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Hydrotreating of Raw Vegetable Oils and Mixed with Gasoil

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Abstract

In micropilot laboratory installation it has been studied the hydrotreating of raw vegetable oil (sunflower oil) and mixed with atmospheric distillation and coking gasoil on Ni-Mo sulphides catalyst alumina supported. Operating conditions were: temperature range 350-450°C, pressure range 30-35 bar, hourly space velocity 2 h^{-1}, hydrogen/raw material 5/1 (molar ratio). Reaction products have been characterized by average properties and physical and chemical characteristics, as well as sulphur content, cetane index, aromatic content. It was emphasized the influence of operating parameters on hydrotreated products properties.

Key words: *hydrotreating process, vegetable oils, supported alumina Ni-Mo sulfides catalyst*

Introduction

The study aim is biofuels production – *biodiesel* – by the hydrotreating of vegetable oils crude and mixed with gasoil, the influence of parameters on the products quality of in micropilot laboratory installation operated in different conditions, using different raw materials.

The present experimental program also studies the improvement of petroleum products quality by hydrotreating [1], and comparing the results of raw material experiments. The biodiesel is a vegetable fuel (obtained from rapeseed oil, sunflower oil, bean oil or palm oil) or animal fuel (from burned oils and animal residues, fats, etc.) [2, 3, 4, 5].

Experimental program

The micropilot laboratory components are: reactor, electric oven, refrigerating apparatus, separator vessel, dosing pump, burette, potentiometer, electric panel, hydrogen gas cylinder and flow meter.

The vertical reactor contents a steel tube available for high temperatures and pressures. The reactor diameter is about 24 mm and the heating is done by electrical resistors. The catalyst is alumina supported Ni-Mo sulphides catalyst [6, 7]. The adjusting of temperature is automatically made by a temperature regulator. Catalyst Ni -Mo/Al_2O_3 characteristics are presented in Table 1.

Table 1. Characteristics of catalyst Ni -Mo/Al_2O_3

Characteristics	Values
Particle diameter , *mm*	6,0
Particle length, *mm*	5,0
Density , *g/cm³*	1,0
Comprising resistance, *kg force/particle*	150
Surface area, m^2/g	107,5
Pore volume, cm^3/g	0,25
Porosity, %	50,5

The experimental program steps:

- Establish the operating conditions and starting reactor heating. Raw material flow is introduced in the reactor using a dosing pump and the gas flow from hydrofining reactions is measured using the flow meter.
- The hydrogen flow is constant.
- The reaction products are condensed and collected and the gases are captured and analyzed.
- The raw material and reaction products are characterized by IR and NMR spectroscopy.

Operation conditions:

- Temperature: 370ºC;
- Hourly space velocity: $2h^{-1}$;
- Pressure range: 30 – 35 atm;
- Hydrogen flow: 0,1 – 0,3 l/mol;
- H_2/raw material: 5/1 (molar ratio).

In Table 2 there are presented the raw materials and reaction products codes.

Table 2. Raw material and reaction products

Raw material (RM) / Reaction product (RP)	Name/ Composition
RM 1	Used sunflower oil
RM 2	75% DA diesel + 25% used sunflower oil
RM 3	75% coking diesel + 25% used sunflower oil
RP 1	Used sunflower oil (hydrotreated)
RP 2	75% DA diesel + 25% used sunflower oil (hydrotreated)
RP 3	75% coking diesel + 25% used sunflower oil (hydrotreated)

Experimental results

In Tables 3, 4 and 5 are presented the properties and sulphur content of raw materials and reaction products from hydrotreating at 370°C (Table 3, 4), respectively diesel properties (Table 5) analyzed with IROX DIESEL instrument (analysis were made in the Petroleum products Analysis Laboratory at University Petroleum and Gas Ploiesti). For IR Spectroscopy analysis it was used GEMINI 300 BB VARIAN equipment in solvent $CDCl_3$.

Table 3. Raw material properties

Raw material type	Mass, g	ρ, g /cm^3	V, cm^3	Viscosity, cSt	Sulphur content, ppm
RM 1	53,53	0,923	58	42,41	3700
RM 2	39,95	0,852	39	47	3564
RM 3	51,54	0.859	60	43	2563

Table 4. Composition of reaction products at 370-375ºC temperature

Product type/ temperature	Mass, g	ρ, g /cm^3	V, cm^3	Viscosity, cSt	Sulphur content, ppm
RP 1 -370^{o}C	41,58	0,904	46	14,14	4600
RP 2- 375^{o}C	43,73	0,825	53	3,25	4013
RP 3 - 370^{o}C	44,56	0,857	52	3,52	2156

Table 5. The determination of diesel properties with IROX DIESEL instrument

Diesel type	Ar %, vol	PNA % vol	Cetane value (CC)	Cetane index (IC)	t 90% ^{o}C	t 95% ^{o}C	additives ppm	ρ, g/ cm^3
DA diesel	25,2	6,7	49,9	48,7	321	342	37	0,827
Coking diesel	29,4	3,3	42,5	37,2	349	382	-	0,837

Spectral characterization of vegetable oil simple and mixed with gas oil

In Figures 1-6 are illustrated the IR spectra for raw materials RM1-3 and RP1-3 around 370^{o}C.

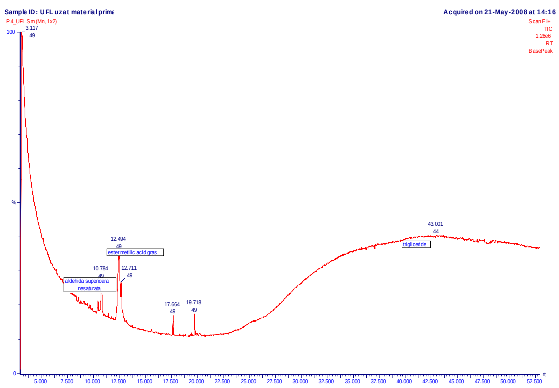

Figure 1. IR spectrum for RM1

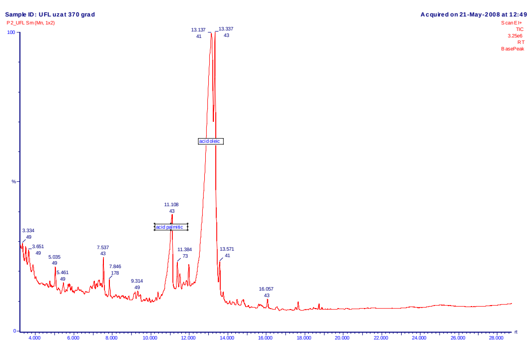

Figure 2. IR spectrum for RP1 (370 ^{o}C)

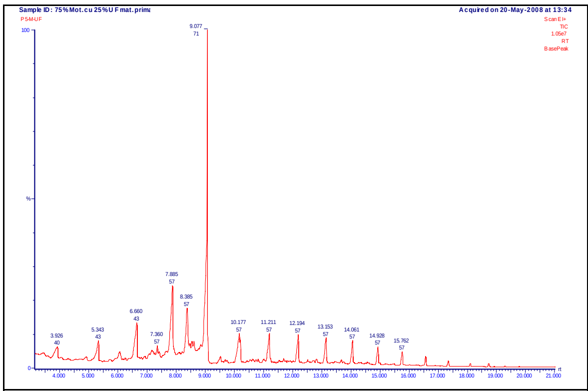

Figure 3. IR spectrum for RM2

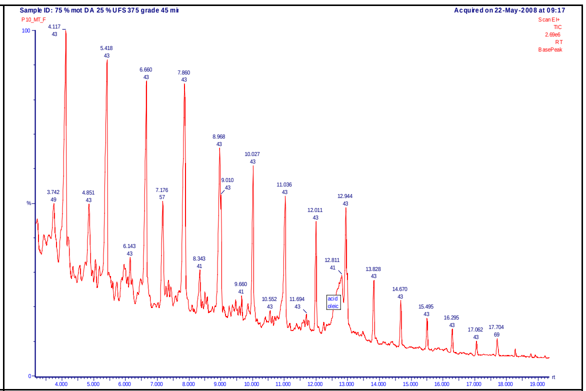

Figure 4. IR spectrum for RP2 (375 °C)

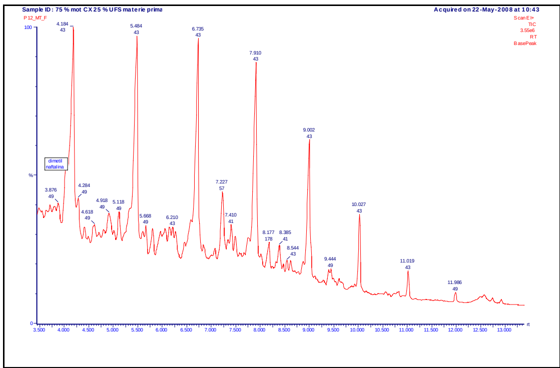

Figure 5. IR spectrum for RM3

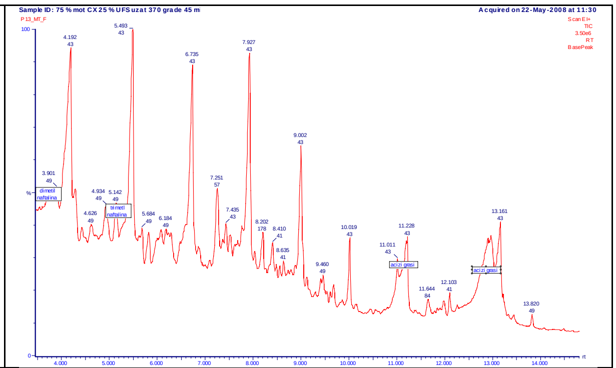

Figure 6. IR spectrum for RP3 (375 °C)

H-NMR characterisation of vegetable oils simple and mixed with gas oil

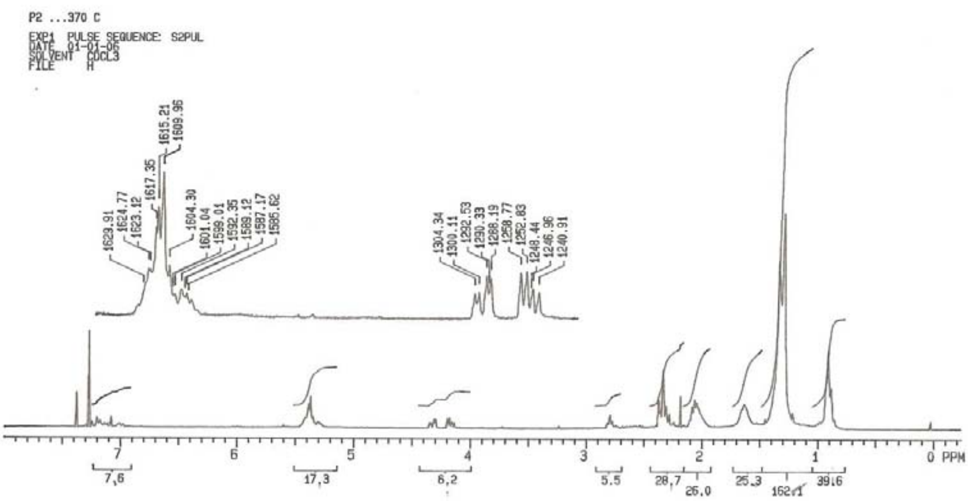

Figure 7. H-NMR for PR1 (370°C)

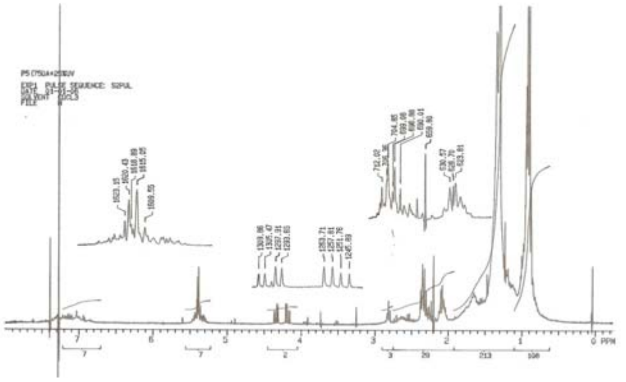

Figure 8. H-NMR for MP2

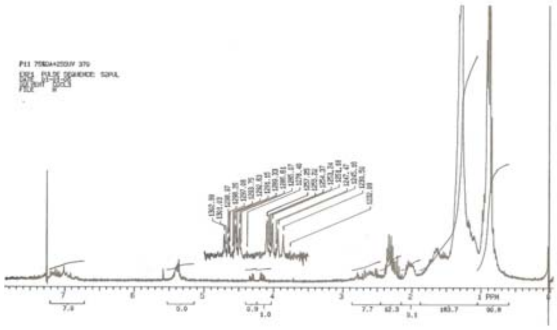

Figure 9. H-NMR for PR2 (370^0C)

Discussion of experimental results

IR spectrum shows that RM1 sample (Figure 1) contains aldehydes derived from unsaturated alcohols, methyl esters of fat acids and triglycerides, compared with PR1 (Figure 2) sample spectrum at temperature of 370°C that presents a mixture of free acids: palmitic, oleic, stearic.

IR spectrum for RM2 (Figure 3) sample showed a content of paraffins without identifying the used oil. It also contains free oleic acid.

The content of dimethyl naphthalene can be observed in the IR spectrum of MP3 (Figure 4) sample.
Starting from the NMR principle, regarding the behavior of atomic nucleus into magnetic field, related to the chemical shift, it could be identified protons types of from the molecule: aliphatic, aromatic, allyl, vinyl, primary, secondary, tertiary.

The spectra for PR1 (370°C - Figure 7) shows the appearance of hydrogenation reactions with methyl esters group decreasing and olefins content reducing. The aromatics appear probably like as precursors of coke formation, meaning that after experiments the particles of catalysts have been coked, probably due to the polar raw material rich in O_2, a probably experiments need to carry out at higher H_2/MP molar ratio and higher pressures.

H-NMR spectrum for MP2 (Figure 8) shows the characteristic signals between 0,2-3 ppm. The spectrum show more thinly signals for H_2, C_2-C_3 alkanes, and the mixture of hydrocarbons and gasoil from atmospheric distillation around 2-3 ppm, characteristic signals spectrum of used sunflower oil. Also, there are protons and methyl esters groups olefins (5-5,5 ppm) and small amounts with low concentrations of bi and tricyclic aromatics in atmospheric distillation gasoil.

For PR2 (370°C – Figure 9) it can be observed that the hydrogen (bonded with ester group) results in a significant concentration. Other reaction products being methyl ester group, respectively aromatics.

Conclusions

Biodiesel obtaining from renewable sources represents a desiderate of our times.

This experimental study is original and the previous results seem to be optimistic.

Raw material types as well as operating conditions lead to significant differences in reaction products type and reaction products distribution.

IR spectra and NMR spectra shows that Ni-Mo catalysts are active for the hydrotreating of crude oil and gasoil mixture.

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Hidrotratarea uleiurilor vegetale simple şi în amestec cu motorina

Rezumat

A fost studiată hidrotratarea unui ulei vegetal (ulei de floarea soarelui) simplu şi în amestec cu motorina de la distilare atmosferică şi cocsare, pe catalizatori sulfuri Ni-Mo depuse pe alumina, pe o instalaţie micropilot de laborator. Parametrii de operare au fost: temperatura 350-450°C, presiunea 30-35 bar, viteza volumare 2 h^{-1}, raport molar hidrogen/materie prima 5/1. Produşii de reacţie au fost caracterizaţi prin proprietăţi medii şi proprietăţi fizice şi chimice, ca şi conţinut de sulf, cifră cetanică, conţinut de aromatice. A fost evidenţiată influenţa parametrilor de operare asupra caracteristicilor fizice şi chimice ale produşilor de reacţie de la hidrotratare.

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