Influence of Glycerol on the Liquid Fossil Fuel Characteristics

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Glycerol market had changes that occurred both in the appearance of a surplus of glycerol on the market, as well as a low-price. These changes occurred due to the emergence and the development of biodiesel production. One variant of interest applied on the capitalisation of glycerol resulting from biodiesel production lies in its use in the preparation of liquid fuel with high demand on the market, considering that this oxygenated compounds ensure a clean combustion. Obtaining emulsified fuels with high stability and improved flow characteristics is the way to introduce this type of fuel on the market. The emulsifying of fossil fuels with glycerol was made in mild conditions by stirring with a mechanical stirrer. In the experimental program were prepared mixtures of fuel emulsions varying glycerol content in the presence of a fatty acid monoglycerides emulsifier. Evaluation of prepared emulsions was targeted to determine stability and the specific characteristics of the main fuel (viscosity, calorific value, flash point, freezing point). Based on data obtained it is suggested the manufacture of fuel emulsions with either low, or high concentrations of glycerol.

Keywords: glycerol, liquid fossil fuel, fuel emulsion, emulsion stability

Fossil fuels such as oil and natural gas are currently one of the main energy sources exploited on the planet. Fossil resources are unevenly distributed around the globe and in limited quantity, while annual consumption is growing. Since biodiesel is made from vegetable oils, renewable resources, the prices compared to the production of petroleum products, it is obvious that this fuel gives a greater security in terms of energy. Biodiesel production technology involves a process of transesterification of glycerides with methanol. In addition to the biodiesel process it is obtained as a byproduct glycerol, with mass ratio glycerol / biodiesel approx. 1/10, glycerol for which should be identified new directions for use. Thus the market for glycerol has changed in recent years both in the appearance of a surplus of glycerin and a low level of its price. These changes are due to the emergence and development of biodiesel production. The amount of glycerol resulting from biodiesel production exceeded consumption by about 100% glycerol from existing industrial units.

Glycerol surplus from the market and range of products made from glycerol strongly influenced the price of glycerol. It is estimated that this could decrease of the price of glycerol can be reduced by increasing the diversity of products that are based on glycerol. One way of recovery is the synthesis of functional derivatives such as 1,2 - and 1,3-propanediol by removal of hydroxyl groups from glycerol molecule through hydrogenolysis processes. Another alternative would be glycerol etherification with other alcohols (eg. methanol or ethanol) or alkenes (eg. isobutene) and the production of branched oxygenated compounds, which may have properties suitable for use as fuel component [1]. Catalytic reforming of glycerol in the aqueous phase to obtain hydrogen is another direction of recovery. A variant of interest applied on the recovery of glycerol resulting from biodiesel production lies in its use in the preparation of liquid fossil fuel with high demand on the market considering that this oxygenated compounds ensure clean combustion. The use of oxygenates compounds such as glycerol in the preparation of outbreaks fuel is required both because of its price competitiveness with petroleum fuel prices in the near future and a contribution that will bring these compounds to reduce pollutant emissions from fuels combustion.

Low mutual solubility of fuels and glycerol is the main impediment to the preparation of liquid fuels containing glycerol [2-6]. Homogenization of the two components can be achieved by emulsification [7]. Estimated disadvantages of fuel emulsification with glycerol is the decrease of the theoretical calorific fuel mixture (glycerol has a lower calorific power than petroleum fuels) and the diminish of the burner flame temperature. This loss of theoretical calorific fuel mixture can be compensated by increasing the effective heat of combustion favored by complete combustion of fuel in the presence of oxygenates compounds such as glycerol. Also, lowering the flame temperature favors the concentration of nitrogen oxides from flue gases.

Glycerol-based fuel emulsions containing two liquid practically insoluble, i.e. fuel oil and crude glycerol resulting from biodiesel production must be stable both during storage and at the temperature of the spraying in burner. Thus the preparation of a glycerol-based emulsion fuel involves the use of suitable emulsifiers, stabilizers or promoters. The identification of a cheap emulsifier to reduce the costs of manufacturing followed emulsified fuel. This study was aimed to reduce manufacturing costs of emulsified fuels by identifying a cheap emulsification method.

Glycerol from biodiesel production contains all the high polarity impurities present in vegetable oil subject to transesterification, eg. mono-, di-and triglycerides. Its use in the preparation of liquid fossil fuel requires no additional purification, only conditioning to correct *p*H.

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Table 1
GLYCEROL CHARACTERISTICS

No.	Characteristic	Value
1.	Boiling point, ˚C	290
2.	Densitate la 20˚C, g/cm^3	1.26
3.	Freezing point, ˚C	18
4.	Thermal conductivity at 0 °C, W m^{-1} K^{-1}	0.29
5.	Flash point, ˚C	176.6
6.	Heat of combustion, J/g	18048
7.	Heat of vaporization, at 195 °C, J/g	826.4
8.	Dynamic viscosity at 20 °C, Pa · s	1.410

Table 2
FOSSIL FUEL CHARACTERISTICS

No.	Characteristics	Value
1.	Density at 20˚C, g/cm^3	0.89
2.	Heat of combustion, cal/g	10339.6
3.	Cleveland inflammation, ˚C	96
4.	Viscosity at 20˚C, °E	4.9

Table 3
MONOGLYCERIDES NONIONIC EMULSIFIER CHARACTERISTICS

No.	Characteristics	Value
1	Appearance at 20 ˚C	dark, viscous, liquid
2	Density at 20 ˚C, g/cm^3	0,92
3	Hydroxyl value, mg KOH/g	155

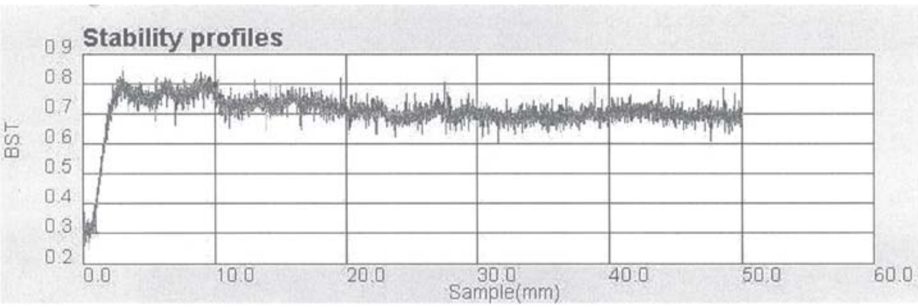

Fig. 1 Stability curve determined on the interval of 10 hours for prepared emulsions

Experimental part

Emulsification process was performed in a laboratory installation, in a batch system, a three-neck glass flask with possibility of programming and maintaining the temperature, fitted with variable speed stirrer. Emulsification process was conducted at the following operating parameters:

-temperature 60°C;

-pressure 1 bar;

-stirrer speed 1200 rpm.

To achieve of the experimental program it had been used technical glycerol whose characteristics are presented in table 1.

The characteristics of liquid fossil fuel and of the emulsifier used in the experiment are presented in tables 2 and 3.

The parameters modified in the emulsified fuels preparation were fossil content, the content of glycerol and nonionic emulsifier. Thus, fossil fuel content of glycerol had values between 5-95% wt., and the emulsifier content compared to the fuel mixture had to range from 0.5-2% wt.

Fuel emulsions prepared were characterized by determining the stability at ambient temperature and the main fuel characteristics: viscosity, heat of combustion, flash point and freezing point.

The stability of the prepared emulsions was evaluated at ambient temperature with Turbiscan Lab apparatus. Radiation transmission profile provides information on the stability of emulsions with clear and cloudy, and the dispersion profile provides information for opaque emulsion stability. Data transmission and dispersion of radiation were recorded every 40 μm, and the period of an analysis was 10 h for each sample.

Viscosity was determined with a rheological viscosimeter of type HAAKE 7 PLUS, caloric power with a calorimetric bomb of type PARR 6200, flash point by means of an inflamommeter Cleveland PETROTEST CL1, and freezing point with a cryostat of type MLW MK70.

Results and discussions

The results obtained in the experimental program are presented in the below graphs. The analysis of data obtained using the Turbiscan Lab Easysoft apparatus shows that prepared emulsions were stable, the stability curves are presented in figure 1.

Dynamic viscosity at 20 °C of the emulsion fuel (fig. 2) shows a variation with a maximum at concentrations of glycerol ranging between 40 and 60%. Maximum viscosity is obtained at higher values of concentration of glycerol to a higher concentration of emulsifier (1.5%). For the area studied concentrations of emulsifier, emulsifier concentration increased the maximum viscosity decreases.

Dynamic viscosity of the emulsion fuel at 45°C temperature (fig. 3) shows a variation with a maximum at concentrations of glycerol ranging from the same values as at 20°C (40-60%). Maximum viscosity is obtained also at a higher concentration of glycerol to a higher concentration of emulsifier (1.5%). For the area studied of

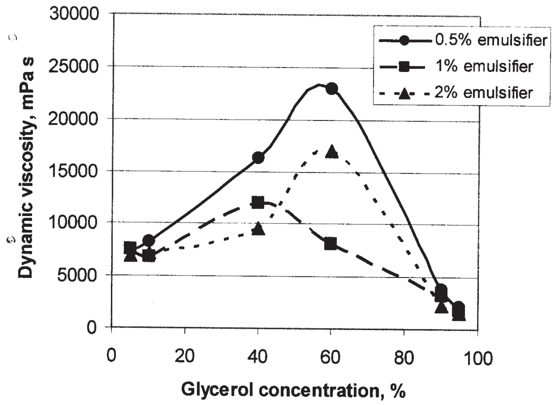

Fig. 2. Influence of glycerol concentration on the dynamic viscosity of the emulsion fuel at 20 °C

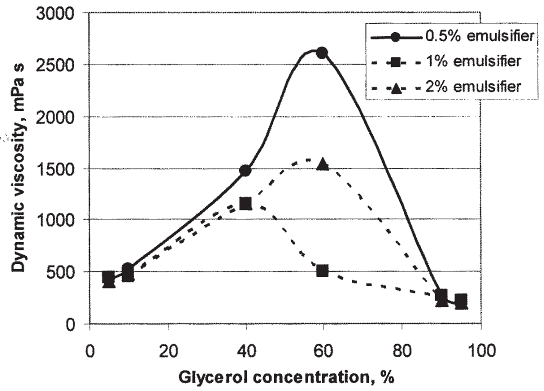

Fig. 3. Influence of glycerol concentration on the dynamic viscosity of the emulsion fuel at 45°C

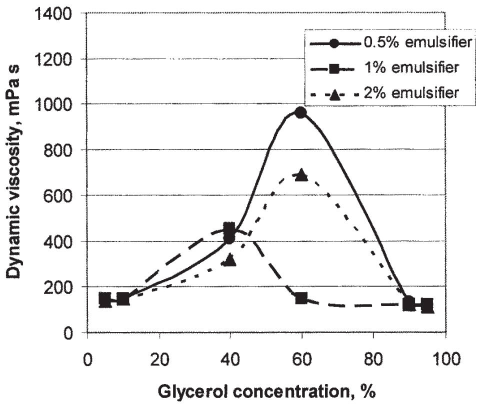

Fig. 4. Influence of glycerol concentration on the dynamic viscosity of the emulsion fuel at °C

the concentrations of emulsifier, emulsifier concentration increased the viscosity and reduces the maximum amount of glycerol concentration at which this maximum is achieved.

Dynamic viscosity at 70°C of the emulsion fuel (fig. 4) shows a variation with a maximum at the same concentrations of glycerol as in tests conducted at temperatures of 20 and 45°C (40-60%); maximum viscosity is obtained also at higher concentration of glycerol to a higher concentration of emulsifier (1.5%). For the area studied concentrations of emulsifier, decreases of the emulsifier concentration lead to an increasing glycerol concentration at which this maximum is obtained as well as the maximum value of viscosity.

For the temperature range studied for the viscosity of the glycerol-based fuel emulsions shows lower values at lower concentrations of glycerol (less than 20%) or high levels of glycerol concentration (85%).

Emulsion fuel heat of combustion decreases with increasing concentration of glycerol, the decrease is almost proportional to the content of glycerol (fig.5); emulsifier concentration insignificantly influencing the calorific power of fuel emulsion.

The flash point of the fuel emulsions shows a complex variation with the content of glycerol emulsion. Thus low values of glycerol content (5-10%) increases exponentially with the flammability emulsion of glycerol content (fig. 6). Variation curve is almost flat at values of glycerol concentration up to 40-60%. For the glycerol concentration values between 60 and 90%, the flash point increases with glycerol concentration after a constant slope, and at concentrations greater than 90% shows up again with a variation. Variation curves are similar to concentrations used in the test emulsifier, emulsifier concentration increased from 0.5 to 2.0% reduces the variation of flammability.

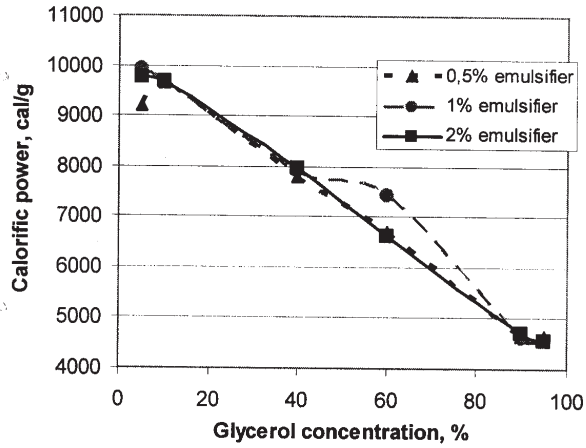

Fig. 5. Influence of glycerol concentration on the heat of combustion of the emulsion fuel

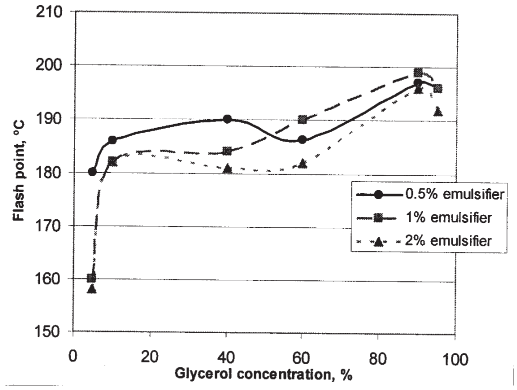

Fig. 6. Influence of glycerol concentration on the flash point of the emulsion fuel

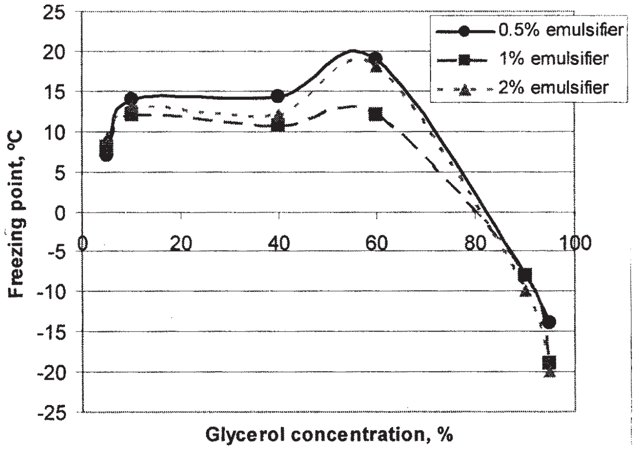

Fig. 7. Influence of glycerol concentration on the freezing point of the emulsion fuel

The freezing point of fuel emulsion based on glycerol (fig. 7) varies with the concentration of glycerol and emulsifier. Thus, at low concentrations of glycerol (less than 10%) the freezing point increases with glycerol content; for glycerol concentrations between 10 and 40%, freezing point varies slightly. For values greater than 40% of glycerol content, variation curve shows a maximum at a concentration of glycerol approx. 60% and for higher concentrations of glycerol 70% the freezing point is negative.

From this point of view it is recommended, as with viscosity, production of emulsions with low concentrations (below 15%) or high concentrations of glycerol (85%). Optimal concentration of emulsifier, in terms of the freezing point is 1%, for which at intermediate concentrations of glycerol, freezing temperature variation is lower than at concentrations of 0.5 and 2% emulsifier.

Conclusions

Characteristics variation of the emulsions fuels with the glycerol content of the emulsion reveals complex changes of the glycerol/ fossil fuel with their glycerol content.

The stability of emulsions prepared with nonionic emulsifier type fatty acid monoglycerides, determined with a Lab Turbiscan Easysoft apparatus is very good, the stability curves are similar for all prepared emulsions.

Emulsion viscosity of glycerol-based fuels varies depending on the concentration of glycerol and emulsifier, so it shows lower values at lower concentrations of glycerol (less than 20%) or greater (85%).

Heat of combustion of glycerol-based fuel emulsions decreases with increasing glycerol content, the decrease is almost proportional with the content of glycerol.

Flash point of glycerol-based fuel emulsions is modified with glycerol content; so the prospect of using these emulsions in combustion processes recommended fuel emulsion with a low content of glycerol which shows a lower flammability.

Freezing point of glycerol-based fuel emulsions varies with glycerol content; in this regard it is recommended manufacture of emulsions or with low concentrations (below 15%) or high concentrations of glycerol (over 85%). After the evaluation it is recommended the manufacture of fuel emulsions to be prepared either at low or at high concentrations of glycerol.

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