TECHNICAL UNIVERSITY OF CLUJ-NAPOCA
Programme: **IDEI**
Proiect ID: **ID_1098;** *Contract no:* **88/01.10.2007**

PHASE 2007

Objectives	Activities
1.1. The analysis of physical-chemical proprieties of fuels ingredients	1.1.1. Acquisition of diesel oil and of bio-fuels
	1.1.2. The analysis of physical-chemical proprieties of bio-fuels ingredients
	1.1.3. The analysis of miscibility and stability limits of the mixtures biodiesel-diesel oil- bioethanol
1.2. Making of researched mixtures biodiesel-diesel oil-bioethanol (BME) recipes	1.2.1. Theoretical evaluation of mixtures proprieties base on constituents proprieties
	1.2.2. Assigning scale of the research fuels B (%) M (%) E (%)

The analysis of physical-chemical proprieties of fuels ingredients
- fuel samples
- the analysis of fuel density, kinematical and dynamic sliminess
- the analysis of the diesel oil main proprieties
- the analysis of sulfur content
- the analysis of minimal inflammability temperature
- the analysis of water content
- the analysis of distillation characteristics
- the analysis of minimal temperature of filtering capacity

The analysis of miscibility and stability limits of the mixtures biodiesel-diesel oil- bioethanol
- materials
- research method
- mixtures making
- the estimation of binary mixtures
- the estimation of ternary mixtures at 15^{o}C degree
- the estimation of ternary mixtures at 0^{o}C degree
- the estimation of ternary mixtures at -8^{o}C degree

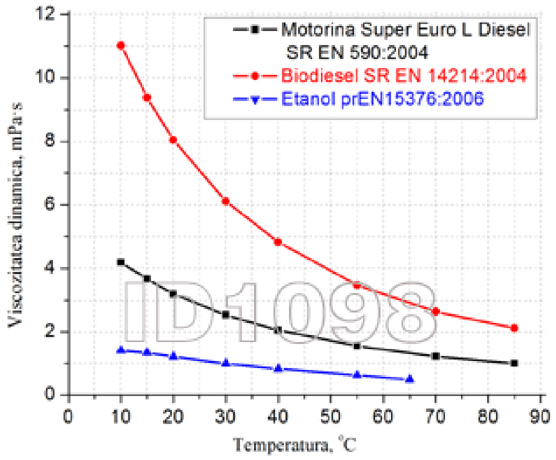
<u>Conclusions regarding the physical-chemical proprieties of fuels ingredients</u>

Fuel samples

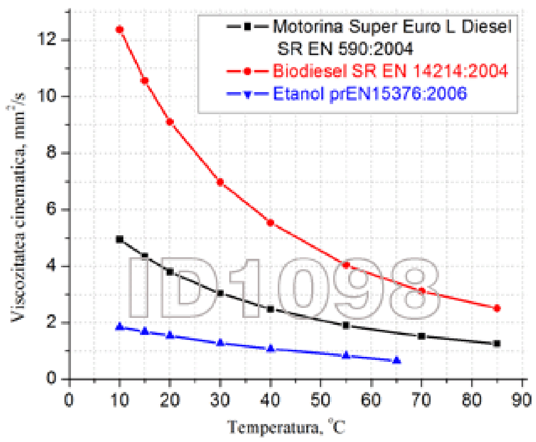
Constituent	Observation
Biodiesel	Made from rapeseed oil by the Analytical Instrumentation Research Institute from Cluj Napoca
Diesel oil	Chosen so that it does not contained EMAG. From technical and operationally reasons on chose diesel oil EURO 5, made by SC PETROTEL LUKOIL SA, under the commercial name “DIESEL OIL SUPER EURO L DIESEL – 0,001”. Fuel sample from type “Diesel oil” was obtained by the mixture of sampling tests from five different gas stations from LUKOIL.
Ethanol	Commerce obtained. Absolute ethylic alcohol (99,3%min) was produced by SC Chemical Company SA

The analysis of fuel density, kinematical and dynamic sliminess

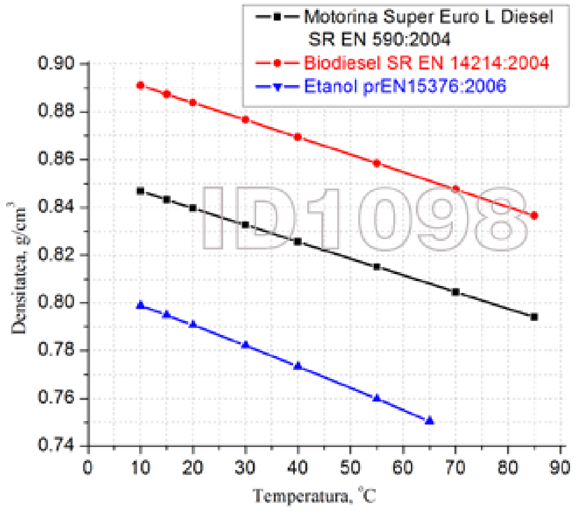
Used equipment : SVM 3000 Stabinger Viscometer
Producer: Anton Paar GmbH, Austria.



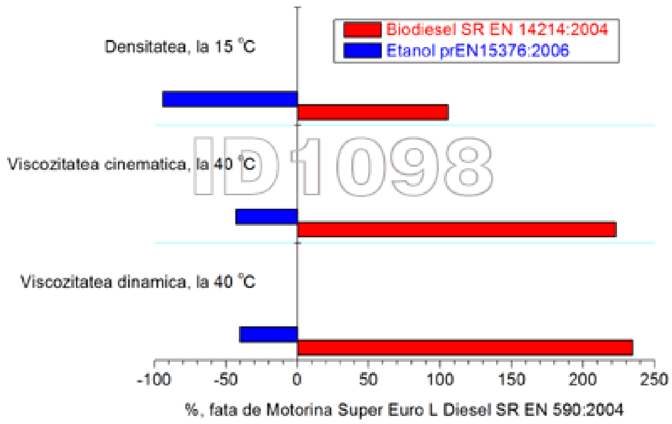
Dynamical sliminess variation with temperature to BME constituents.



Kinematical sliminess variation with temperature to BME constituents.



Sliminess variation with temperature to BME constituents



Density, dynamical and kinematical sliminess variation of used BME constituents compared with diesel oil.

The analysis of the diesel oil main proprieties

Used equipment: IROX 2000 DIESEL
Producer: GRABNER INSTRUMENTS, Austria

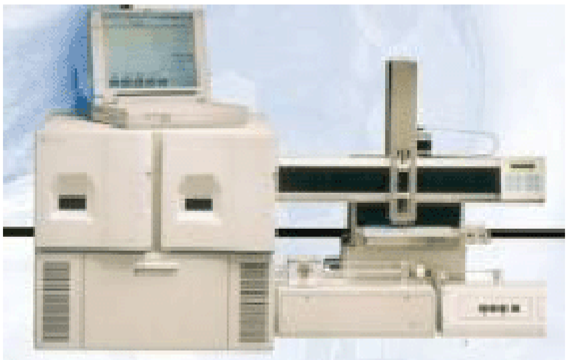
Analysis procedure:

- EN/DIN 22719
- cetane number – ASTM D 613
- cetane index – SR EN ISO 4264, ASTM D 976
- aromatic polycyclic hydrocarbon content – EN 12916
- EMAG content – EN14078
- distilling proprieties: t_{85}, t_{90}, t_{95} (EN ISO 3405, ASTM D 86)

Main proprieties of diesel oil obtained with IROX 2000 DIESEL equipment

No.	Characteristic	Value
1	Aromatic hydrocarbon content	**42.57**
2	Aromatic polycyclic hydrocarbon content	**7.5**
3	Cetane number	**49.3**
4	Cetane index	**48.47**
5	Additives for rising of cetane number	**0**
6	T90	**328.33**
7	T95	**346.67**
8	EMAG content	**0.17**
9	Density at 27,8 °C	**0.854**

The analysis of sulfur content



Used equipment: ANTEK 9000
Producer: PAC, SUA

Analysis procedure: Piro chemiluminescence's, ASTM D 5453

The medium values obtained after the sulfur content analysis for the considered fuels

Fuel	U.M.	Predicted value	Measured value
DIESEL OIL SUPER EURO L DIESEL SR EN 590:2004	mg/kg	Max. 10	**6.8**
BIODIESEL SR EN 14214:2004	mg/kg	Max. 10	**14.95**
BIOETHANOL prEN15376:2006	mg/kg	Max. 10	**1.62**

The analysis of minimal inflammability temperature

Used equipment: MINIFLASH FLP
Producer: GRABNER INSTRUMENTS, Austria

Analysis procedure: EN/DIN 22719

Medium values obtained after minimal inflammability temperature measurement of the considered fuels

Fuel	U.M.	Predicted value	Measured value
DIESEL OIL SUPER EURO L DIESEL SR EN 590:2004	°C	Min. 55	**68**
BIODIESEL SR EN 14214:2004	°C	Min. 120	**>140**
BIOETHANOL prEN15376:2006	°C	Is not provided	**13**

The analysis of water content

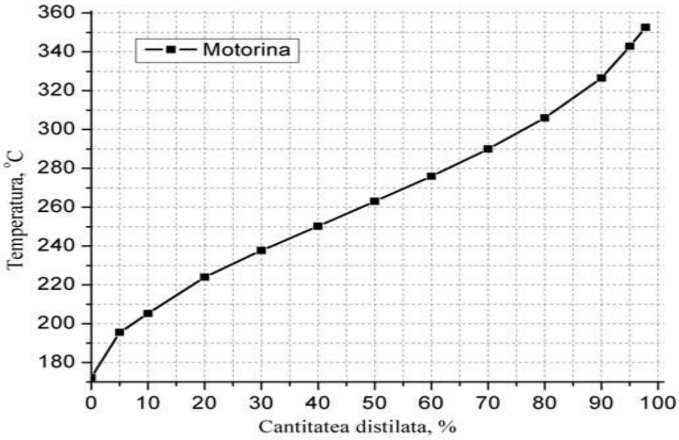
Used equipment: Predicta OM 1000, Model CA21
Producer: a1-envirotech,
Analysis procedure: titration Coulometer Karl-Fischer, EN ISO 12937

Medium values obtained after water content measurement of the considered fuels

Fuel	U.M.	Predicted value	Measured value
DIESEL OIL SUPER EURO L DIESEL SR EN 590:2004	mg/kg	Max. 200	**114**
BIODIESEL SR EN 14214:2004	mg/kg	Max. 500	**1600**
BIOETHANOL prEN15376:2006	% (m/m)	3	**2.3**

The analysis of distillation characteristics

Used equipment: PMD 100
Producer: ISL, France
Analysis procedure: EN ISO 3405

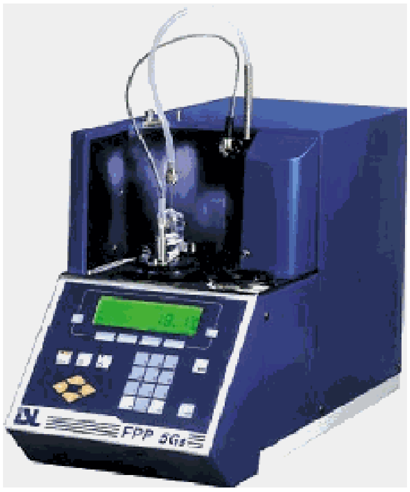


Diesel oil distillation curve in temperature-distillated quantity coordinate.

The analysis of minimal temperature of filtering capacity

Medium values obtained after minimal temperature of filtering capacity measurement of the considered fuels

Used equipment: FPP 5Gs
Producer: ISL, France
Analysis procedure: SR EN 116

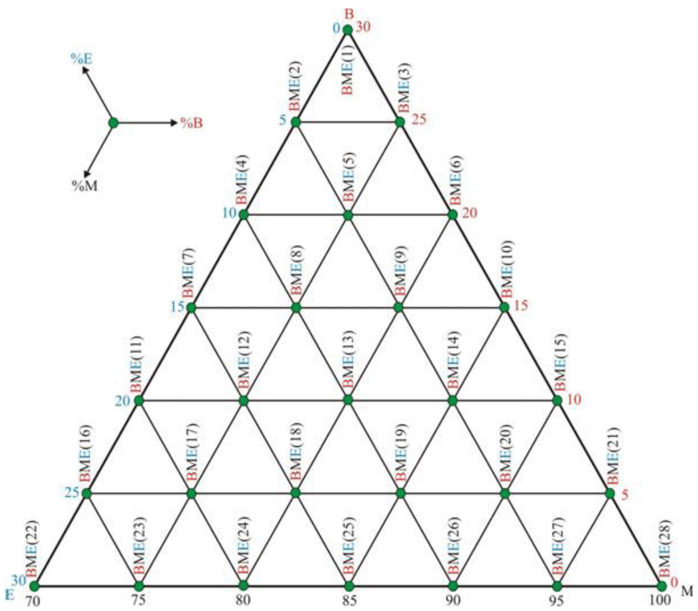


Fuel	U.M.	Predicted value	Measured value
DIESEL OIL SUPER EURO L DIESEL SR EN 590:2004	°C CLASE	-5	**-9 CLASA C**
BIODIESEL SR EN 14214:2004	°C CLASE	Is not provided	**-14 CLASA D**
BIOETHANOL prEN15376:2006	°C CLASE	Is not provided	

The analysis of miscibility and stability limits of the mixtures biodiesel-diesel oil-bioethanol

Materials

The researches aim the mixtures composed by:
– commercial diesel oil without EMAG components,
– biodiesel obtained from rapeseed oil (RME),
– bioethanol.
Having biofuel content (biodiesel + bioethanol) of max. 30%(v/v), in 5%(v/v) steps.
In this phase of the research there are no co solvents used.



Representation of mixtures biodiesel-diesel oil-bioethanol.

Noting of mixtures biodiesel-diesel oil-bioethanol

Mixture	Fuel cod	Mixture	Fuel cod	Mixture	Fuel cod	Mixture	Fuel cod
BME(1)	B30M70	BME(8)	B15M75E10	BME(15)	B10M90	BME(22)	M70E30
BME(2)	B25M70E5	BME(9)	B15M80E5	BME(16)	B5M70E25	BME(23)	M75E25
BME(3)	B25M75	BME(10)	B15M85	BME(17)	B5M75E20	BME(24)	M80E20
BME(4)	B20M70E10	BME(11)	B10M70E20	BME(18)	B5M80E15	BME(25)	M85E15
BME(5)	B20M75E5	BME(12)	B10M75E15	BME(19)	B5M85E10	BME(26)	M90E10
BME(6)	B20M80	BME(13)	B10M80E10	BME(20)	B5M90E5	BME(27)	M95E5
BME(7)	B15M70E15	BME(14)	B10M85E5	BME(21)	B5M95	BME(28)	M100

Research method

Fuel constituents were introduced in the laboratory one day before of mixtures making for them to reach at the 20 degree Celsius existent in the laboratory, and before dosing they were homogenized by agitation.

For mixtures dosing were used 5 and 10 ml squirts and a graduated cylinder of 100 ml, class A.

The samples were homogenized in a balloon which has micro section and glass cork by were strongly agitated. After the disappearance of surface formed foam, the samples were moved in 150 ml glass jars, having a label and a rubber cork, which assure their tight closures.

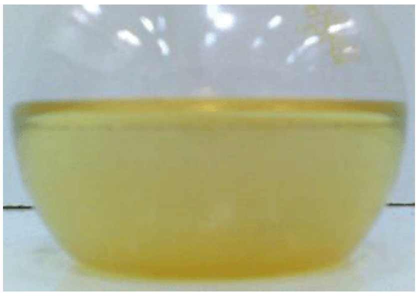
After the making, the mixtures were visual examined, noting down their aspects. The mixtures, kept for 30 hours at the 20 degree Celsius temperature, were visual examined again, after that they were cool down at the temperature of 0 degree Celsius. The experiment has repeated for the -8 degree Celsius temperature (with one degree Celsius above diesel oil riot temperature, which is the biggest one).

For the mixtures cooling on use the deep-freeze compartment of a refrigerator. Findings were write down in cards, and fuel samples were photographed (Appendix 1.11–1.16).

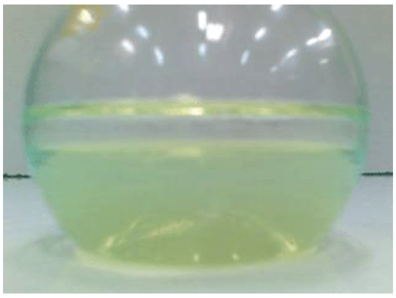
Mixtures making

In the making time on note their aspects before and after homogenization. On seen the followings:

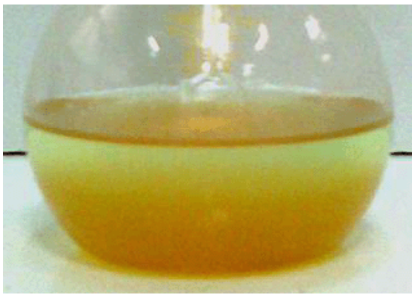
- in dosing time, fuels components make successive layers in the mixture ball, after their density,
- the bioethanol is partially spread in the diesel oil layer making a whitely dispersion,
- the mixtures having a higher biodiesel content that 10% without bioethanol after homogenization makes a milky mixture, half opaque
- the mixtures which contained bioethanol become clear and shade after homogenization, even at lower bioethanol ratio (5% v/v),
- after appreciatively 30 hours of keeping them at 20 degree Celsius temperature all the mixtures become homogenize and clear.



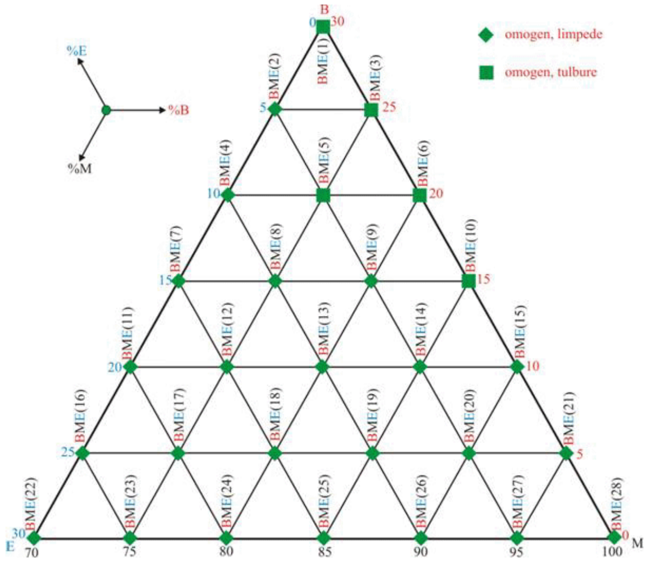
Mixture BME07 (B15M70E15) aspect before homogenization.



Mixture BME22 (M70E30) aspect before homogenization.

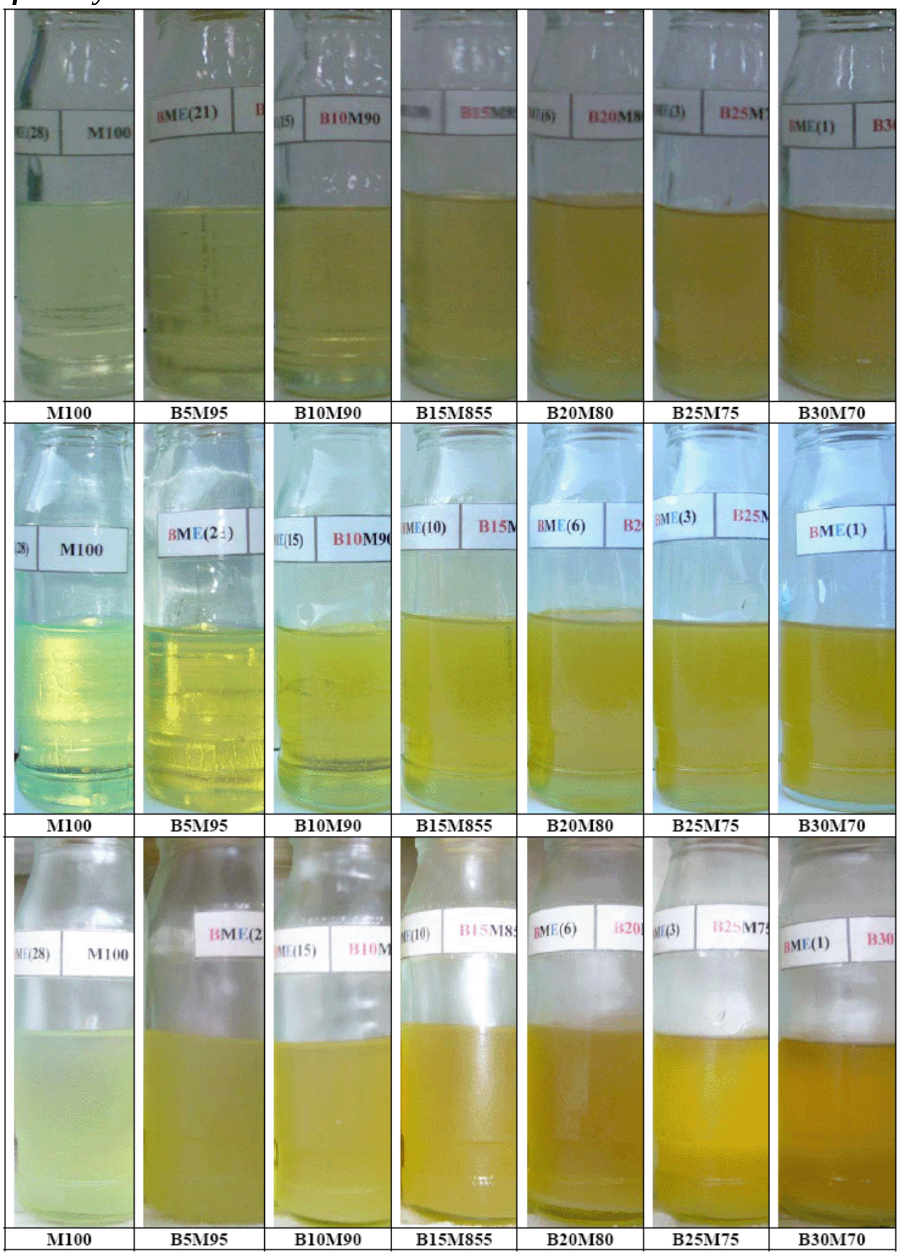


Mixture BME01 (B30M70 aspect before homogenization.

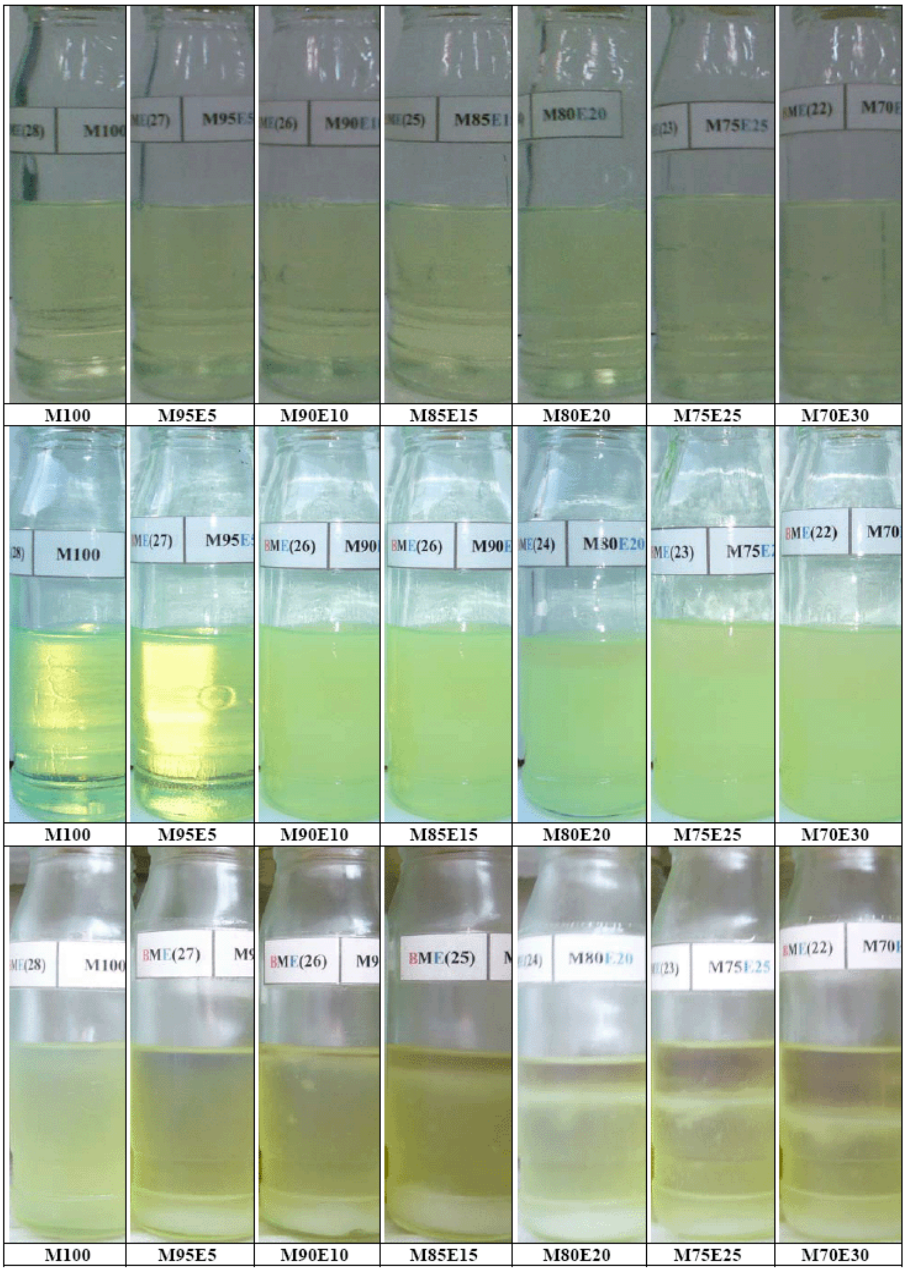


Making of mixtures appreciation.

The estimation of binary mixtures

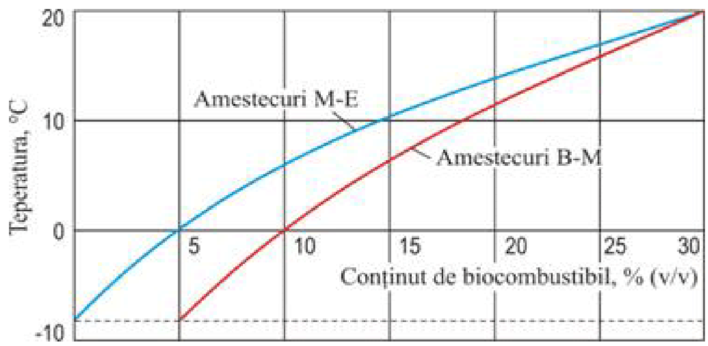


Binary mixtures diesel oil-biodiesel at different temperatures (20°C up; 0°C middle; -8°C down).



Binary mixtures diesel oil-bioethanol at different temperatures (20°C up; 0°C middle; -8°C down).

The binary mixtures diesel oil-biodiesel forming homogeny mixtures when they are prepared and they are stable at the 20 degree Celsius temperature. Once with the temperature decrease, the mixtures become milky, so as at the temperature of -8 degree Celsius only the B5M95 mixture remained clear and shade. The phenomenon is explained by than the minimal filter capacity of used diesel oil temperature is -9 degree Celsius and the milky temperature is only -3 degree Celsius.

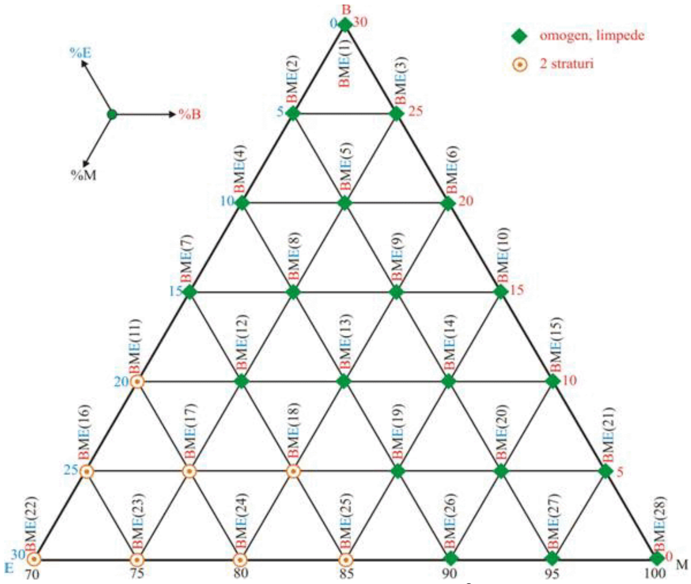


The variation of binary mixtures miscibility toward temperature.

The estimation of ternary mixtures at 15°C degree

On seen the followings:

- only mixtures with a lower bioethanol content until 10% keeps their stability with two exceptions: BME(7)–B15M70E15 and B10MM75E15,
- others mixtures makes two layers: mixture bioethanol-diesel oil easy fractions and mixture biodiesel-diesel oil.



The estimation of mixtures at 15°C degree.

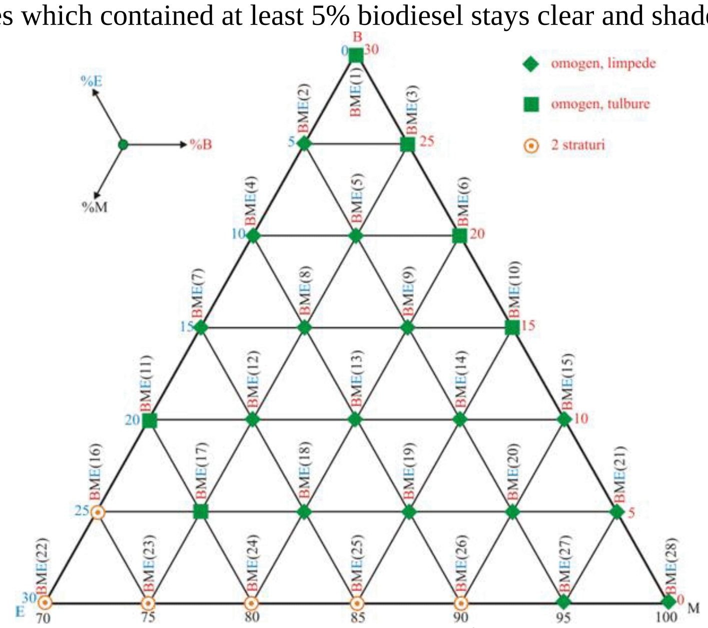
The estimation of ternary mixtures at 0°C degree

The BME mixtures at 0 degree Celsius temperature on can group them in:

- homogeny and clear,
- homogeny and milky,
- Separated in two layers (bioethanol + mixture diesel oil–biodiesel).

On seen the followings:

- The mixtures having until 5% v/v bioethanol stays clear;
- Those who contained 25, respective 30% v/v bioethanol devises them selves in two layers (bioethanol + mixture diesel oil–biodiesel), same as the binary mixture bioethanol–diesel oil with a content higher than 5% v/v bioethanol,
- Ternary mixtures which contained at least 5% biodiesel stays clear and shade.



The estimation of mixtures at 0°C degree.

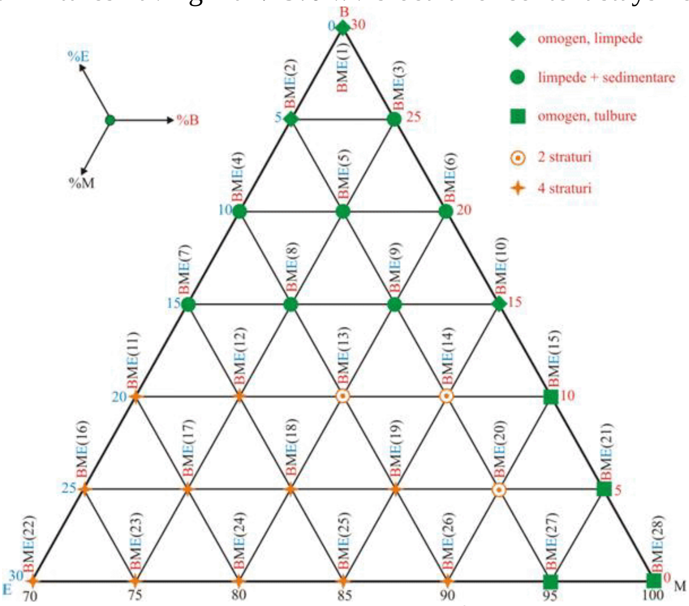
The estimation of ternary mixtures at -8°C degree

At -8°C degree temperature of BME mixtures on have 5 situations:

- Clear and homogeny mixture,
- Clear mixture and whitish sediment (ice crystals),
- Homogeny mixture but milky,
- Separated in two layers (bioethanol + mixture diesel oil–biodiesel),
- Separated in four layers.

This last category is composed from a ethanol layer, follow by a layer of paraffin emulsion, mixture diesel oil-biodiesel and emulsion composed from ice crystals and mixture diesel oil-biodiesel.

Due to higher water content of biofuel components, at this temperature only the M70B30 mixture stayed clear, with no aqueous emulsion sediments (ice).
On seen also that only the mixtures having max.15% v/v bioethanol content stays homogeny.



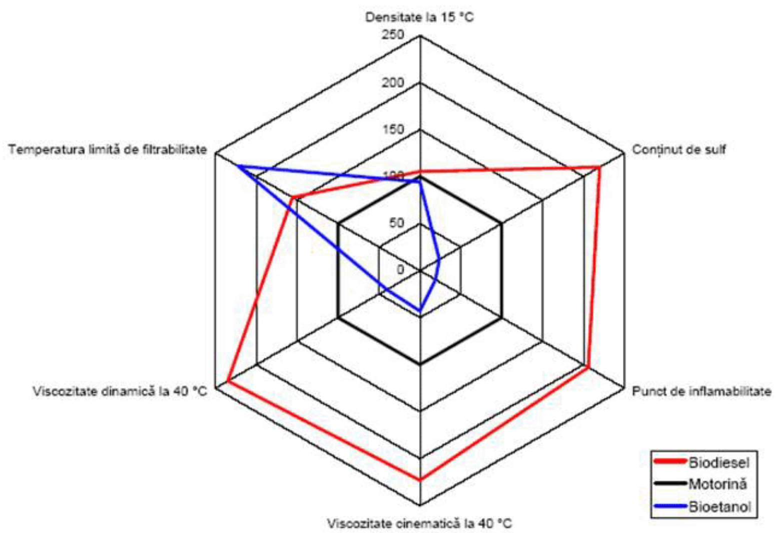
The estimation of mixtures at -8^{o}C degree.

Storage stability refers at fuel capacity of chemical resistance to the changes which appears for long time storage. It is a factor of major importance for biodiesel. Air contact (oxidizing stability) and water contact (water stability) are responsible of storage stability affection. Generally oxidizing is accompanied by fuel sliminess and acidity increasing. Often, the changes are completed by biodiesel color intensity from yellow to brown and the appearance of a paint smell. In the water presence, the esters can hydrolysis to long FFA molecules, which also guide to acidity raise. Generally, the applied methods for diesel oil to solve these problems (ASTM D2274) showed themselves incompatible with biodiesel. Any fuel which will be storage for a long period of time has to be treated with anti oxidizing additives.

Conclusions regarding the physical-chemical proprieties of fuels ingredients

After the research made in this phase on can conclusion the followings:

- Density, kinematical and dynamical sliminess, sulfur content are the most reduced in case of bioethanol, followed by diesel oil, and the measured values for biodiesel are the higher ones,
- On appreciated that this proprieties will compensated each others, higher measured values in biodiesel case will be compensated by lower measured values in bioethanol case,
- Also, minimal filtering capacity temperature is the most lower to bioethanol, follow by biodiesel, the mast high value measured in diesel oil case.



Relative values obtained at the main proprieties analysis of biodiesel and bioethanol toward diesel oil (100%).

Regarding miscibility on can conclude the followings:

- bioethanol–diesel oil–biodiesel mixtures can be made in the proportion presented in table 1.24, them become homogeny and clear after appreciatively 30 hours after they were made,
- the mixtures stability depends on their temperature,
- at 20 degree Celsius the mixtures with a content until 15% v/v bioethanol stay constant,

at 15 degree Celsius

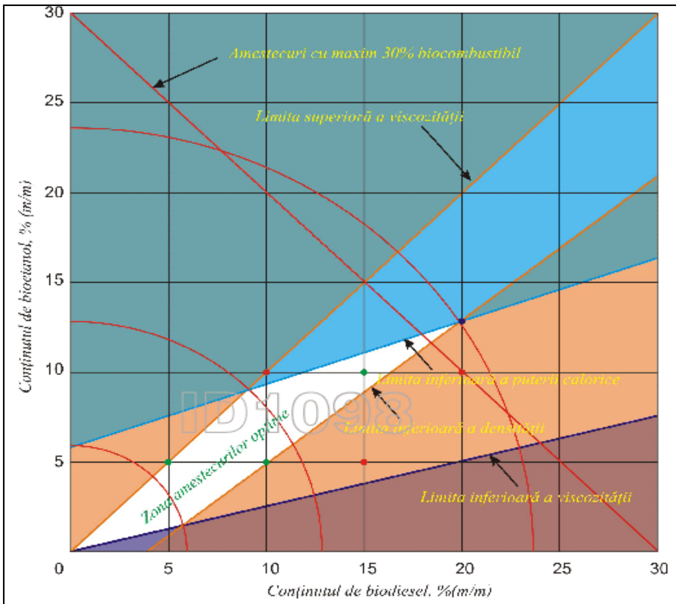
- only mixtures with a content lower than 10% bioethanol keep their stability, with two exceptions BME(7)-B15M70E15 and B10M75E15,
- the others mixtures devise themselves in two layers: mixture bioethanol-diesel oil easy fraction and mixture biodiesel-diesel oil.

at 0 degree Celsius

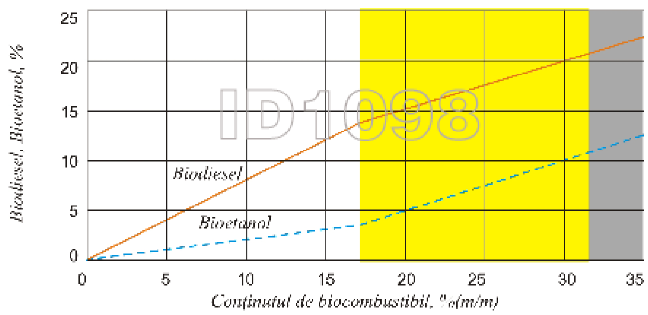
- the mixtures with a content lower than 15% bioethanol stays homogeny (clear or milky), with the exception of binary mixtures, on which the alcohol devise himself,
- over 15% v/v bioethanol on have the devise of alcohol.

at -8 degree Celsius

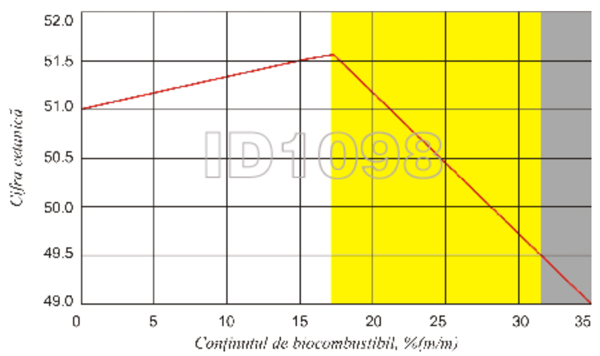
- only BME(1) and BME(2) mixtures can be considered clear, the rest of the mixtures become milky and shows in sediments an emulsion of ice and fuel,
- in the case of mixtures with a middle biofuel content it shows the devise of bioethanol in a superior layer, and at the rest appears also a paraffin emulsion layer.



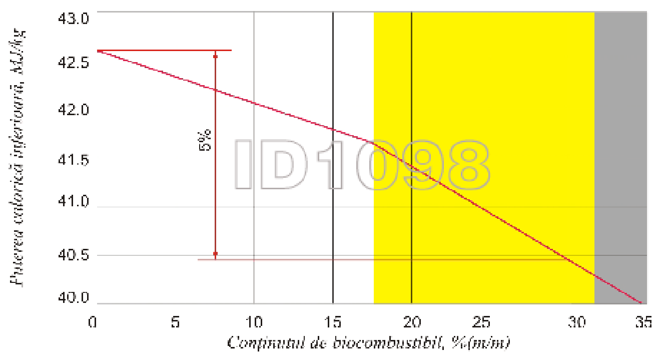
Energetically point of view of optimal mixtures limits.



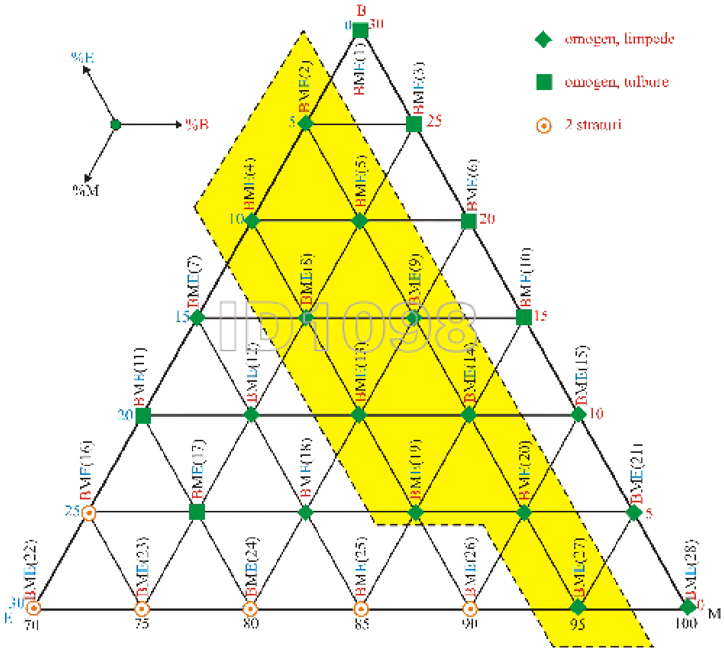
Biodiesel and bioethanol content variation toward biofuel content.



BME mixture cetanic number variation toward biofuel content.



Lower fuel BME caloric power variation toward biofuel content.



Chosen fuel scale.

Mixtures proprieties

Nr.crt.	Mixture	Fuel cod	Biofuel content	Cetanic number	CC variation toward diesel oil	Density, kg/dm^3	Caloric power, MJ	Equivalent coefficient
1	BME(2)	B25M70E5	30	52.60	1.6	0.852	41.10	0.96
2	BME(4)	B20M70E10	30	49.70	-1.3	0.847	40.45	0.95
3	BME(5)	B20M75E5	25	51.85	0.85	0.850	41.24	0.97
4	BME(8)	B15M75E10	25	48.95	-2.05	0.845	40.59	0.95
5	BME(9)	B15M80E5	20	51.10	0.1	0.847	41.38	0.97
6	BME(13)	B10M80E10	20	48.20	-2.8	0.843	40.74	0.96
7	BME(14)	B10M85E5	15	50.35	-0.65	0.845	41.53	0.97
8	BME(19)	B5M85E10	15	47.45	-3.55	0.843	40.88	0.96
9	BME(20)	B5M90E5	10	49.60	-1.4	0.841	41.67	0.98
10	BME(27)	M95E5	5	48.85	-2.15	0.841	41.81	0.98
11	BME(28)	M100	0	51.00	0	0.843	42.60	1.00

Mixtures chemical composition

Nr.crt.	Mixture	Fuel cod	Biofuel content	Water content mg/kg	Sulfur content, mg/kg	Carbon content, % (m/m)	Hydrogen content, % (m/m)	Oxygen content, % (m/m)
1	BME(2)	B25M70E5	30	594.8	8.578	81.496	14.069	4.434
2	BME(4)	B20M70E10	30	629.8	7.912	80.255	14.114	5.631
3	BME(5)	B20M75E5	25	520.5	8.171	81.909	14.197	3.894
4	BME(8)	B15M75E10	25	555.5	7.504	80.667	14.242	5.091
5	BME(9)	B15M80E5	20	446.2	7.764	82.320	14.325	3.355
6	BME(13)	B10M80E10	20	481.2	7.097	81.079	14.369	4.552
7	BME(14)	B10M85E5	15	371.9	7.356	82.733	14.452	2.816
8	BME(19)	B5M85E10	15	406.9	6.689	81.491	14.496	4.013
9	BME(20)	B5M90E5	10	297.6	6.949	83.144	14.579	2.276
10	BME(27)	M95E5	5	223.3	6.541	83.556	14.707	1.736
11	BME(28)	M100	0	114.0	6.800	85.210	14.790	0