained as a sub-product from fish processing, can be used as raw material for production of diesel type biofuel.

The objective of the present paper is to utilize the FO obtained as a by-product resulting from fish wastes processing for the production of diesel type biofuels through hydrotreatment. The FO and FO mixed with SRGO have been subjected to hydro-treatment reactions. The experiments aimed to establish the influence of the hydrotreatment process parameters over the characteristics of the obtained bio-diesel. Two types of catalysts have been used for the hydroprocess: CoMo/Al₂O₃ and CoMoRe/Al₂O₃.

Experimental part

Materials

For the experimental study, a FO (Nutrivet wild salmon) and SRGO were used. Table 1 presents the main characteristics of FO and SRGO and Table 2 shows the composition of FAs of FO.

Table 1
CHARACTERISTICS OF FO AND SRGO

Characteristics	Density at 20°C	Viscosity at 40°C	Pour Point	Flash point
Units	g/cm ³	mm ² /s	°C	°C
SRGO	0.845	4.41	-12	64.1
FO	0.896	12.60	4	164.0

Table 2
THE CHEMICAL COMPOSITION OF FO

Peak	RT	Scientific name of acid	(%) wt
1	12.566	myristic	1.88
2	15.890	palmitoleic	2.58
3	16.317	palmitic	8.71
4	19.742	linoleic	14.90
5	19.966	oleic	48.33
6	20.345	stearic	2.96
7	23.121	cis 5,8,11,14,17 eicosapentaenoic	2.86
8	23.493	8,11,14,17, eicosatetraenoic	1.07
9	23.764	cis 11,14,eicosadienoic	1.80
10	23.900	cis 11 eicosenoic	5.85
11	26.798	4,7,10,13,16,19 docosahexaenoic	4.45
12	27.068	7,10,13,16,19 docosaheptaenoic	1.58
13	27.746	13 docosenoic (erucic)	3.03

In order to determine the composition of FAs, the FO was esterified with methanol and then was subjected to gas chromatography / mass spectrometry analysis on a CP-3800 Triple Quad Agilent Technologies GC-MS system a NIST library was used to identify and analyse the reaction mixtures and the used parameters are presented in Table 3.

The result of the GC / MS analysis of FO is shown in Figure 1.

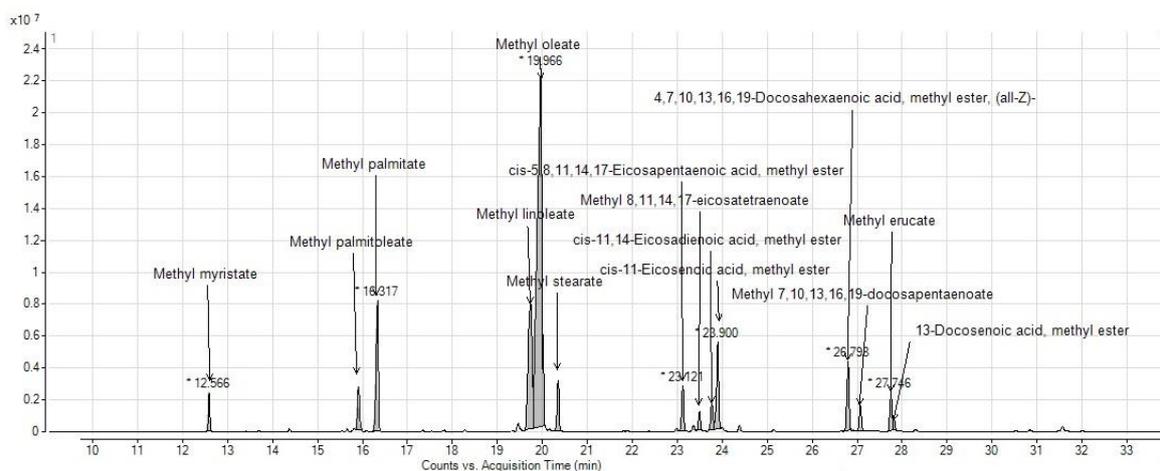


Fig.1.Chemical composition of FO

Table 3
THE PARAMETERS FOR GS/MS ANALYSIS

GS Method	MS Method
Column DB-WAX (L=30m, D=250 μ m, d=0.25 μ m)	Collision cell QQQ: Flow Quench Gas (He) = 2.2 ml/min; collision gas flow (N ₂) = 1.5 ml/min;
Oven program: 50°C for 1min., then 7°C /min. until 180°C	Source type: EI;
Carrier gas: He, debit 1ml/min	Electrons energy: 70eV;
Injector temperature: 250°C	Source temperature: 230°C; Temperature Aux 2: 280°C

Two catalysts were used, CoMo/Al₂O₃ type and CoMoRe/Al₂O₃ type obtained by successive impregnations with aqueous solutions of the catalytic precursors, applying the method of filling the support pores. Catalyst precursors were cobalt nitrate Co(NO₃)₂, ammonium heptamolybdate tetrahydrate (NH₄)₆Mo₇O₂₄·4H₂O and perhenic acid (H₄O₉Re₂), respectively. The precursor concentrations from impregnation solutions were calculated according to the proposed metal content (4% Co, 8% Mo), respectively (4% Co, 8% Mo, 0.5% Re) as well as the catalyst support pore volume.

Catalysts reconditioning between impregnations has been carried out by oven drying at 160°C for 4 hours and the final conditioning has been completed in the following sequence: 1) Oven drying at 160°C for 8 hours; 2) Calcination at 450°C for 6 hours, followed by activation in a hydrogen stream at 450°C for 6 hours. The chemical composition of the catalysts used in the experiment was confirmed by atomic absorption. Catalysts textural data (specific surface, pore volume, mean pore diameter, pore size distribution) were determined on an Autosorb1 Quantacrome (Table 4). The texture data were obtained by automatic recording and processing of the adsorption-desorption nitrogen isotherms. The specific surface was calculated using the BET equation in the linear part of the adsorption isotherm. To evaluate the pore distribution and the pore size, desorption branch of the isothermal with hysteresis was used applying the BJH method.

The adsorption isotherms for the prepared catalysts (Fig. 2) are V type with a H3 loop hysteresis characteristic of mesoporous materials, with low affinity for the adsorbed molecules and a tight distribution of the pore size. The specific surface of the two catalysts has a typical value for γ -alumina catalysts. Thus, the specific surface is relatively large, the volume of the pores is large and the distribution of the mesoporous sizes indicates a good accessibility of the active centres, compatible with the FO triglycerides diameter.

Table 4
PHYSICAL PROPERTIES OF CATALYSTS

Property	CoMo/Al ₂ O ₃	CoMoRe/Al ₂ O ₃
Surface area (m ² /g)	274.145	257.162
Pore volume (cm ³ /g)	0.486	0.466
Average pore size (nm)	6.300	6.400

BJH pore size distribution reveals that the two catalysts contain a trimodal pore size distribution at an average pore distribution of 5.2 nm, 6.3 nm respectively 7.5 nm.

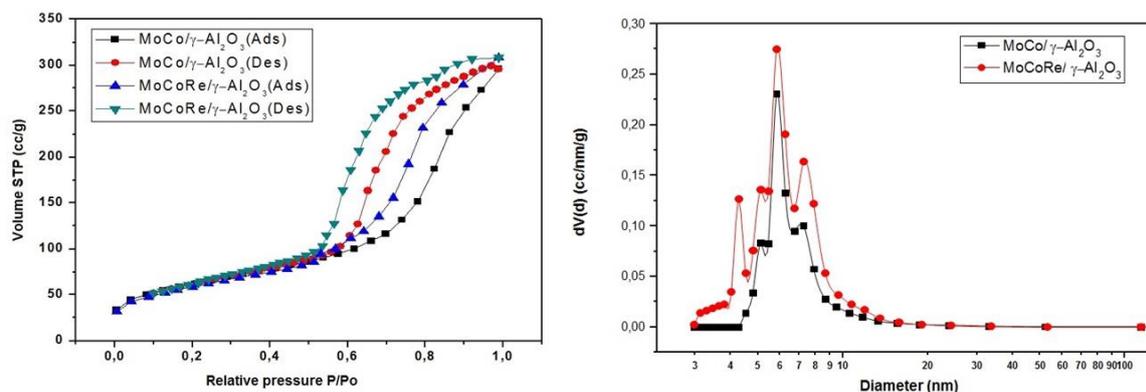


Fig. 2. N₂ adsorption isotherms of catalysts

The catalysts were activated by sulfurization with dimethyl-disulphide (DMDS) solubilized in SRGO, to 4% wt concentration, in the presence of hydrogen at a flow rate of 15 l/h, 280°C and 15 bar. Activation is completed after the H₂S formation in the reaction gases is revealed at the appearance of the yellow colour of cadmium acetate 5% aqueous solution, used as indicator.

Micro-pilot plant

The hydrotreating experiments were performed on a micro-pilot plant (Fig. 3) by using a fixed bed reactor with a volume of 40 cm³.

The hydrotreating experiments have been carried out for, FO and a mixture of FO with 5 and 10% SRGO at 380°C and 50 bar with hourly space velocity 1.5 h⁻¹ and 1000 cm³/cm³H₂/feedstock ratio.

The experiments ran for 3 hours. The liquid phase is dried with CaCl₂ in order to remove the traces of water, as a result of FO FAs deoxygenation reactions and then it is weighed to establish the yield in hydrotreated product.

The chemical composition of the liquid product obtained from FO hydrotreating, was determined by GS/MS on a GC-MS CP-3800 Triple Quad Agilent Technologies. Biofuel resulting from hydrotreatment was characterized to determine: density (EN ISO 12185), pour point (SR 13552), flash point (SR 5489) and viscosity (SR EN ISO 3104)

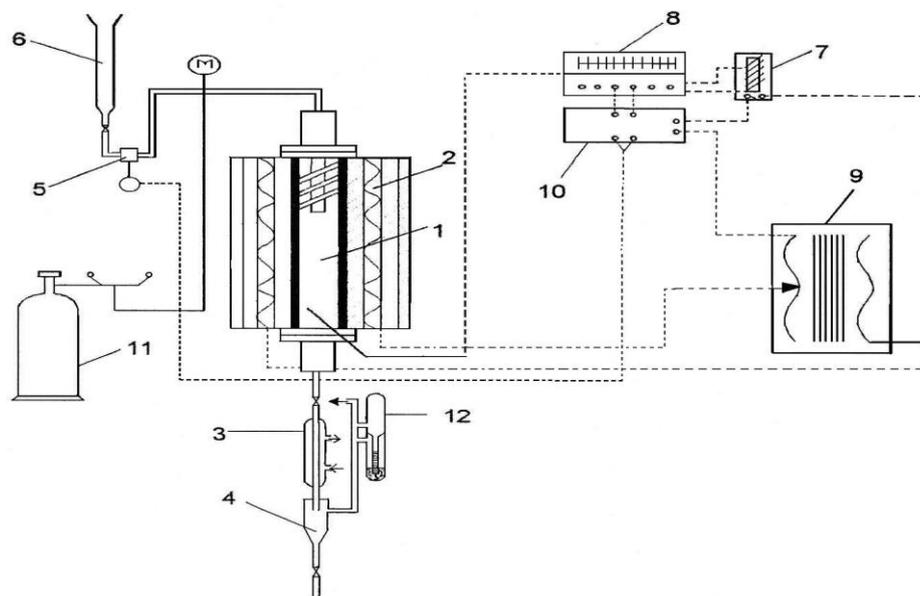


Fig. 3. The Hydrotreating Micro-pilot Plant

(1-reactor, 2-electrical furnace, 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)

Results and discussions

As shown in Table 2 the FO used in the hydrotreatment process contains 13.55% wt of saturated FAs, 59.79% wt monounsaturated and 26.66% wt polyunsaturated FAs. The saturated FAs contain mainly palmitic acid and the unsaturated ones, oleic acid. Distribution by number of carbon atoms highlights the very high content of FAs with 18 carbon atoms (66.19%), followed by 20 atoms (11.58%) and 16 atoms (8.71%). The material balance for each experience is presented in Table 5.

The yields in the products were determined by the mass balance for each experiment, as a result of knowing the amount of raw material and of weighing the organic product resulting from hydrotreatment, after water absorption on CaCl_2 . The gases were established by difference.

Table 5
PRODUCTS YIELDS OBTAINED BY HYDROCONVERSION OF FO AND OF
FO WITH SRGO MIXTURES

Catalyst	CoMo/Al ₂ O ₃			CoMoRe/Al ₂ O ₃		
	5	10	100	5	10	100
FO content in mixture FO-SRGO (%)						
Hydrotreated Product	95.47	94.65	84.94	96.38	94.12	84.09
Gas	4.05	4.44	6.14	3.08	4.76	5.85
Water	0.48	0.91	8.92	0.54	1.12	10.06

Hydroconversion of FO alone determined lower hydrotreated product yields, due to water and gas (propane, CO, CO₂) formation. This is due to hydrocracking of triglycerides and hydrodeoxygenation, hydrodecarbonylation and hydrodecarboxylation reactions of FAs. Hydrodeoxygenation reactions favoured by the more acidic CoMoRe catalyst generate more water. In the hydroconversion of SRGO mixtures with 5% and 10% of FO respectively, the yields in the hydrotreated liquid product are higher, than in the case of hydrogenation of FO alone. SRGO does not contain oxygen compounds and gases originate only as a result of the hydrogenation of the compounds with sulphur and nitrogen and of the hydrocracking reactions.

Decreasing yields are accentuated by an increase in the proportion of FO added ratio to the SRGO, as a result of FA content increase, which generates more water and gases through hydroconversion reactions.

The chemical composition of the bio-oil resulting from the hydrotreating of FO on CoMo/Al₂O₃ and CoMoRe/Al₂O₃ catalysts was determined by the GC-MS method and is shown in Tables 6, 7 and Figures 4, 5.

Peak	Components	RT	Wt%
1	Tridecane	6.518	1.26
2	Tetradecane	8.152	3.68
3	Pentadecane	9.808	2.14
4	Hexadecane	11.285	4.15
5	Heptadecane	11.553	10.37
6	7 MethylHexadecane	12.923	2.72
7	Eicosane	13.134	7.78
8	Octadecane	14.716	42.38
9	Nonadecane	16.055	2.56
10	Heneicosane	17.536	8.41
11	1 Octadecanol	18.951	1.12
12	6 Octadecenoic acid	19.582	3.88
13	Octadecanoic acid	19.819	1.92
14	n Docosane	20.141	4.45
15	Tetracosane	22.503	0.91
Sum			100.00

Table 6
THE CHEMICAL COMPOSITION OF THE
PRODUCT RESULTING
FROM THE HYDROTREATING OF FO ON
CoMo/Al₂O₃

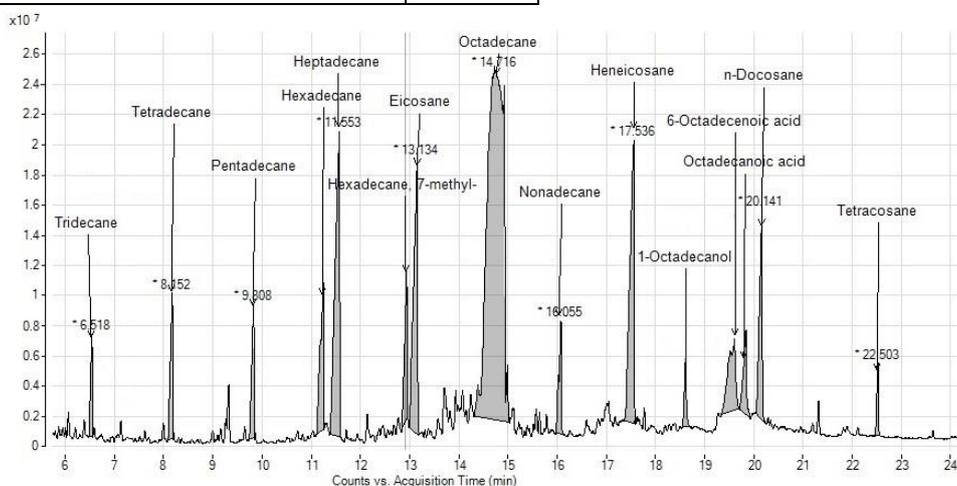


Fig.4. Chemical composition of hydrotreated biofuel on CoMo/Al₂O₃ catalyst

Table 7
CHEMICAL COMPOSITION OF PRODUCT RESULTING
FROM HYDROTREATING OF FO ON A CoMoRe/Al₂O₃

Peak	Components	RT	Wt%
1	Tridecane	6.648	0.75
2	Tetradecane	7.874	1.72
3	Pentadecane	9.160	3.73
4	Hexadecane	10.595	8.62
5	7 MethylHexadecane	11.245	2.26
6	4 MethylPentadecane	11.347	0.55
7	4 methylHexadecane	11.449	0.52
8	8 HexilHentadecane	11.550	0.50
9	3 MethylHexadecane	11.679	0.43
10	Heptadecane	12.214	16.19
11	8 MethylHeptadecane	12.891	4.61
12	7 HexilTridecane	12.952	1.39
13	8 HexylPentadecane	13.020	1.32
14	3 Methyl Heptadecane	13.135	1.43
15	2 Methyl Heptadecane	13.250	1.16
16	4 MetilHeptadecane	13.392	1.39
17	Octadecane	14.022	36.82
18	1 Octadecanol	15.166	1.17
19	2 DodecylCiclohexane	15.274	1.39
20	n Dodecyl Benzene	15.626	0.97
21	Eicosane	15.802	3.42
22	Heneicosane	17.786	6.35
23	Docosane	21.829	3.31
Sum			100.00

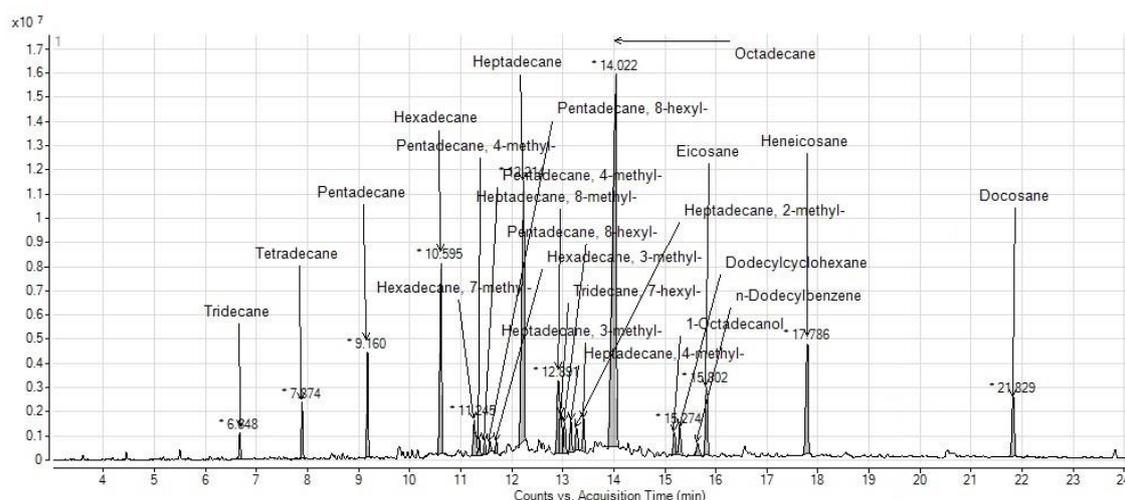


Fig. 5. Chemical composition of hydrotreated biofuel on CoMoRe/Al₂O₃ catalyst

The data presented in Tables 6, and 7 demonstrate that the hydrotreating of FO results mainly in obtaining paraffin with the same number of carbon atoms as FAs as a consequence of triglycerides transformation from oil, by hydrodeoxygenation reactions and paraffin with a less carbon atom as a result of hydrodecarboxylation or hydrodecarbonilation reactions. In all three mentioned reactions: propane, CO₂, CO and water are generated. Figure 6 shows a general scheme of reactions occurring in the FO hydroconversion process.

The triglyceride double bonds are hydrogenated and then by hydrocracking, triglycerides break down with propane and free FAs formation, which after that, through a series of reactions indicated in the scheme, they convert to normal and isoparaffin with 13-22 carbon atoms, which can constitute components for fuel formulation. FAs with 18 carbon atoms (66.19%) are transformed by hydrodeoxygenation into: 42.38% octadecane on the CoMo and 43.91% octadecane on CoMoRe (Fig. 7).

Taking into consideration the low content in acids with 17-carbon atoms (2.58%), most of the C17 paraffin come from the hydrodecarbonylation and hydrodecarboxylation reactions of acids with 18 carbon atoms. Also, by hydrocracking and isomerization reactions, facilitated by the acidity of the catalyst, paraffin with fewer carbon atoms and isoparaffin respectively, are produced. In addition to the support acidity (Al₂O₃), Rhenium added to the catalyst as perrhenic acid (H₄O₉Re₂), increases its acidity (generating Lewis acid centres). Higher acidity justifies formation by

isomerization reactions of branched paraffin in a proportion of 15.36% on the CoMoRe catalyst compared to only 2.72% on the CoMo type.

The presence of alkyl cyclohexane (2-dodecylcyclohexane) and alkyl benzenes (n-dodecylbenzenes) is explained by cyclization and dehydrogenation reactions of olefin-like intermediate products, which occur in the cracking reactions on the acidic centres of the catalyst.

The lower hydrogenation activity of the CoMo/Al₂O₃ catalyst compared to the CoMoRe type, justifies the presence of FAs and fatty alcohols (octadecanoic acid, 6-octadecenoic acid and octadecanol) in the hydrotreated product.

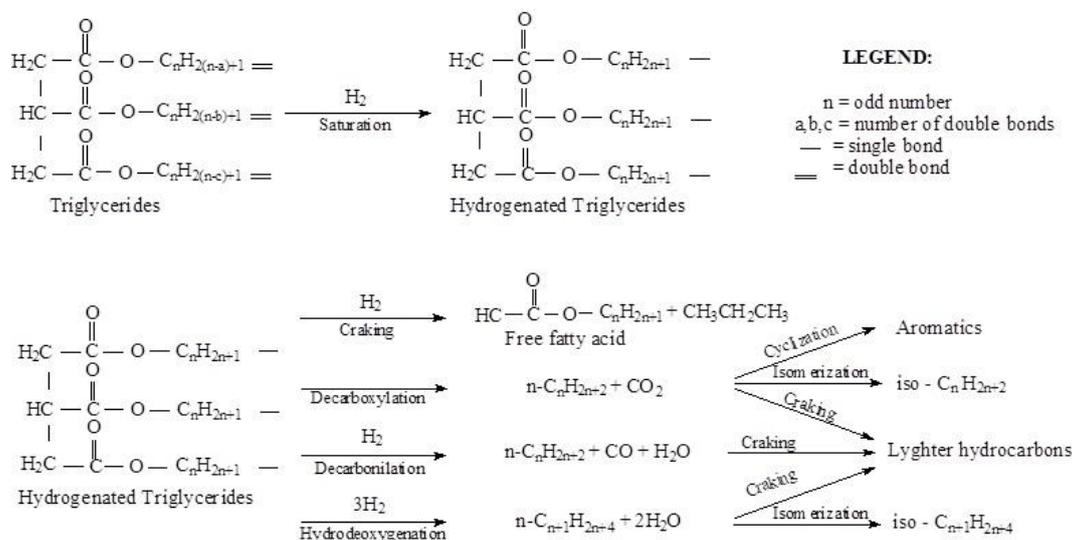


Fig. 6. Hydroconversion of FO into Biofuel Scheme

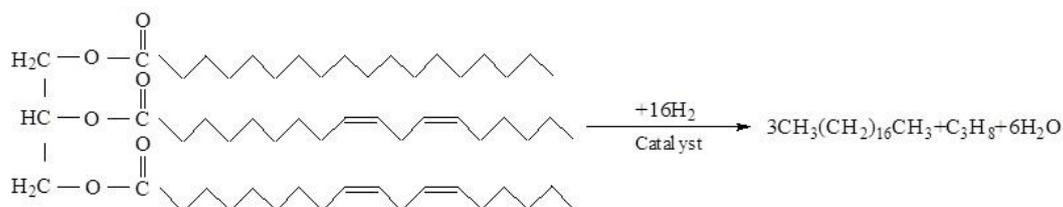


Fig. 7. Hydrodeoxygenation of C18 FA Scheme

The hydrotreatment experiments aimed to convert the FO into a bio component for diesel fuel and to directly obtain bio fuel by hydrotreating of FO-SRGO mixtures. The main physicochemical characteristics of liquid product, resulting from hydrotreatment are shown in Table 8.

Table 8
 PHYSICOCHEMICAL PROPERTIES OF THE HYDROTREATED PRODUCT

Catalyst	CoMo/Al ₂ O ₃			CoMoRe/Al ₂ O ₃		
	5	10	100	5	10	100
FO content in mixture FO-SRGO	5	10	100	5	10	100
Properties						
Density (g/cm ³) at 15°C	0.8423	0.8396	0.8037	0.8407	0.8381	0.7928
Viscosity (mm ² /s) at 40°C	3.92	3.78	3.59	3.86	3.74	3.21
Flash Point, (°C)	77	71	58	79	73	54
Pour Point, (°C)	-10	-7	4	-14	-13	-8

The physicochemical characteristics of the hydrotreated product are influenced by the FO content in mixture FO-SRGO as well as by the catalyst used.

Table 8 data reveal a significant decrease in the hydrotreated FO density (0.7928 or 0.8037g/cm³ respectively) vs the density of the crude FO (0.896g/cm³) as a result of the hydrogenation reactions which eliminate the groups containing oxygen from the oil structure [31]. The products resulting from the hydroconversion of FO and FO-SRGO blends have

densities ranging from 0.8381 to 0.8423g/cm³, within the limits imposed by the EN590 standard for diesel fuel (density 0.820-0.845g/cm³). The conversion of FO into a mixture of mostly paraffinic hydrocarbons, with a lower density in relation to the other hydrocarbon classes, with the same number of carbon atoms as hydrotreated gas oil, explains the decreasing of the hydrotreated product density, along with the increasing of the added ratio. Due to the higher acidity, which intensifies the hydrocracking reactions, by hydroconversion on the CoMoRe catalyst, there results biofuels of a lower density as compared to CoMo catalyst case.

Rhenium doped catalyst allows a slight improvement of the properties due to the n-paraffin hydroisomerization reactions. Thus, the pour point decreases from 4°C for mixtures with 5%FO to 6°C for mixtures with 10% FO and to 12°C for the hydrotreated FO (Table 3.7). The decrease is justified mainly due to the increasing in isoparaffin content, from 2.72% on the CoMo/Al₂O₃ catalyst, to 15.36% on the most acidic CoMoRe/Al₂O₃ catalyst, as a result of paraffin hydroisomerization reactions. Since the value of the cold flow properties are below EN 590 requirements, the following steps are suggested the hydroisomerisation of hydrotreated products on catalysts with higher acidity [28] and the adding of pour point depressants additives.

The transformation of triglycerides from FO, into paraffinic hydrocarbons with 13-22 carbon atoms in the molecule (Table 6,7), results in a significant decrease of product kinematic viscosity, obtained by hydroconversion from 12.6mm²/s for pure FO to respectively 3.21mm²/s and 3.59mm²/s for the hydrotreated oils on the two catalysts.

Biofuel viscosity obtained from the hydrotreatment of FO-SRGO blends, decreases as compare to the viscosity of the two feedstocks up to values below 4.5mm²/s. Viscosity decrease is bigger for the more acidic CoMoRe catalyst.

The elimination of carboxyl bonds by hydrogenation of FAs, causes a significant decrease in the flash point, from 164°C for pure FO at 54-58°C for hydrotreated FOs.

Conclusions

Oil recovery from by-products obtained in the fish industry is a cost effective strategy for fuel production and it is also an efficient solution to the pollution problems generated by their storage.

Hydrotreatment of FOs is a technologically accessible and a cost-effective process for the production of diesel biofuels.

Hydrogenation of double bonds and carboxyl groups of FAs, accompanied by secondary hydrocracking and isomerization reactions, results in the formation of a predominantly paraffinic hydrocarbon mixtures with 13-22 carbons in the molecule with physicochemical characteristics in conformity with to the requirements of quality standard for diesel fuel EN590.

Hydrotreated product composition is strongly influenced by the catalyst acidity. The isoparaffins content is 15.36% on the more acidic CoMoRe/Al₂O₃ type catalyst compared to 2.72% on the CoMo/Al₂O₃ type.

Hydrotreatment of FO-SRGO mixtures with different FO content in mixture FO-SRGO is an efficient method to produce biofuels.

References

1. MRAD, N., VARUVEL, E.G., TAZEROUT, M., ALOUI F., Energy **44**, (2012), p. 955–963.
2. USHAKOV, S., VALLAND, H., ČSŔY, V., Energy Conversion and Management **65**, (2013), p. 228–238.
3. GÜLÜM, M. BILGIN, A., Fuel Processing Technology **134**, (2015), p. 456–464.
4. MONYEM, A., VAN GERPEN, J.H., Biomass and Bioenergy **20**, (2001), p. 317–325.
5. DWIVEDI, G., JAIN, S., SHARMA, M.P., Renewable and Sustainable Energy Reviews **15**, (2011), p. 4633–4641.
6. TOMOS, B., NOVELLA, R., GARCIA, A., GARGAR, K., Renewable Energy **35**, (2010), p. 368–378.
7. KARL, T.R., TRENBERTH, K.E., Science **302**, (2003), p. 1719–1723.
8. DAHLQUIST, E., THORIN, E., YAN, J., International Journal of Energy Research **31**, (2007), p. 1226–1236.
9. ESCOBAR, J.C., LORA, E.S., VENTURINI, O. YÁÑEZ, E. E. CASTILLO, E.F. ALMAZAN, O., **13**, (2009), p. 1275–1287.
10. MISRA, R.D., MURTHY, M.S., Renewable and Sustainable Energy Reviews **14**, (2010), p. 3005–3013.
11. OPRESCU, E.E., STEPAN, E., DRAGOMIR, R.E., RADU, A., ROSCA, P., Fuel Processing Technology **110**, (2013), p. 214–217.
12. NAUTIYAL, P., SUBRAMANIAN, K.A., DASTIDAR, M.G., Fuel Processing Technology **120**, (2014), p. 79–88.
13. Romanian Energy Strategy 2016-2030, with perspectives for 2050, 15 november, 2016.
14. DEMIRBAS, A., Energy Conversion and Management **50**, (2009), p. 14–34.
15. NIGAM, P.S., SINGH, A., Progress in Energy and Combustion Science **37**, (2011), p. 52–68.
16. BEHÇET, R., YUMRUTAS, R., OKTAY, H., ENERGY **71**, (2014), P. 645–655.
17. AGHBASHLO, M., TABATABAEI M., HOSSEINPOUR, S. Energy Conversion and Management **64**, (2018), p. 385–398.
18. MA, F.R., HANNA, M.A., Bioresource Technology **70**, (1999), p.1–15.
19. MATH, M.C., KUMAR S.P., CHETTY, S.V., Energy for Sustainable Development **14**, (2010), p. 339–345.
20. MARCHETTI, J.M., MIGUEL, V., ERRAZU, O.F., Renewable and Sustainable Energy Reviews **11**, (2007), p. 1300–1311.
21. MEHER, L.C., SAGAR, D.V. NAIK S.N., Renewable Sustainable Energy Reviews **10**, (2006), p. 248–268.
22. HAMA, S., YAMAJI, H., KAIEDA, M., ODA, M., KONDO, A., FUKUDA, H., Biochemical Engineering Journal **21**, (2004), p. 155–160.
23. DEVENDRA, S., SUBRAMANIAN, K.A., GARG. M., Renewable and Sustainable Energy Reviews **81**, (2018), p. 2947–2954.
24. SAKTHIVEL, R., RAMESH, K., PURNACHANDRAM, P., SHAMEER, P.M., Renewable and Sustainable Energy Reviews **82**, (2018), p. 2970–2992.

25. MONTEIRO, R.M., KUGELMEIER, L.C., PINHEIROS, S.R., BATALHA O.M., CESAR, S.A., *Renewable and Sustainable Energy Reviews* **88**, (2018), p. 109–122.
26. ANTUNES, W.M., VELOSO, C.O., HENRIQUES, C.A., *Catalysis Today* **133**, (2008), p. 548–554.
27. DRAGOMIR, R.E., ROSCA, P., *Rev. Chim. (Bucharest)* **65**, 2014, p. 485–488.
28. DRAGOMIR, R.E., ROSCA, P., OPRESCU, E.E., *Rev. Chim. (Bucharest)* **65**, 2014, p. 616–619.
29. J. WALENDZIEWSKI, J., STOLARSKI, M., LUZNY, R., KLIMEK, B., *Fuel Processing Technology* **90**, (2009), p. 686–691.
30. GUSMAO, J., BRODZKI, D., DJEGA-MARIADASSOU, G., FRETY, R., *Catalysis Today* **5**, (1989), p. 533–544.
31. KUBIČKOVÁ, I., SNĀRE, M., ERĀNEN, K., MĀKI-ARVELA, P., MURZIN, D.Y., *Catalysis Today* **106**, (2005), p.197–200.
32. BEZERGIANNI, S., KALOGIANNI, A., VASALOS, I., *Bioresource Technology* **100**, (2009,) p. 3036–3042.
33. SINGH, D., SUBRAMANIAN, A.K., GARG, O.M., *Renewable and Sustainable Energy Reviews* **81**, (2018), p. 2947–2954.
34. BEZERGIANNI, S., KALOGIANNI, A., *Bioresource Technology* **100**, (2009), p. 3927–3932.
35. ZHANG, Y., DUBÉ, M.A., MCLEAN, D.D., KATES, M., *Bioresource Technology* **90**, (2003), p. 229–240.
36. DRAGOMIR, R.E., ROSCA, P., JUGANARU, T. OPRESCU, E.E., *Rev. Chim. (Bucharest)*, **66**, 2015, p. 277–281.
37. RUBIO-RODRÍGUEZ, N., DIEGO, S.M., BELTRÁN, S., JAIME, I., SANZ, M.T., ROVIRA, J., *Journal of Food Engineering* **109**, (2012), p. 238–248.

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