Glycerol Based Fuel Emulsions

DORIN BOMBOS[1]*, ION BOLOCAN[1], MIHAELA BOMBOS[2],GABRIEL VASILIEVICI[2], EMIL ZAHARIA[3]
[1] Petroleum - Gas University of Ploiesti, 39 Calea Bucuresti,100520, Ploiesti, Romania
[2] National Institute for Research Development for Chemistry and Petrochemistry- ICECHIM-Bucuresti, 202 Splaiul Independetei, 060021, Bucuresti, Romania
[3] Atica Chemicals, 202 Cazanesti Str., Rm Valcea , Romania

Fuel emulsions using represents a method of diminution of pollutant emissions resulted from burning of liquid petroleum fuels. The selection of fuel emulsions with a high stability and improved flowing characteristics represents the introducing method of this type of fuels on market. Emulsifying of liquid stoker fuels was achieved by using glycerol in mild working conditions by a mechanical stirrer mixing. In the experimental part there were prepared fuel emulsions which differ by glycerol and fuel oil proportion and by emulsifier type. Characterization of prepared emulsions considered in the first step determination of stability for prepared emulsions and then, determination of main characteristics specific to fuels (caloric power, flash point, viscosity, freezing point).

Keywords: glycerol, fuel emulsion, emulsifier, emulsion stability

Fossil fuels evolve polluting emissions after burning, whose toxicity increases with aromatic hydrocarbons content (especially of polycondensated aromatics), with petroleum resins content and most of all, with asphaltenes content increasing. The perfection of oil processing technologies has as a goal the increase of yield to fuels (automobile gasoline and diesel oil), process which restricts the actual range of residual fractions resulted from these processes [1]. Thus, in compositions of these fractions there are found ordinarily high molecular weight hydrocarbons with a complex chemical structure (naphtyl-aliphatic hydrocarbons with branched chains, alkyl-aromatic hydrocarbons with mono- and polycondensed nuclei, etc.), petroleum resins and asphaltenes, compounds which limit the perspective that these fractions would be superior valorificated, but only for stroke fuels preparation. No matter the development of technique in domain of fuels, these classes of compound can not burn completely both due to a lower inflammability and of a complex structure.

Preocupations regarding diminution of polluting emissions from burning gases were focused especially to exhaust gases, being neglected the contribution of burning gases eliminated from industrial furnances, which operate with liquid fuels, to environmental pollution [2-4]. Thus, in composition of automobiles gasoline there were introduced oxygenated compounds as methyl-tert-buthyl ether, ethyl-tert-buthyl ether, tert- amyl-methyl ether and recently, bioethanol and ethers of glycerol with isobutene [5]. Likewise, diesel engines fuel contains methyl esters of fatty acids. All these biofuels are oxygenated compounds, their use favorizing the complete burning of fuels.

The use of biofuels for combustibles preparation was possible when their price became competitive to petroleum fuels price. The implementation of this policy to stroke fuels is possible as long as there are identified on market oxygenated compounds which can be used as biofuels and whose price is competitive to that of fossil liquid stroke fuels [6]. This tendency will permit the improvement of burning process by reducing of noxious burning gases content and implicit by reducing environmental pollution.

In this paper there is proposed the use of a renewable oxygenated compound, available on market, for preparation of stroke fuels which can assure a complete burning, obtaining glycerol as a secondary product from biodiesel production. The availability of glycerol on market is determined by the increase of biodiesel production, glycerol being the secondary product resulted from biodiesel production, which is obtained in proportion of about 10% compared to this. Thus, glycerol production as a biofuel for preparation of liquid stroke fuels is important both because of this contribution to reducing of pollutant emissions resulted from burning by a high oxygen content, and due to this price competitiveness compared to price of petroleum fuels.

The implementation of this method of fabrication of stroke fuels presents the following advantages:

-maximum temperature from the furnance and implicit NO_x content from burning gases are reduced because of the lower caloric power of glycerol compared to that of classic stroke fuels;

-presence of water or another additives in system (bioethanol, biobuthanol) favorizes reducing of glycerol freezing point and implicit of emulsions containing glycerol and increases vapor pressure of mixture;

-glycerol viscosity decreases significantly with temperature increasing, depression diminuting with the increase of mixture water content.

Difficulties of apllying of this liquid stroke fuels preparation method are determined by some glycerol characteristics:

-reciprocal solubility to petroleum fuels is low;

-glycerol density is over 25% higher than that of petroleum fuels;

-boiling point is relatively high and it will influence negatively the inflamability of fuel to be mixed;

-freezing point is also higher than that of usual petroleum fuels and influences negatively the manipulation of fuel at temperatures lower than 15°C.

Because of a very low reciprocal solubility and a high density difference between the two components[7], homogenization of petroleum fuels containing glycerol can be achieved only by emulsification. Thus, emulsification

---

Tel.: (+40) 0745637623

Table 1
CHARACTERISTICS OF RAW MATERIALS USED FOR THE EXPERIMENTS

Component	Flash point, °C	Freezing point, °C	Caloric power, cal/g
Fuel oil	53	-3.2	10100
Glycerol	177	17	5000

represents an efficient method of homogenization of mixture fuel oil-glycerol and it eliminates disadvantages generated by the accidental presence of water in stroke fuels reservoirs.Such mixtures would permit a better dispersion of the vaporized fuel in the burning area, favorizing a complete combustion and the pollution reducing by presence of oxygenated compounds in this area.

In order to evidence this aspect, in present work we achieved an experimental study regarding testing of some different emulsifier classes to obtain some emulsifiers formulations for preparation of emulsified stroke fuels with improved characteristics. The selection of surfactants used for obtaining of glycerol based fuel emulsions considered their emulsioning capacity and obtaining of superior characteristics after emulsification of respective fuel [8,9].

There were selected two imidazoline type cationic emulsifier of some fatty acids and a non ionic surfactant of nonilfenol ethoxylate type with nine ethyleneoxide molecules.

Experimental part

The experiments were performed in steady regime, on a Berghof autoclave type reactor made of stainless steel, with a capacity of 600 mL and provided with mechanical stirring. The autoclave heating was electrically performed, with the automatic temperature setting. Glycerol was of analytical grade, the most important characteristics of glycerol and fuel are presented in table 1.

In the experimental programme there were used two cationic emulsifiers of type 2-alkyl, 1-polyethylene-polyamine-imidazoline (ROT 1 and ABR from Atica Chemicals), with an amine nitrogen content of 7.52% wt and 3.58% wt. and a non ionic emulsifier NF 9 from Huntsman Company. The conditioning of cationic emulsifier before using was made in glycerol phase at an acid pH. The emulsifier concentration in the reaction mixture had values between 0.75 and 2% wt.

The experiments were performed at 80°C, during 2.5 h and stirring turation was maintained at 1300 rot/min for all experiments. Glycerol content of emulsions varied between 60-75% wt. The prepared fuel emulsions were characterized by determination of the most important characteristics specific to fuels (flash point, freezing point, caloric power and viscosity) and testing of emulsions stability at room temperature.

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

For study of some emulsions stability it was used an apparatus TURBISCAN LAB EASYSOFT. The light source is an electroluminiscent diode in the domain of near IR (λair=880nm). An optical sensor receives light transmitted to sample at 45°C; there were used 55 mm height cells, data for transmission and dispersion of radiation being registered for each 40 μm, and duration of an analysis was of 10 h for each sample.

Results and discussions

The influence of emulsifier content

The influence of emulsifier content upon emulsification process of mixture glycerol- fuel oil was studied for a cationic emulsifier of imidazoline type (ABR) and for a mixture of emulsifiers containing 67% wt. emulsifier ABR and 33% wt. emulsifier NF 9.

Variation of main characteristics of these emulsified fuels is presented in figures 1-6. From figure 1 it is observed that for emulsion containing 65% glycerol, flash point varies with content of cationic emulsifier of type ABR after a curve which presents a maximum at a value of about 1% wt. emulsifier. Lower or higher values of the emulsifier content favorize the decrease of emulsified fuel inflammability; thus, from this point of view it is preferred a content of 0.75% wt. of emulsifier ABR, for that flash point is lower which represents an advantage for combustion installations.

This behaviour can be explained by the influence of emulsion type upon vaporization rate for more volatile molecules; thus, cationic emulsifier which was used favorized the obtaining of a direct emulsion and evaporation rate for volatile compounds from the discontinous phase depends on the size of this phase and on the thickness of the emulsifier film around discountinous phase drops (fuel oil). Thus, at low emulsifier concentrations, the size of fuel oil drops is higher , diminishing the mass transfer of volatile fractions from fuel oil, and at higher emulsifier concentrations increases also the thickness of emulsifier film around the fuel oil drops, stopping mass transfer of volatile fractions from fuel oil.

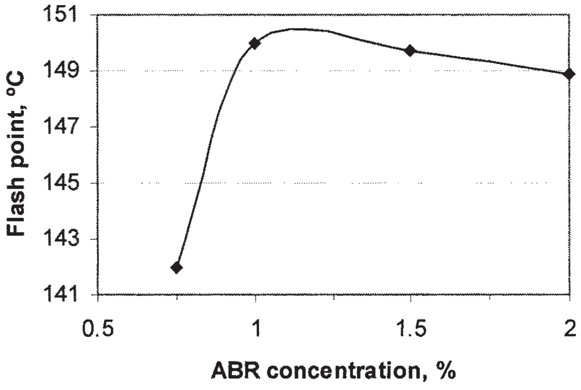

Fig.1. Variation of emulsion flash point versus ABR emulsifier content, for an emulsion content of 65% glycerol

From figure 2 it is observed that freezing point of fuel emulsion containing 65% glycerol increases with cationic emulsifier content increasing, which is attenuated at higher values of the emulsifier content; thus, for a ABR emulsifier content of 0.75%, freezing point of emulsion is lower, which represents an advantage for use in combustion installations during winter. This behaviour can be awarded to higher solubility of the emulsifier in glycerol phase, the emulsifier favorizing glycerol crystalization after micellization.

A lower value of the emulsion viscosity favorizes a more efficient combustion of fuel in burner. From figure 3 it is observed that viscosity of the fuel emulsion is influenced by the cationic emulsifier concentration for an emulsion content of 65% glycerol. Thus, viscosity of the fuel emulsion

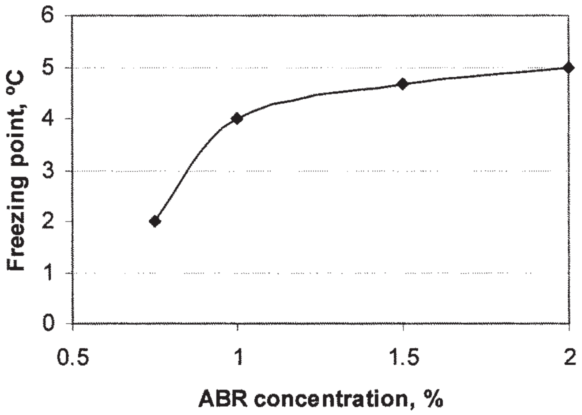

Fig.2. Variation of freezing point of the emulsion versus ABR emulsifier content, for an emulsion content of 65% glycerol

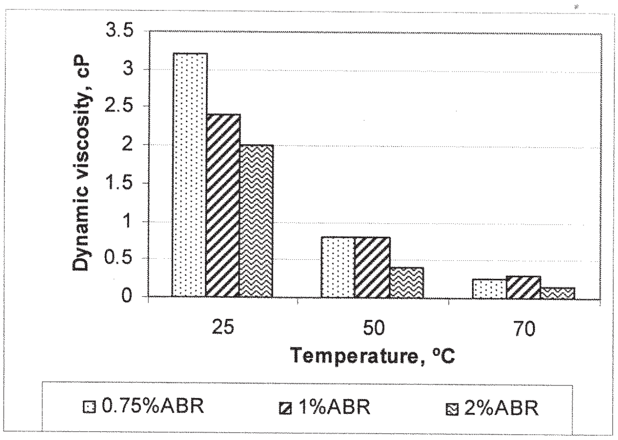

Fig.3. Variation of the emulsion viscosity at 25, 50 and 70°C versus ABR emulsifier content, for an emulsion content of 65% glycerol

containing 2% emulsifier is lower than that of emulsions with a lower emulsifier content, both at 25 and at 50, 70 °C. The increase of ABR emulsifier favorizes the obtaining of a larger distribution of drops size, which determines diminution of frictions between emulsion layers and implicit, a better flowing.

From figure 4 it can be observed the same aspect as in case of use of cationic emulsifier - nonionic emulsifier mixture, for emulsion containing 65% glycerol, flash point varies with the emulsifier content, but after a curve which presents a minimum at a value of about 1% wt. emulsifier. Lower or higher values of the emulsifier content favorize the increase of fuel emulsion inflammability, thus from this point of view it is preffered a content of about 1% wt. emulsifier mixture.

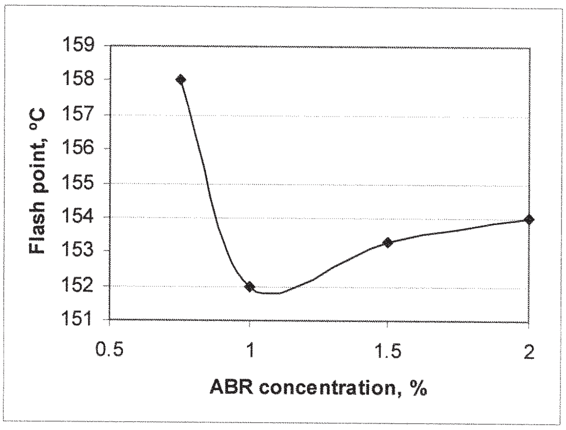

Fig.4. Variation of flash point versus ABR +NF 9 emulsifiers mixtures, for an emulsion content of 65% glycerol

This behaviour can be explained by the influence of nonionic emulsifier upon evaporation rate of more volatile molecules from fuel oil; thus, even if both emulsifier favorize the obtaining of a direct emulsion, presence of nonionic emulsifier increases migration rate of volatile fraction from fuel oil at concentrations of about 1% emulsifier mixture.

From figure 5 it is observed that freezing point of fuel emulsion prepared with a mixture of cationic and non ionic emulsifiers, presents a variation to minimum; thus, for emulsifiers mixture content of about 1%, freezing point of emulsion presents a minimum variation. This modification of the emulsion behaviour after non ionic emulsifier adding can be awarded to interractions between hydroxil groups of glycerol and those of nonilfenol ethoxylate molecules. These interactions diminutes glycerol crystallization tendency for low values of ethoxylate molecules and at higher values of non ionic emulsifier concentration this interraction is reduced.

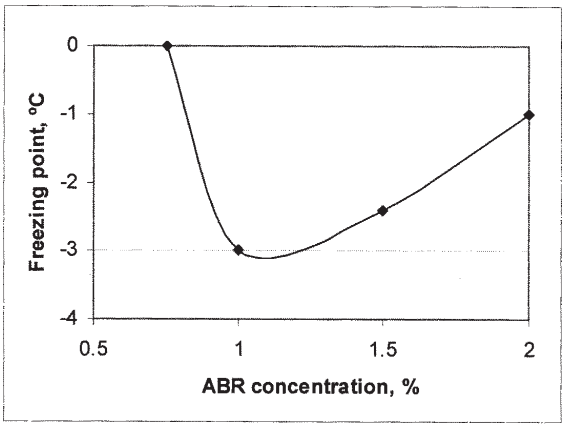

Fig.5. Variation of emulsion freezing point versus ABR+NF 9 emulsifier content, for an emulsion content of 65% glycerol

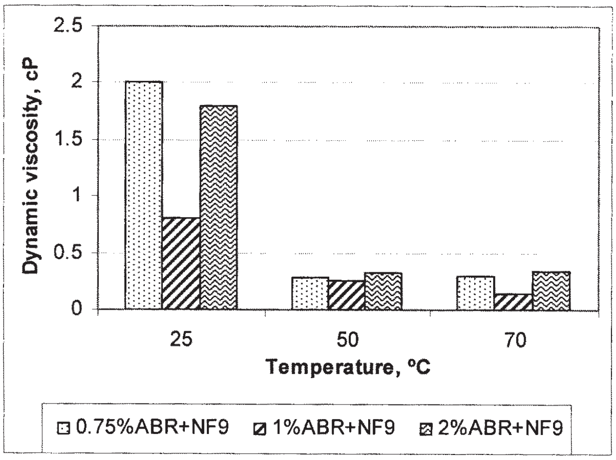

Fig.6.Variation of emulsion dynamic viscosity at 25°C, 50°C and 70°C versus emulsifiers content of 67% ABR and 33% NF9

Presence of nonionic emulsifier has modified variation of fuel emulsion viscosity to content of emulsifiers mixture for the same content of 65% glycerol as it can be observed from figure 6. Thus, viscosity of fuel emulsion containing an intermediary concentration of emulsifier (1%) is lower both at 25 and at 70°C. It is possible that nonionic emulsifier presence to favorize the obtaining of a large distribution of drops size and implicit it determined diminution of frictions between layers, improving flowing.

The influence of glycerol content

From figure 7 it can be observed that for emulsion prepared with ROT cationic emulsifier, which presents a

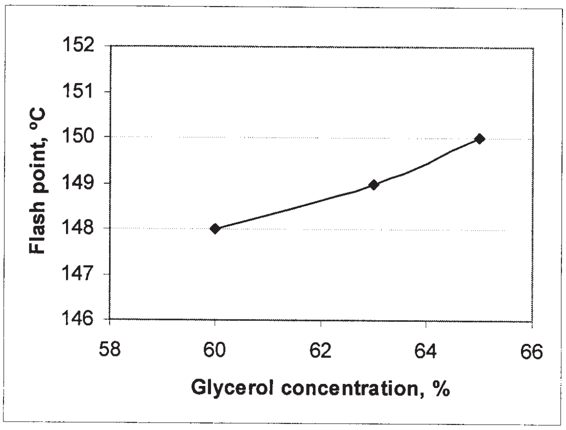

Fig.7. Variation of emulsion flash point temperature versus glycerol content (for a ROT emulsifier content of 1%)

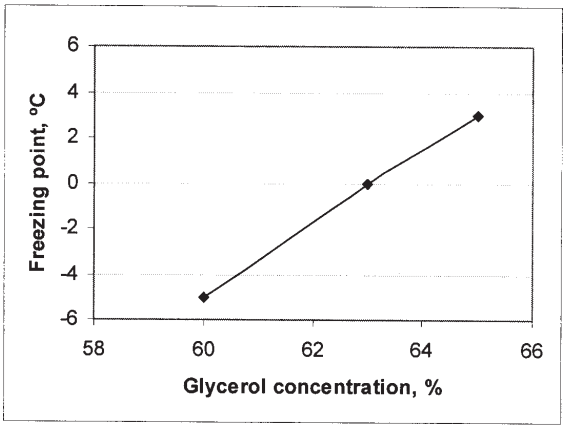

Fig.8.Variation of emulsion freezing point to glycerol content (for a ROT emulsifier content of 1%)

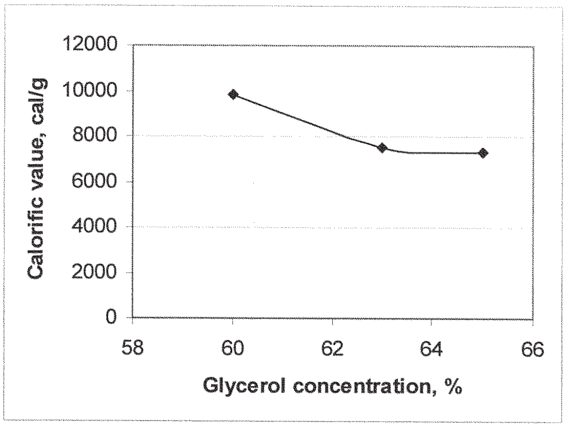

Fig.9.Variation of emulsion caloric power versus glycerol content (for a ROT emulsifier content of 1%)

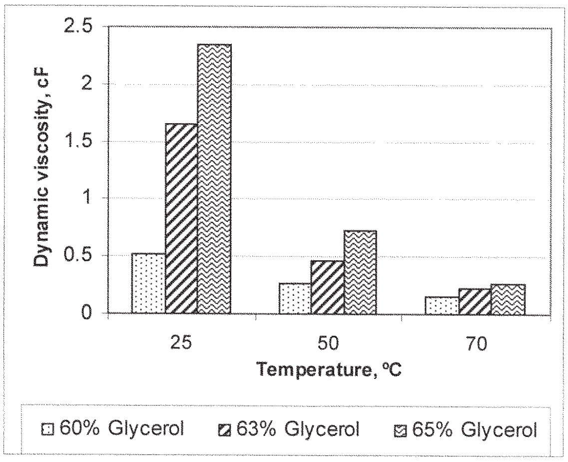

Fig.10.Variation of dynamic viscosity at 25°C, 50°C and 70°C versus glycerol content (for a ROT emulsifier content of 1%)

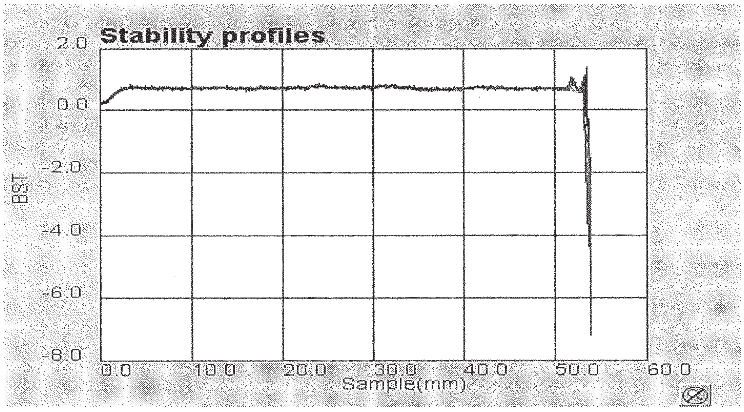

Fig.11.Stability curve determined on the interval of 10 hours for prepared emulsions

higher emulsioning capacity than ABR, flash point increases proportionally with glycerol content. This behaviour is explained by diminution of penetration rate of glycerol continous phase by volatile compounds from discontinous phase to increase the glycerol emulsion content.

Freezing point of fuel emulsion increases with glycerol content as it can be observed from figure 8. This behavior is due to higher value of freezing point of the continous glycerol phase, increase of its concentration favorizing emulsion freezing at higher temperatures.

Caloric power of emulsion decreases with glycerol content, this decrease being attenuated by glycerol content rising, as it can be observed from figure 9; considering that glycerol presents a lower caloric power than that of fuel oil, this behavior is normal.

It is observed from figure 10 that viscosity of fuel emulsion decreases with temperature increasing, this being more evidenced for a higher glycerol content; for the same temperature, viscosity increases with glycerol content, the increase being more accentuated at lower temperatures. This variation is encouraging for users of these types of fuels, who would use emulsions with a higher glycerol degree, correction of viscosity at burner being achieved at non significant increases of temperatures for that emulsion.

After testing on a Turbiscan type apparatus designed for emulsions stability determination, it was demonstrated that all prepared emulsions were stable, stability curves presenting a similar shape (fig.11).

Conclusions

Flash point of glycerol based fuel emulsions increases with glycerol content, but it varies function of type and concentration of emulsifiers used for preparation of these emulsions. Thus, when using ABR cationic emulsifier, inflammability of fuel emulsion varies to maximum and in case of use of a cationic emulsifier – nonionic emulsifier mixture inflammability varies to a minimum, for concentrations domain of studied emulsifiers.

Freezing point of glycerol based fuel emulsions increases with glycerol content, but it varies also function of type and concentration of emulsifiers used for preparation of these emulsions. Thus, in case of ABR cationic emulsifier using, freezing point of fuel emulsion varies to a maximum and in case of use of a cationic emulsifier – nonionic emulsifier mixture its freezing point varies to a minimum.

Viscosity of glycerol based fuel emulsions varies function of type and concentration of emulsifiers used for preparation of these emulsions; thus, this decreases with temperature increasing and it increases with emulsions glycerol content and caloric power of glycerol based fuel emulsions decreases with glycerol content increasing.

Stability of prepared emulsions was high both in case of using of a cationic emulsifier with a lower emulsification capacity, and in case of using a cationic emulsifier – non ionic emulsifier mixture.

The backscattering profiles of the emulsions prepared performed with the Turbiscan Lab denote a satisfactory stability of all emulsions
studied

References

1. SUCIU, Gh., s. a., Ingineria Prelucrării hidrocarburilor, Ed. Tehnică, Bucureşti, 1999
2. KADOTA, T., YAMASAKI, H., Progress in Energy and Combustible Science, 2002, 28, p. 385
3. NENSHO, TARO, HANNO, HANAKO, KEISOKU, KAZUO, JIKKEN, Kenichi, www.combustionsociety.jp
4. BUZUKOV, A. A., TIMOSHENKO, B. P., Combustion, Explosion, and Shock Waves (Historical Archive), 1995, 31(4), p.419
5. MANGOURILOS, V., BOMBOS, D., JUGANARU, T., BOLOCAN, I., BOMBOS, M., CIUPARU, D., Rev. Chim. (Bucharest), **60** , no. 12, 2009, p.1338
6. GARO , J.P. , VANTELON, J.P., SOUIL, J.M., BREILLAT, C., Experimental Thermal and Fluid Science, 2004, 28, p.753
7. *** Ullman's Encyclopedia of Industrial Chemistry, Fifth Edition on CD-ROM, 1998
8. OLDFIELD, A. S., THOMPSON, L., MAYER, B., ROWE & MAW LLP, US Patent 20050060928 / 2005.
9. D'ELIA, L., SCORLETTI, P., RAUSA, R., RIVOLTA, G., De AMICIS, A., AMBROSINI, T., OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., US Patent 20060123695 / 2006.

Manuscript received: 16.11.2009