# Diesel Biofuels - Preparation, Characterization and Testing

**CRISTINA DUªESCU[1]*, ANCA BORCEA[1], VASILE MATEI[1], ION POPA[2], IRINA GABRIELA RĂDULESCU[1]**
[1] Oil Gas University of Ploieºti, 39, B-dul Bucureºti, Ploieºti, 100680, Ploiesti, Romania
[2] Academy of Economical Sciences, 6 Piata Romana, 010374, Bucharest, Romania

*The present paper studies biodiesel samples preparation by transesterification and compares their physical and chemical properties (biofuels prepared from different raw materials - vegetable oils: sunflower oil, crocus oil and soya bean oil) and the biodegradability degree, as well as the possibilities of the integration of such production unit in industrial diagram of auto fuels production.*

*Key words: biodiesel, transesterification, vegetable oil, biodegradability*

Spectacular development of the production of machines and equipments with heat engines determined the increasing of fossil fuels consumption. Even if they continue to dominate the energy market, transportation – the most important consumer – using priority classical fuels, the pessimistic evaluations concerning crude oil resources and damaging effects of all the activities related to petroleum products (crude-oil production, treatment and advantage) determined a dramatically restructuring of petroleum processing industrial sector and has oriented the attention unto alternative energy sources, biodiesel being one of them [1, 2]. This fact determined important mutations, in economical and technical terms, concerning certain quality fuels demands. The wide variety of feed stocks, the diversity of preparation receipts, determines different qualities for clean fuels. The key of petroleum processing industry is represented by the degree of using clean fuels in transportation [3]. The directions to follow envisage the necessity of security and resources diversification increasing, and finding the best fuels and their production technologies, in order to offer the best environment protection, from the point of view of urban aspects and global warming effects. For motors ignition by compression, the laws in force stipulate reformulated fuels with 5% vol. biodiesel (up to 20% vol. till 2010) [4, 10]. The international convention is to note with BXX the mixture of mineral diesel and biodiesel (methyl or ethyl esters of the acids from vegetal glycerides), B representing the biodiesel content in variable proportion (ester percent). Thus, B10 represents 90% mineral diesel and 10% biodiesel, and B100 represents 100% biodiesel. A common way of vegetable oils utilization for diesel fuels is the transesterification [12] of the glycerides of unsaturated vegetal fat acids in methyl and ethyl esters by acid or basic [5, 9, 11] catalysis, e.g. on KOH catalyst [6]. Reaction systems presented in the literature as well as in industry are discontinuous. It is very important to identify from the wide spectrum of potential raw materials, those whereby it could be obtained biodiesel with best combustion qualities.

In this paper are presented experimental data regarding preparation, physical, chemical and biodegradability characterization of certain methyl esters of corresponding acids for vegetable oils such are: sunflower oil, crocus oil and soya bean oil.

## Experimental part

The experimental program focused on biodiesel preparation by transesterification, the products characterization and biodegradability degree tests. From every vegetal oil type biodiesel samples were prepared by basic catalysis transesterification method, in discontinuous system. Raw materials were vegetable oil refined for alimentary use. Physical and chemical characteristics of raw materials are presented in table 1.

Methanol was used as transesterification agent and KOH pellets as catalysts. Catalyst proportion related to oil was 0.4-1.2% wt.; this was dissolved in methanol and introduced in the system under continuous stirring at 65°C. Molar ratio methanol/oil was between 2-4. After 3 h, system temperature decreased to room temperature, stirring was stopped and two phases separated. Biodiesel was distilled to atmospheric prssure in order to remove unreacted methanol. Biodiesel samples prepared and conditioned were analyzed (table 2).

Respecting UE regulations concerning biodiesel utilization in mixture with mineral diesel, physical and chemical characterizations were determined for methyl esters obtained by crude sunflower oil transesterification with methanol and mixtures of gasoil with 10% biodiesel

**Table1**

PHYSICAL AND CHEMICAL CHARACTERIZATION OF VEGETAL OILS

| Property | sunflower oil | crocus oil (crocus banaticus) | soya bean oil (soja hispida) |
|---|---|---|---|
| Density, g/cm$^3$ | 0,8889 | 0,9136 | 0,8893 |
| Viscosity, at40°C, mm$^2$/s | 8,31 | 6,47 | 6,52 |
| Degree of unsaturation, mgKOH/g | 4,033 | 2,900 | 3,877 |
| Refraction index, 20°C | 1,4780 | 1,4785 | 1,4775 |
| Freezing point,°C | -8 | -18 | -16 |
| Flash point, °C | 290 | 305 | 300 |
| Oil saponification value, mg KOH/g | 58 | 44 | 65 |

---

**Tel.: 0726757053*

**Table 2**
BIODIESEL SAMPLES CHARACTERIZATION

| Property | Biodiesel from sunflower oil | Biodiesel from crocus oil (crocus banaticus) | Biodiesel from soya bean oil (soja hispida) |
|---|---|---|---|
| Density, g/cm$^3$ | 0,8788 | 0,8783 | 0,8788 |
| Viscosity, at 40°C mm$^2$/s | 17,12 | 11,16 | 17,12 |
| Degree of unsaturation, mgKOH/g | 9,1857 | 9,038 | 6,794 |
| Refraction index, 20°C | 1,4370 | 1,4763 | 1,4370 |
| Freezing point, °C | -5 | -7 | -9 |
| Flash point, °C | 154 | 163 | 172 |
| Oil saponification value, mg KOH/g | 51 | 72 | 86 |

(B10) and 20% biodiesel (B20). These samples analysis carried out with GC-MS QMD-1000, Carlo Erba Instruments on a capillary column FactorFour VF-5 ms, length 30m, internal diameter 0,25 mm and stationary phase film 0.25 µm, according to ISO 5508/1990 and ISO 5509/2000. Identification was realized with database NIST and WILEY.

Experimental data regarding composition characterization, on components and hydrocarbons types, are presented in table 1 for B100, table 2 for B05, table 3 for B10 and table 4 for B20. Mixtures were also analyzed by $^1$H-NMR. The $^1$H-NMR spectra for B100, B05, B10 and B20 samples are presented in figures 1-4.

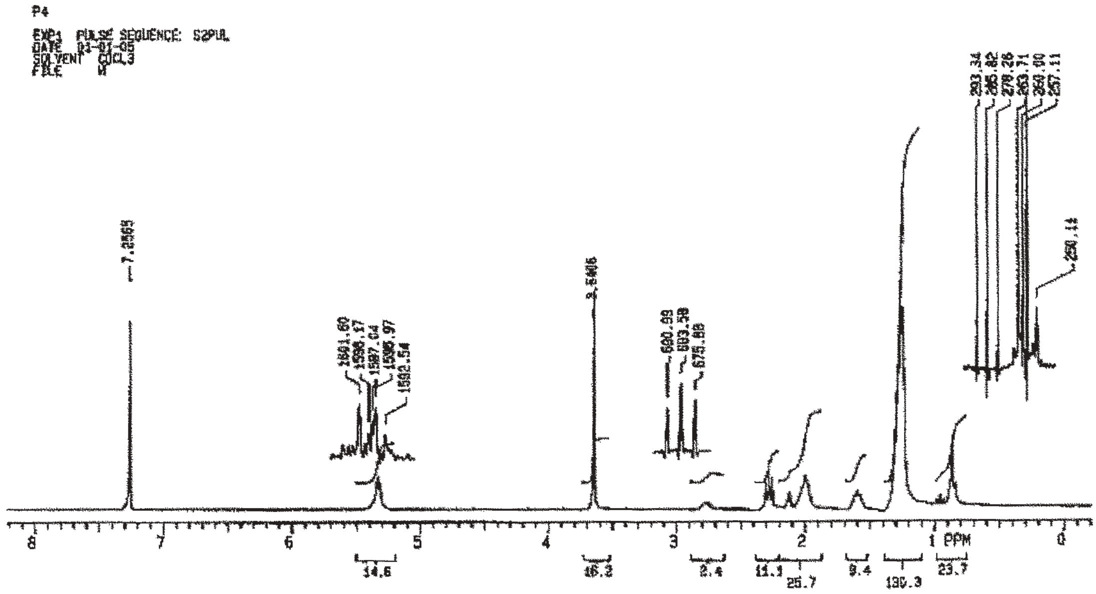

Fig. 1. $^1$H-NMR spectrum for B100

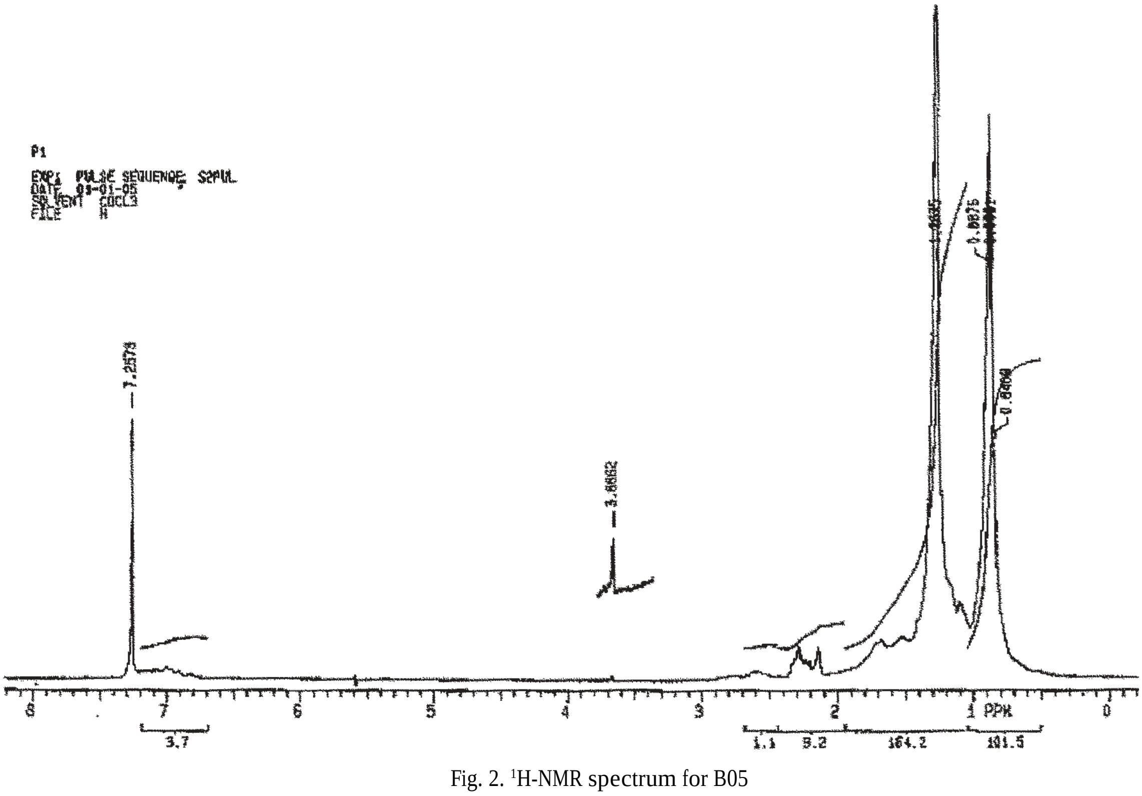

Fig. 2. $^1$H-NMR spectrum for B05

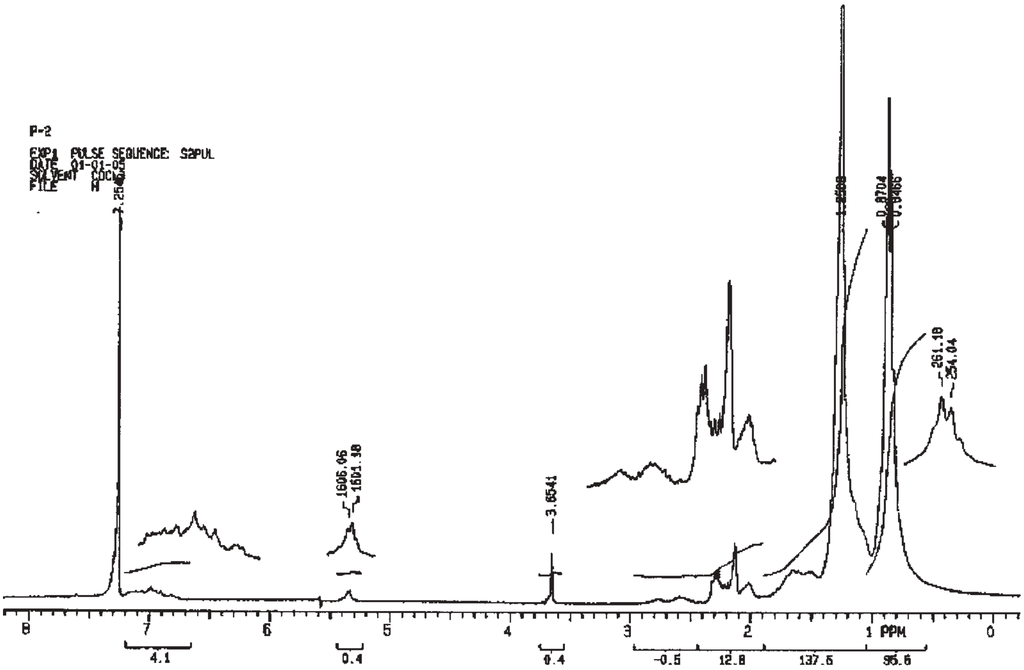

Fig. 3. $^1$H-NMR spectrum for B10

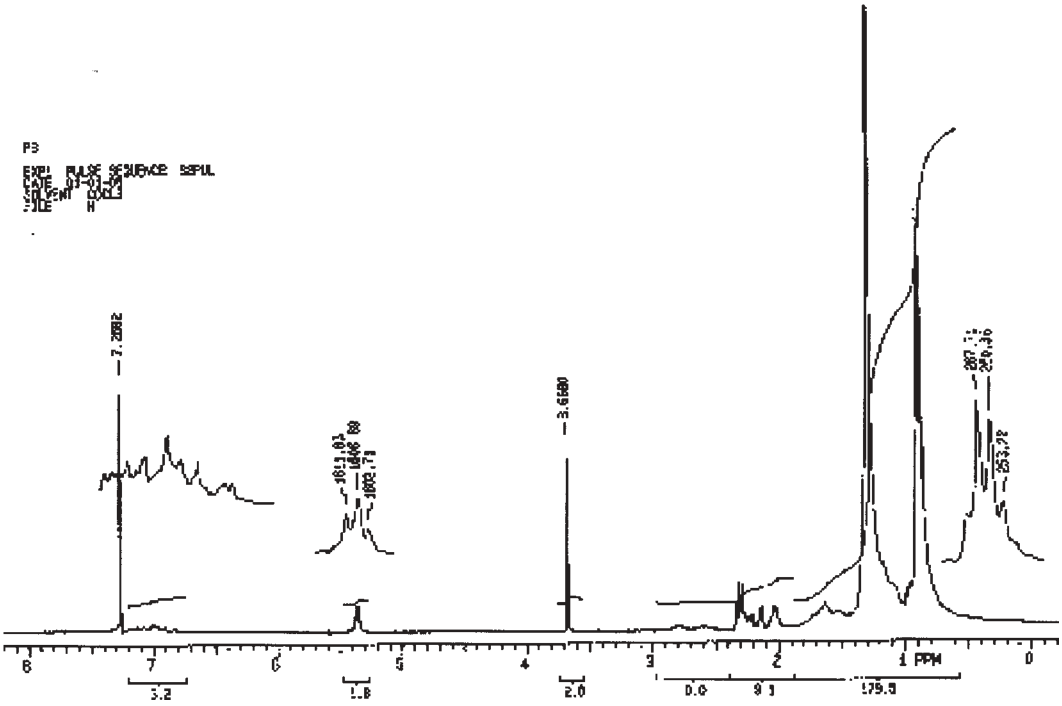

Fig. 4. $^1$H-NMR spectrum for B20

**Table 3**
CHARACTERIZATION OF SAMPLES FOR BIODEGRADATION

| Test | Before biodegradation | | | | After biodegradation | | | |
|---|---|---|---|---|---|---|---|---|
| Properties | M | B1 | B2 | B3 | M | B1 | B2 | B3 |
| $d_4^{20}$ | 0,8629 | 0,8318 | 0,8389 | 0,8859 | 0,8282 | 0,8416 | 0,85175 | 0,9133 |
| $n_D^{20}$ | 1,4550 | 1,4545 | 1,4542 | 1,4530 | 1,4575 | 1,4579 | 1,4590 | 1,4598 |
| $\upsilon_{40°C}$, cSt | 2,2261 | 2,3296 | 2,6920 | 4,1416 | 2,3814 | 2,8991 | 3,3133 | 12,7354 |
| S, ppm | 38 | - | - | - | - | - | - | - |
| % P | 34,02 | 29,78 | 28,51 | 28,14 | 30,38 | 27,41 | 25,43 | 25,61 |
| % N | 42,21 | 39,78 | 42,25 | 41,58 | 45,82 | 40,83 | 42,03 | 41,35 |
| % Ar | 27,75 | 25,44 | 21,24 | 29,24 | 23,73 | 21,76 | 11,74 | 33,04 |

**Table 4**
BIODEGRADATION PROCESS YELDS

| Test | Gas oil | B1 | B2 | B3 |
|---|---|---|---|---|
| Initial amount, g | 50 | 50 | 50 | 50 |
| Final amount, g | 43 | 42 | 44 | 36,5 |
| Yield, % | 14 | 16 | 12 | 27 |

For fuels biodegradability degree characterization, there were prepared mixtures of gas oil and 5% biodiesel (B1 - biofuel with 5% biodiesel from sunflower, B2 - biofuel with 5% biodiesel from cocusa oil, B3 - biofuel with 5% biodiesel from soya bean oil). 50g from each probe have been used for biodegradation tests (165 h under continuous stirring with 100 mL aqueous solution of bacterial SuSa cells). The samples have been analyzed and characterized before and after biodegradation and the results are presented in table 3. To compare them, it has been used as control sample a commercial diesel.

## Results and discussion

From data presented in tables 5-8, it can be observed that biodiesel contains methyl esters of different unsaturated oils that are part of sunflower oil. The most part are esters of erucat, oleic, linoleic and 11-eicosenoat. In mixture with mineral diesel from hydro-treated gasoil in industrial plant of great performance, it could be observed the decreasing of majority acids esters and rare components.

The analysis GC-MS indicates the presence of different mixtures of acids methyl esters from vegetable oils in biodiesel, having the same characteristics as for diesel gasoil. In tables 1-2 there are presented some properties of vegetable oils and biodiesel samples. In tables 3-4 there are presented the results from biodegradation study. As it can be observed in $^1$H-RMN spectra, chemical shifts are characteristic for hydrogens in methyl and methylene from iso, normal and cycloparaffines. It can also be observed the chemical shift due to vinylic hydrogen, from vegetable oils. Aromatic hydrocarbons are not detectable for transesterified vegetable oil in $^1$H-NMR spectra. Diffuse signals appears at chemical shifts $\delta$ between 6.8-7.2 ppm in mineral gasoil, and decrease in mixtures with esters content increasing. These small signals could be assigned to aromatic hydrogens, and because of the reduced amounts they appear as band signals not isolated signals as for pure substances [7]. In all $^1$H-NMR spectra it appears a straight signal at $\delta$=7.25 ppm that could be assigned, according to literature ($\delta$=7.34 ppm for benzene, fig. 5), to a proton from benzene, probably remained in vegetable oil from petroleum solvent refining of vegetable oils.

Biodiesel has been characterized from the point of view of viscosity, unsaturation degree, freezing and flash points and saponification values (table 2).

**Table 5**
B100 CHARACTERIZATION BY GC-MS

| Nr.crt. | Components | Retention time, s | Concentration % |
|---|---|---|---|
| 1. | Methyl ester of palmitic acid C16-0 | 32,743 | 4,00 |
| 2. | Methyl ester of linoleic acid C18-2 | 36,487 | 15,00 |
| 3. | Methyl ester of oleic acid C18-1 | 36,670 | 26,00 |
| 4. | Methyl ester of palmitic acid C18-0 | 36,297 | 1,50 |
| 5. | Methyl ester of 11-eicosenoat acid C20-1 isomer | 40,330 | 12,31 |
| 6. | Methyl ester of 11-eicosenoat acid C20-1 isomer | 40,385 | 1,16 |
| 7. | Methyl ester of arahidic acid C20-0 | 40,669 | 0,80 |
| 8. | Methyl ester of erucat acid C22-1 | 44,026 | 35,50 |
| 9. | Methyl ester of behenic acid C22-0 | 44,237 | 0,60 |
| 10. | Methyl ester of nervonat acid C24-1 | 47,062 | 1,73 |
| 11. | Methyl ester of lignoceric acid C24-0 | 47,401 | 1,40 |

**Table 6**
B05 CHARACTERIZATION BY GC-MS

| Nr.crt. | Components | Retention time, s | Concentration % |
|---|---|---|---|
| 1. | Methyl ester of palmitoleic acid C16-1 | - | 0,244 |
| 2. | Methyl ester of palmitic acid C16-0 | 32,743 | 0,288 |
| 3. | Methyl ester of linoleic acid C18-2 | 36,487 | 0,656 |
| 4. | Methyl ester of oleic acid C18-1 | 36,670 | 1,487 |
| 5. | Methyl ester of palmitic acid C18-0 | 36,297 | 0,647 |
| 6. | Methyl ester of 11-eicosenoat acid C20-1 | 40,330 | 0,208 |
| 7. | Methyl ester of erucat acid C22-1 | 44,026 | 0,151 |
| Total methyl esters of fat acids | | | 3,681 |
| n-paraffin and isoparaffin | | | 96,319 |

**Table 7**
B10 CHARACTERIZATION BY GC-MS

| Nr.crt. | Components | Retention time, s | Concentration % |
|---|---|---|---|
| 1. | Methyl ester of palmitic acid C16-0 | 32,743 | 0,710 |
| 2. | Methyl ester of linoleic acid C18-2 | 36,487 | 1,487 |
| 3. | Methyl ester of oleic acid C18-1 | 36,670 | 5,628 |
| 4. | Methyl ester of palmitic acid C18-0 | 36,297 | 2,065 |
| 5. | Methyl ester of 11-eicosenoat acid C20-1 | 40,330 | 0,167 |
| 6. | Methyl ester of arahidic acid C20-0 | 40,669 | 0,103 |
| 7. | Methyl ester of erucat acid C22-1 | 44,026 | 9,120 |
| Total methyl esters of fat acids | | | 19,270 |
| n-paraffin and isoparaffin | | | 80,730 |

| Nr.crt. | Components | Retention time, s | Concentration % |
|---|---|---|---|
| 1. | Methyl ester of palmitic acid C16-0 | 32,743 | 4,417 |
| 2. | Methyl ester of linoleic acid C18-2 | 36,487 | 3,388 |
| 3. | Methyl ester of oleic acid C18-1 | 36,670 | 9,525 |
| 4. | Methyl ester of palmitic acid C18-0 | 36,297 | 1,566 |
| 5. | Methyl ester of 11-eicosenoat acid C20-1 isomer | 40,330 | 9,726 |
| 6. | Methyl ester of erucat acid C22-1 | 44,026 | 9,120 |
| Total methyl esters of fat acids | | | 31,921 |
| n-paraffin and isoparaffin | | | 68,079 |

**Table 8**
B20 CHARACTERIZATION BY GC-MS

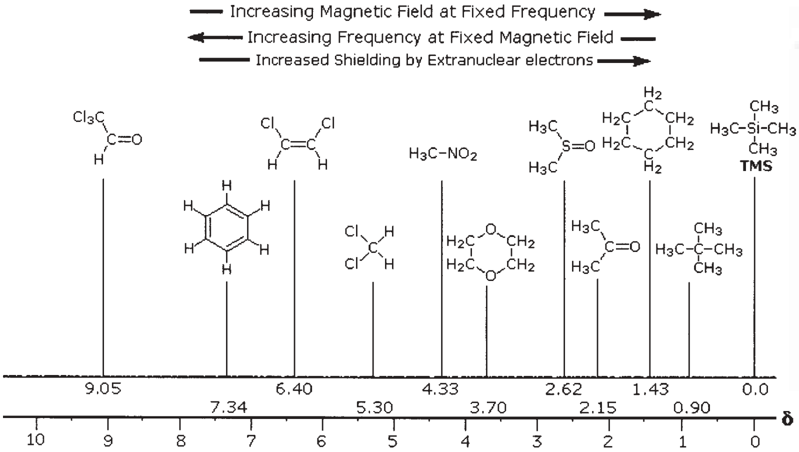

Fig.5. 1H-NMR spectrum for pure substances

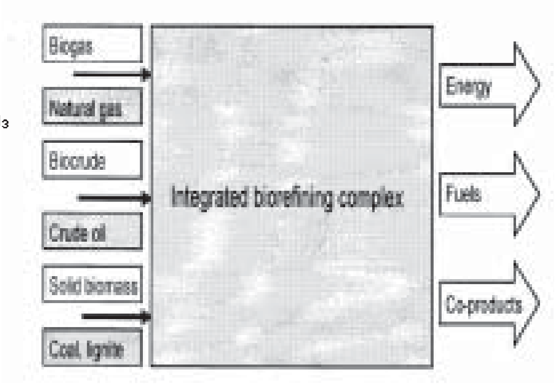

Fig. 6. Integrated biorefining complex

It was established which of vegetable oil used as raw materials could lead to biofuels with better combustion qualities. It has been proved that prepared biofuels have a superior degree of biodegradability and a biodegradability high rate related to all classical petroleum fuels (tables 3-4). For conventional gasoil biodegradability yields are between 10-15% in 21 days (short cycle). For biodiesel, biodegradability yields are between 27-30% in 21 days and for gasoil-biodiesel mixtures biodegradability yields are between 15-27% in 21 days. For long cycles, biodegradability yields are even higher for biodiesel and mixtures gasoil-biodiesel.

Laboratory researches will be finalized by passing to pilot level and than industrial level. In Romania are already a lot of technologies for biofuels preparation from vegetable oil. Biofuels diesel type production at the level forecasted by European Union recommendations for 2010 could be estimated to be 400000 tones /year. This production is based on small and medium enterprises integrated in oleaginous agricultural crops of high productive rate [8]. Although the main component of Diesel fuels remains gasoil produced in refineries – large enterprise. Enterprises that produce biodiesel are considered to be Small and Medium Enterprises.

In the future, biofuels industry will develop continuously together with petroleum industry (fig. 6) – and this is a wise economical decision. The important producers of auto fuels (the great refineries) could build their own biofuels fabrication units, acceding to integrated biorefineries modern concept.

## Conclusions

Technological choice for clean fuels preparation from sunflower oil and crocus oil allowed high yields in useful product (over 90%). The proposed formula could be applied having the same performances for different types of vegetable oils from Romania. Biodiesel prepared from crocus oil has the lowest values for viscosity and freezing point and the highest flash point. Biofuel obtained from soya bean has the better oxidation stability. Samples prepared with biodiesel from sunflower and crocus have a high biodegradability degree. For analyzed raw materials, the best results concerning biofuels properties and biodegradability degree were obtained for crocus oil.

## References

1. MATEI, V., Romanian Auto Fuels and Perspectives for Alternatives", Informative Symposium on Fuel Standards & Regulations "Required Structure of National Standards & Norms for Promoting Biofuels in Romania, 4th of May 2007 – Bucharest – Romania

2. HIS, S., European Energy and Transport Trends to 2030, total consumption for passenger cars in the EU should remain relatively stable between now and 2030, Panorama IFP 2005, Institut Français du Pétrole

3. MATEI, V.,ANTONESCU, N.N., MIHAI.O., DUªESCU,C., BORCEA, A., Petrol si Gaze, 2007, 9, p.58

4. ONUÞU,I.,CONSTANTINESCU,GH. ZGÂIA, I.,STIRIMIN,S., Rev. Chim.(Bucure°ti), **55**, 2004, nr.11, p.924

5. Y. LIN , C., A.LIN, S., Fuel, 86, 2007, p.210

6. KNOTHE, G., JAOCS, 83, 2006, p.823

7. KNOTHE J., J. Am. Oil Chem. Soc, 78, 2001,p. 1025

8. STANICA-EZEANU,D., ONUTU, I., MATEI,V., MATEI, D., Integrated refinery: A complex structure of fossil and bio fuels production - Conference Renewable Resources and Biorefineries Gent, Belgium, 4-6 June 2007

9. WAWRZYNIAK, R., WASIAK, W. AND FRACKOWIAK, Chem. Pap, 59 (6b), 2005, p. 449

10. DEMIRBAS, A, Int.J.Mol. Sci., 8, 2007

11. ABREU, F.R., LIMA, D. G., HAMU, E.H., WOLF C., SUAREZ, P.A.Z., J. Mol. Cata., 2003

12. SCHUCHARDT, U., SERCHELI, R., VARGAS, R. M., J. Braz. Chem. Soc., 9-1, 1998, p. 199

---

Manuscript received: 25.06.2008