

# Processing of the glycerol fraction from biodiesel production plants to provide new fuels for heat generation

Nerijus Striūgas<sup>1</sup>,

Anupras Šlančiauskas<sup>1</sup>,

Violeta Makarevičienė<sup>2</sup>,

Milda Gumbytė<sup>2</sup>,

Prutenis Janulis<sup>2</sup>

<sup>1</sup>Laboratory of Combustion Processes, Lithuanian Energy Institute, Breslaujos 3, LT-44403 Kaunas, Lithuania  
E-mail: striugas@mail.lei.lt

<sup>2</sup>Laboratory of Chemical and Biochemical Research for Environmental Technology, Lithuanian University of Agriculture, Studentų 11, LT-53361 Akademija, Kaunas district, Lithuania  
E-mail: agrotech@lzuu.lt

With the increasing production of biodiesel fuel, we encounter the problem of how to make use of the glycerol by-product. The purpose of this research was to evaluate the possibility of using technical glycerol (80% purity) and the glycerol fraction (up to 60% purity) for heat generation.

The research examined the use of glycerol to produce “fuel emulsions” which are emulsions containing heavy fuel oil. The use of these HFO directly as heat sources is limited because of their high sulphur content. In this study, the stability of the emulsions was assessed based on their composition. The results show that stable emulsions can be prepared when they contain 27–34% of glycerol and 27–34% of heavy fuel oil. Emulsifiers can also be used to increase the stability of emulsions; two examples of emulsifiers are fatty acid monoglycerides (optimal concentration, 1.5–3%) and soaps (optimal amount, 1.3%), both being found in the glycerol fraction obtained as a by-product during the production of biodiesel fuel.

This article presents the results and analysis of comparative combustion investigations carried out on samples of stable emulsions and of technical glycerol. Over the entire load range used during the experimental combustion tests of technical glycerol, the concentrations of NO<sub>x</sub> (~90 mg/m<sup>3</sup>), CO (40–130 mg/m<sup>3</sup>), and SO<sub>2</sub> (0–10 mg/m<sup>3</sup>) in the flue gases did not exceed the permissible levels of pollutants emitted from fuel combustion plants, as specified in EU Council Directives.

Burning these fuel emulsions leads to the production of 993–1074 mg/m<sup>3</sup> sulphur dioxide (SO<sub>2</sub>) in the oxides, which is up to six-fold less than the concentration produced by burning pure heavy fuel oil. In addition, as the concentrations of nitric oxides (NO<sub>x</sub>) in the flue gases fall into the range 250–280 mg/m<sup>3</sup>, the emission of particulates also significantly decreases.

**Key words:** glycerol, heavy fuel oil, fuel emulsion, combustion, emission.

## 1. INTRODUCTION

The volume of biodiesel fuel produced around the world continues to increase. Declining fossil fuel supplies and climate change due to greenhouse gas emissions are driving this expansion in production. Indeed, these factors led the EU and national governments to issue new regulations, among them one of the most important: Directive 2003/30/EC of the European Commission, which calls for fulfilling 5.75% of total fuel consumption with biofuels by 2010 [1].

Currently, the volume of biodiesel fuel – specifically, fatty acid methyl esters – produced in the European Union is rapidly increasing. The EU has undertaken to provide the market with at least 11 million tons of biodiesel fuel per year until 2010 [2, 3]. Germany leads in this area: its production capacities in 2007 exceeded 4 million tons per year. The production of biodiesel fuel also yields by-products such as free fatty acids and raw glycerol [4–6]. Raw glycerol makes about 10 wt% of the total amount of biodiesel fuel produced. Since biodiesel fuel production is increasing rapidly, the amount of glycerol produced will also grow. In fact, it may exceed 1.16 million tons per year in the EU

Member-States in 2010. If the supply of glycerol in the market increases, its price and demand will decrease. This is proven by Europe’s experience with biodiesel. When the production volume of biodiesel suddenly increased from 1997 to 2000, the price of glycerol tumbled almost 40%. In contrast, in 2001, biodiesel production diminished, and the price significantly recovered [7].

The physical and chemical properties of the by-product glycerol depend on the method used to produce the biodiesel fuel. The glycerol can be assigned to one of three categories based on its purity. Raw glycerol contains up to 63.3% of glycerol, up to 26.8% of water, and approximately 26.7% of methanol. In addition, it contains organic substances (FAME) and salts of potassium and sodium (soaps). Glycerol of average purity (technical glycerol) contains approximately 80% of glycerol and much lower percentages of water and methanol. Glycerol of the highest purity (>99.8%) is received in glycerol distillation plants. In the largest biodiesel production plants, methanol is evaporated from the glycerol fraction, and the free fatty acids are purified away, producing technical glycerol of ~80% purity. Usually this technical glycerol is collected and purified up to 99.8%. This incurs additional costs in energy and materials, and the demand

for it is limited because of a large surplus in the market. Thus, we are searching for new possible uses of non-purified glycerol [8]. One of the most attractive ones is to use the liquid fuel in various combustion plants to produce heat energy.

Using raw or technical glycerol directly as a fuel in combustion plants raises certain problems. For one thing, it is difficult to atomize with conventional atomizers because of its high density and viscosity, which means that it must be heated in advance. In fact, glycerol has quite a high auto-ignition temperature (370 °C) compared to other liquid fuels, so it flames up with difficulty [9]. Another important consideration is that when glycerol is heated above 280 °C, toxic acrolein is produced [10]. As glycerol is highly flammable and combusts at a higher temperature, a high temperature should be maintained in glycerol combustion processes. One way to solve these problems would be to produce fuel emulsions using raw or technical glycerol. These emulsions could contain the fatty acid methyl esters that are formed while making biodiesel fuel. From the economic and environmental perspectives, it would also be good for the emulsions to include heavy fuel oil (HFO) because the use of this fuel in boiler houses is currently limited because of its high sulphur content.

To implement the provisions of Directive 2001/80/EC of the European Parliament and Council [11, 12] regarding emission restrictions on certain pollutants from fuel combustion plants, the Republic of Lithuania now allows the use of HFO in its fuel combustion plants, although, when it is burned, the amount of SO<sub>2</sub> in flue gases cannot exceed 1700 mg/nm<sup>3</sup>. This low value is reached when HFO containing up to 1 wt% of sulphur is combusted. The inexpensive heavy fuel oil imported from Russia and Belarus does not satisfy these requirements: the content of sulphur exceeds 2 wt%. If HFO were mixed with the glycerol fraction, it would reduce the sulphur content and SO<sub>2</sub> concentration in flue gases emitted while burning the fuel oil. In addition, it would provide a cheap liquid fuel for boiler houses.

According to the literature and analysis of patents, it appears that little research has been done on using glycerol in emulsions containing HFO. The foreign authors are intensively exploring the possibility of making emulsions with water. In fact, the composition of heavy fuel oil-and-water emulsions and the emulsifiers used for their production have been patented [13–17]. Authors of patents stress, however, that the emulsions have a negative feature: a low stability during long-term storage.

The purpose of our work was to analyse the possibilities of using technical glycerol and glycerol emulsions as a liquid fuel in fuel combustion plants. While trying to achieve this goal, emulsions of different compositions were tested for their stability. The physical and chemical characteristics of technical glycerol and glycerol emulsions were evaluated, as well as their combustion and environmental effects.

## 2. METHODS

### 2.1. Preparation of emulsions

Reference fuel emulsions containing glycerol were made from pure glycerol (Sigma), fatty acid methyl esters locally produced according to EN 14214 specifications, heavy fuel oil (mazut M100) prepared according to GOST 10585-75 specifications, AB “Mažeikių nafta” (Mazeikiai Oil Ltd.), methanol (Sigma), and

the emulsifiers fatty acid monoglycerides and sodium oleate (Sigma). The monoglycerides (Palsgaard0093® pellets) were heated until they melted, then they were poured into the already prepared mixture of glycerol, fatty acid methyl esters, HFO, methanol, and sodium oleate. The mixture was homogenized for 15 minutes using the adjustable large-scale IKA T25 Digital Ultra-Turrax homogeniser at a frequency of 20 000–24 000 revolutions per minute. The viscosity and density of stable emulsions produced in this study were measured, respectively, with a viscometer (Cannon-Fenske Rutine) or aerometer (Russia). To evaluate the reliability and applicability of the reference test results, another set of reference emulsions were prepared from the industrial raw glycerol fraction.

### 2.2. Analysis of emulsion properties and stability

The physical and chemical characteristics of emulsions were examined using standard analytical methods. To evaluate the stability of the prepared emulsions, they were stored at room temperature in cone-shaped glass tubes with 0.1-ml graduations and tightly covered with PTFE lids. Whether the emulsions formed layers was assessed every hour.

### 2.3. Analysis of industrial applications and environmental characteristics of technical glycerol and glycerol emulsions

Combustion investigations of technical glycerol and glycerol emulsions were carried out in an organic fuel combustion setup (Fig. 1). In this setup, a gear pump transfers glycerol or glycerol emulsion from the fuel reservoir to the atomizer. A constant pressure in the glycerol supply system is maintained with the help of a pressure relief valve. The amount of glycerol is controlled by adjusting the pressure using a three-way control valve situated upstream of the atomizer. The valve is fitted with calibrated openings with diameters of Ø 0.35 mm (used for glycerol) or Ø 0.22 mm (used for the emulsion of glycerol and liquid fuel). Before reaching the atomizer, the fuel passes through two filtration steps, one involving a rough cleaning filter with a filtering element with an average diameter of Ø 700 µm, and a fine cleaning filter (Ø 140 µm). In addition, it is heated to 60–85 °C using an electric heater.

When the fuel enters the atomizer, it flows through the distributor, where three tangentially arranged grooves pass it to the swirling chamber. The tangential grooves give rise to an intense vortexing in the swirling chamber. The rotated liquid is atomized through the exit outlet. The burner is fed air from a compressor, and the air flow is regulated by a needle valve and a special diaphragm of flow measurement equipped with a differential manometer. Before the glycerol or its emulsion is released, an adiabatic combustion chamber is heated to 1000 °C with the help of natural gas. Heating the combustion chamber in this way guarantees fuel gasification in advance, and good burning is easily achieved with a proper regulation of the air supplied to the combustion chamber. This chamber is equipped with two thermocouples of S type (PtRh10-Pt) and two of K type (NiCr-Ni). These thermocouples supply data to the computer through the TC-08 (Pico) data collection system, and the data are displayed on the monitor.

The setup contains a cyclone device for removing solid particles from the flue gas. After the flue gases enter the cyclone, the

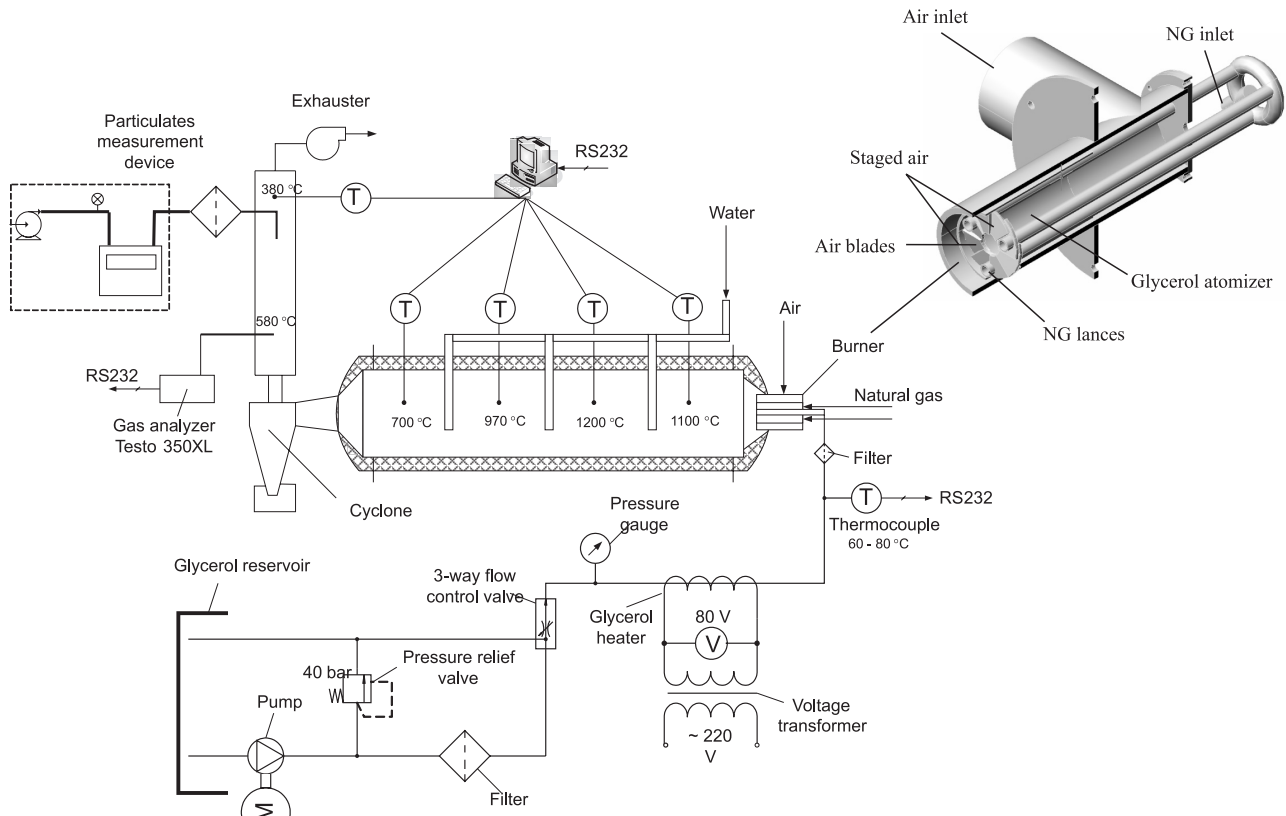


Fig. 1. Fuel combustion setup

largest particles are thrown by centrifugal force closer to the wall where they lose energy and fall into the particle accumulation chamber mounted at the bottom of the cyclone. The flue gases exiting the cyclone then pass into the gas analysis chamber. This chamber contains the Testo 350 XL flue gas analyzer and a device to measure solid particles. The gas analyzer measures emissions of  $O_2$ ,  $CO$ ,  $CO_2$ ,  $NO$ ,  $NO_2$ , and  $SO_2$  gas. The concentration of solid particles in smoke is determined by the weight method [18].

### 3. RESULTS AND DISCUSSION

#### 3.1. Production of emulsions

Several factors make the inclusion of heavy fuel oil in emulsions challenging. Because of differences in polarity, HFO and glycerol mix to only a limited extent. It is possible to disperse one fraction in another, but it is nevertheless necessary to search for the other components that improve the miscibility of these substances and the stability of the emulsions. In addition, both HFO and glycerol are characterized by a high viscosity and density. This makes it necessary to heat them prior to combustion, yet the emulsions are unstable at high temperatures. Thus, it is necessary to search for other components that reduce the density and viscosity of the emulsions so that they can be passed to the combustion chamber at lower temperatures.

During the production of biodiesel fuel, there is an oil transesterification by methanol, after which raw glycerol is separated from the desired products. Besides glycerol (~60%), the raw glycerol fraction contains methanol, fatty acid methyl esters (FAME), sodium or potassium soaps, and water. This fraction is

usually purified after the methanol is evaporated off and free fatty acids have been separated away by processing with mineral acids. The evaporation and rectification of methanol to recycle it back into the biodiesel production process is costly in terms of energy and materials, so the overall cost effectiveness of the process would increase if raw glycerol could be used to produce emulsions.

To evaluate the possibility of producing emulsions from raw glycerol that would be suitable for use as fuel in boiler houses, the stability of emulsions with different compositions was tested. All or some of the components present in the glycerol fraction were used to produce the emulsions, and the proportion of heavy fuel oil was always 35% or less to avoid more than 1% sulphur in the emulsions.

Ionic and non-ionic emulsifiers were selected for emulsion production, namely sodium oleate and fatty acid monoglycerides. Soaps are made in the process of biodiesel fuel production, while fatty acid monoglycerides may be produced from the glycerol fraction through glycerolysis of free fatty acids or oil.

For preliminary experiments, emulsions were prepared with the following components: glycerol, 23–35%; fuel oil, 28–48%; fatty acid methyl esters (FAME), 16–22%; water, 15–23%; soap, 1–2%; fatty acid monoglycerides (MG), 0.4–1.5%. The initial set of emulsions was found to be unstable: they formed layers either immediately or upon storage for up to one day. The amount of emulsifier (fatty acid monoglycerides) was increased up to 7% in an attempt to stabilize the emulsions, but the stability was still insufficient, and the fatty acid monoglycerides made the emulsions significantly thicker. This thickening effect could be reduced if some of the water (8%) was substituted with methanol or

Table 1. Composition and stability of glycerol–heavy fuel oil emulsions

Polar compounds (glycerol, water, methanol), %	Non polar compounds (fuel oil, RRME), %	Monoglycerides, %	Sodiumoleate, %	Stability
40.0	51.5	7.0	1.5	Hardened
48.7	48.0	1.5	1.8	Stable 3 h
48.6	46.2	3.5	1.7	Stable 3.5 h
48.7	45.5	4.0	1.8	Stable 48 h
48.7	46.3	3.5	1.5	Stable for 6 days
48.6	47.1	3.0	1.3	Stable for 6.5 days
35.2	62.0	1.5	1.3	Stable for 4 days
39.1	58.1	1.5	1.3	Stable for 4 days
35.2	60.5	3.0	1.3	Stable for 44 days
42.0	55.2	1.5	1.3	Stable for 30 days
42.0**	56.5	1.5	–	Stable more than 100 days
35.5**	61.5	3.0	–	Stable more than 100 days

\*\* Glycerol phase was used for production of emulsions.

if water was omitted entirely from the emulsions. The optimal amount of fatty acid monoglycerides was found to be 1.5–3%. The low stability of this initial set of emulsions was probably caused by the ~50 : 50 proportion of polar and non-polar components. The proportion was moved closer to the optimal one for stable emulsions, which was 40 : 60 when the main polar components consisted of water, methanol, and glycerol, and the non-polar components were fuel oil and FAME. Some of the testing results are presented in Table 1.

Further tests showed that stable emulsions could be produced with 27–34% of glycerol and 27–34% of HFO. Thus, different emulsion compositions can be selected depending on whether the goal is increased consumption of glycerol or of heavy fuel oil. The high water content destabilizes emulsions, while methanol stabilizes emulsions. If the glycerol fraction is used without the evaporation of the methanol or removal of fatty acids, it contains a sufficient amount of ionic emulsifier, so it is unnecessary to add more Na soap.

### 3.2. Combustion experiments of technical glycerol and glycerol emulsions

The technical glycerol used in this study was taken from one of the largest biodiesel production plants in Lithuania, JSC “Rapsola.” The glycerol-heavy fuel oil emulsion was prepared in the laboratory. The technical glycerol contained 80% of glycerol, 9% of water, 0.5% of methanol, 9% of sodium phosphate, and 1.5% of FFA. The resulting emulsion contained 8% of methanol, 3% of MG, 1.3% of soap, 27.2% of glycerol, 34% of fuel oil, and 26.5% of FAME. Tables 2 and 3 present the quality indexes of glycerol and the glycerol-heavy fuel oil emulsion.

Table 2. Quality parameters of glycerol used for production of emulsions

Parameter	Value
Ash content, % (m/m)	0.085
Sulphur content, mg/kg	381
Flash point, °C	109
Viscosity at 80 °C, mm <sup>2</sup> /s	15.2
Density at 15 °C, kg/m <sup>3</sup>	1260
Calorific value, MJ/kg	12.2

Table 3. Quality parameters of glycerol–heavy fuel oil emulsion

Parameter	Value
Ash content, % (m/m)	0.16
Sulphur content, % (m/m)	0.7
Freezing temperature, °C	–6
Viscosity at 20 °C, mm <sup>2</sup> /s	116.8
Density at 20 °C, kg/m <sup>3</sup>	932

Before the experimental combustion studies, the thermal stability of the glycerol and the glycerol-heavy fuel oil emulsion was determined for the range of 30–1000 °C (Fig. 2). Direct thermal analysis was not possible, since the glycerol was a liquid. Boiling liquid substances, which could wet the thermocouples, could distort the readings or damage the device. To avoid this problem, the present study used the following method: the samples of glycerol were mixed in a 1 : 1 weight proportion with inert aluminum oxide ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) and stirred until the mixture took on the consistency of paste. A sample (50 mg) was analysed in the NETZSCN STA 40S PC/P6 device in an air atmosphere. The temperature was increased at the rate of 15 °C/min.

The thermogravimetry (TG) and differential thermogravimetry (DTG) curves of technical glycerol show four major mass losses (Fig. 2a): a small mass loss up to 190 °C (loss of 11.04% of the initial mass), an extensive mass loss up to 303 °C (36.48%), a small mass loss from 303 °C to 375 °C (1.5%), and a slight decrease in mass up to 1000 °C (2.31%). The first mass loss is the water in the glycerol, as well as the additional moisture that it had absorbed. This is proven by the endothermic reaction seen in the curve from differential scanning calorimetry (DSC), which shows a peak at 153.2 °C. From 152 °C onwards, the pressure of glycerol vapour increases sharply from the starting value of 0.67 kPa [19], and it reaches atmospheric pressure (101.3 kPa, i. e. begins to boil, at 290 °C. The second mass loss may be explained by the evaporation of the glycerol itself. This is supported by the DSC analysis where a strong endothermic peak at 285.3 °C is seen. At the third mass loss, DSC analysis shows a weak endothermic reaction with a peak at 356 °C. This peak may explain the decomposition of Na<sub>3</sub>PO<sub>4</sub> · 12H<sub>2</sub>O, by a dehydration reaction. The final, slow mass loss may be due to the thermal decomposition or oxidation of coke.

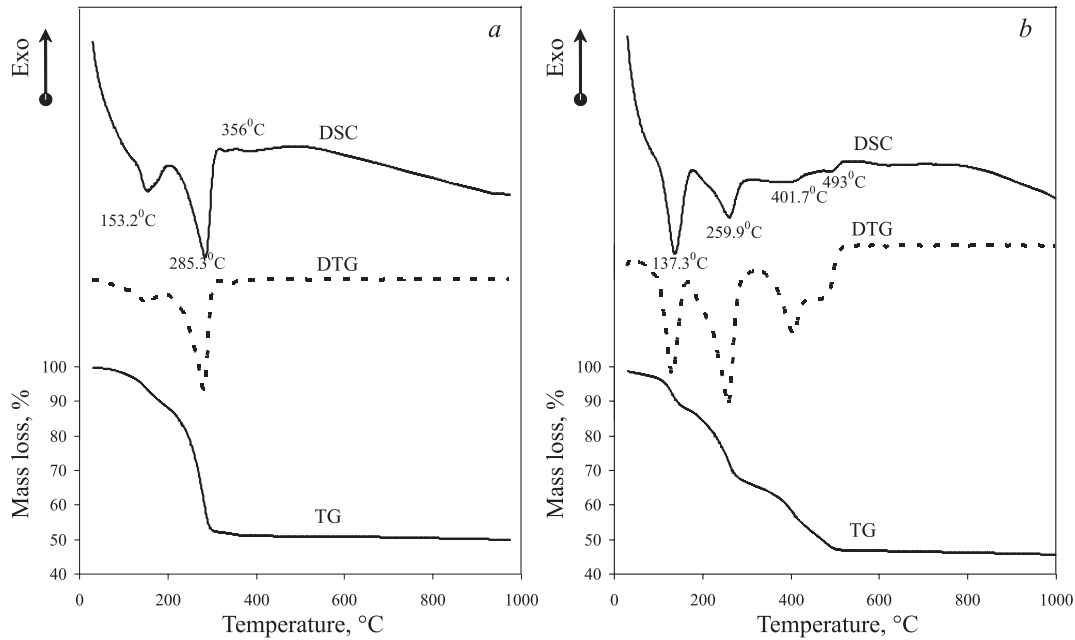


Fig. 2. Thermal analysis of technical glycerol (a) and glycerol–heavy fuel oil emulsion (b)

The thermogram of the glycerol–fuel oil emulsion (Fig. 2b) is similar to that of technical glycerol and heavy fuel oil [20]. The thermal analysis of the emulsion shows five principal mass losses. The first decrease in mass up to 166 °C occurs as a result of the larger amount of water and methanol present in the sample (loss of 11.24% of the original mass), then the evaporation of glycerol and FAME occur up to 286 °C (loss of 21.27% of the initial mass).

The DTG and DSC curves of the glycerol emulsion show two additional endothermic reactions with peaks at 401.7 °C and 493 °C. These peaks are caused by the introduction of HFO into the emulsion. It seems likely that, at temperatures between 286 °C and 432 °C (loss of 12.68% of initial mass), the lighter fractions of HFO begin to decompose, while from 432 °C to 530 °C (loss of 6.72% of initial mass) heavy fuel oil is rapidly destroyed in the air environment. This destruction involves hydrocarbon decomposition and dehydrogenation, which consume a lot of heat energy [21]. As the temperature increases, the hydrocarbon molecules cleave more frequently at the end of the chain, forming shorter radicals that gasify following stabilization. As the alkyl groups become shorter, the molecular weight of the decomposition products becomes smaller. Though the rate of decomposition does not increase with increasing temperature, the speed of mass loss in the residual sample at temperatures over 530 °C slows significantly. More stable aromatic hydrocar-

bons and solid asphalt materials become enriched in the residual sample, and they begin to condense into the polycyclic aromatic structures that form coke. Formation of the coke, as well as its partial decomposition, takes place over the temperature range of 530–1000 °C (loss of 1.26% of the initial mass). From 800 °C onwards, decomposition of coke occurs (Fig. 2b).

Thus, the thermal analysis of glycerol and its emulsion shows that the introduction of heavy fuel oil and other additives slightly affect the thermal stability of the mixture. The evaporation process of the mixture becomes slower at temperatures up to 500 °C.

The modern boilers used in thermal and industrial plants work at high temperatures, but the adiabatic temperature of glycerol is by ~100–250 °C lower than the adiabatic temperature of the other liquid fuels. To guarantee stable combustion, glycerol should be mixed with another type of fuel, or it must be introduced directly into the hot zone. In the present experiments, natural gas was used to create the hot burning zone; the gas helped to raise the temperature in the combustion chamber to 1000 °C. The gas was turned off once this temperature was reached. The glycerol fraction entered the zone of high temperature and gasified, while the distribution of streams created by the burner formed a flammable mixture of gasified glycerol vapour and air that easily ignited, thereby guaranteeing a stable combustion regime. The quality indexes of glycerol combustion are presented in Table 4.

Table 4. Combustion quality of technical glycerol

Parameter	Unit	Measured error	Regime			
Heat power	kW	±2	35	45		
Glycerol supply	kg/h	±2	11	13		
Glycerol pressure before atomizer	bar	±2	20	28		
Air supply	m <sup>3</sup>	±5	41	46		
Oxygen content in flue gases	%	±0.5	3.6	1.6	1.9	2.4
Air excess coefficient	–	±0.02	1.21	1.09	1.1	1.13
Carbon monoxide emission	mg/m <sup>3</sup>	±20	41	90	73	130
Nitrogen oxide emission	mg/m <sup>3</sup>	±14	88	87	88	88
Particulate emission (Na salts)	g/m <sup>3</sup>	±25%	10.5	14.5	11.9	9.6

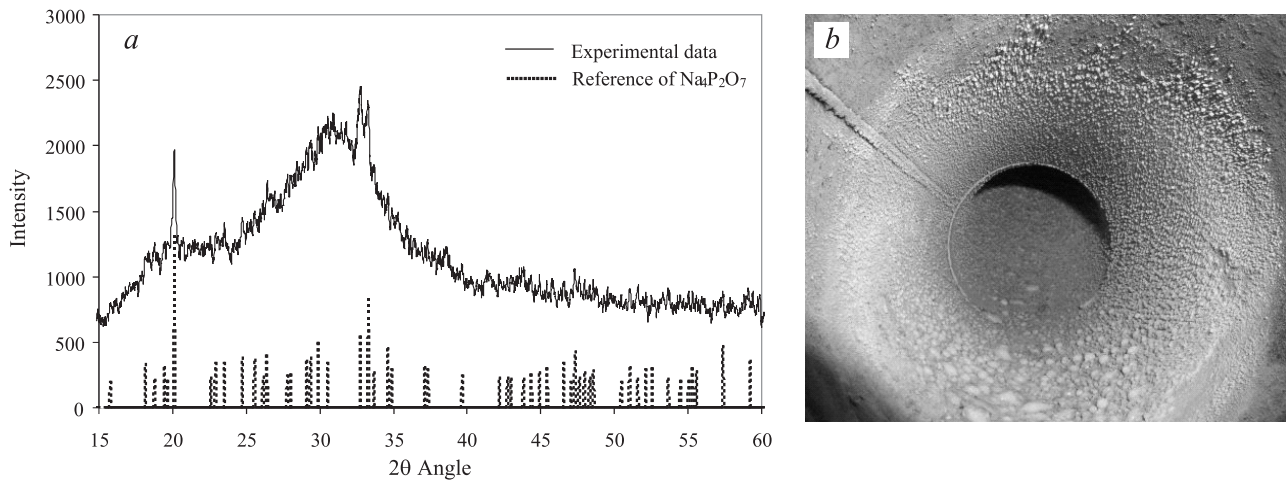


Fig. 3. Curves of X-ray diffraction analysis (a) and sediment of solid particles on the cooled surfaces of boilers (b)

In the experiments on the combustion of technical glycerol, the boiler operated efficiently from 35 to 45 kW. Over the entire loading range, the air excess coefficient behind the boiler changed from 1.21 to 1.09. The concentrations of emitted pollutants at 3% of oxygen content in the flue gases did not exceed the limits established by the EU Directive 2001/80/EC; the concentrations were as follows:  $\text{NO}_x$ ,  $\sim 90 \text{ mg/m}^3$ ;  $\text{CO}$ ,  $41\text{--}130 \text{ mg/m}^3$ ; and  $\text{SO}_2$ ,  $\sim 10 \text{ mg/m}^3$  (Table 4). When technical glycerol was burned, the flue gases showed an especially high concentration of solid particulates (Na salts), which reached as high as  $14.5 \text{ g/m}^3$ . They appear in glycerol during the production of biodiesel fuel when the alkaline catalyst is used for the transesterification reaction. As water is removed during the combustion process, salts in the glycerol condense and form polycondense compounds. X-ray diffraction analysis of these solid particles showed that the structure of the white powder produced most closely resembles the crystallographic structure of sodium pyrophosphate  $\text{Na}_4\text{P}_2\text{O}_7$  (Fig. 3a). These compounds have been shown to stick to the cooled surfaces of boilers (Fig. 3b) and to reduce the heat transfer efficiency of combustions carried out in boilers.

To comply with the provisions of Directive 2001/80/EC of the European Parliament and Council [11, 12] regarding emission limits for certain pollutants from fuel combustion plants, the burning of sulphurous fuel ( $S^u > 1\text{wt}\%$ ) is prohibited in Lithuania. Using glycerol together with another liquid fuel high in sulphur, such as heavy fuel oil or oil shale can reduce the emission of hazardous  $\text{SO}_2$  and  $\text{NO}_x$  into the environment. This reduction was verified in the combustion trials with the glycerol–heavy fuel oil

emulsion in which the content of sulphur oxides in the flue gases was found to be  $\sim 1000 \text{ mg/m}^3$  (Table 5) and the concentration of nitric oxides was measured at  $250\text{--}280 \text{ mg/m}^3$ . For comparison, extensive experience has shown that burning sulphurous HFO ( $S^u$  up to 3%) leads to a concentration of  $\text{SO}_2$  of up to  $6000 \text{ mg/m}^3$  in flue gases, and  $\text{NO}_x$  levels in flue gases as low as  $250\text{--}300 \text{ mg/m}^3$  can be achieved without additional methods only when the combustion process is well coordinated.

The reduction in sulphur oxides is due to the reduction parting the proportion of sulphurous fuel needed to achieve the same amount of thermal energy. In contrast, the reduction in  $\text{NO}_x$  may be explained by the low adiabatic flame temperature of glycerol. In other words, when glycerol is introduced into the combustion process, the flame temperature decreases, leading to a reduced formation of the so-called thermal nitric oxides. The content of  $\text{CO}$  in flue gases depends on the coefficient of air surplus, and it may vary between 60 and  $130 \text{ mg/m}^3$ . In addition, the fact that each fuel was diluted into another decreased the formation of solid particles. In the present study, the concentration of solid particles in smoke averaged  $0.5 \text{ g/m}^3$  over the entire load range.

#### 4. CONCLUSIONS

1. To solve the problem of how to use the glycerol formed while making biodiesel fuel, this study analyzed the possibility of using it directly as a fuel or in an emulsion with other combustible products. A glycerol–heavy fuel emulsion was investigated

Table 5. Combustion quality of glycerol–heavy fuel oil emulsion

Parameter	Unit	Meas. error	Regime			
Heat power	kW	$\pm 2$	37			
Emulsion supply	kg/h	$\pm 2$	5.8	5.5	6	6.1
Emulsion pressure before atomizer	bar	$\pm 2$	10			
Air supply	$\text{m}^3$	$\pm 5$	65	60	62	62
Oxygen content in flue gases	%	$\pm 0.5$	4	3.6	3	2.5
Air excess coefficient	–	$\pm 0.02$	1.23	1.21	1.16	1.13
Carbon monoxide emission	$\text{mg/m}^3$	$\pm 20$	60	75	100	134
Nitrogen oxide emission	$\text{mg/m}^3$	$\pm 14$	251	234	277	257
Sulfur dioxide emission	$\text{mg/m}^3$	$\pm 30$	1025	945	993	1074
Particulate emission (Na salts)	$\text{g/m}^3$	$\pm 25\%$	0.5			

because of the limited use of heavy fuel oil in combustion plants due to its high sulphur content.

2. Stable emulsions are produced when they contain 27–34% of glycerol and 27–34% of heavy fuel oil. In addition to these products, the emulsions contain methanol present in the glycerol fraction. Fatty acid monoglycerides can be used as stabilizers (optimal amount 1.5–3%) together with soaps (optimal amount, 1.3%). Both of these emulsifiers are present in the green glycerol received after fatty acid methyl esters and glycerol fractions have been separated.

3. Initial combustion experiments suggest that, once solid particles can be eliminated from the glycerol fraction or the salts remaining in the glycerol after dissolving of the soaps can be removed, the glycerol fraction can be used directly as a fuel to generate heat energy. The concentrations of  $\text{NO}_x$  ( $\sim 90 \text{ mg/m}^3$ ), CO ( $40\text{--}130 \text{ mg/m}^3$ ), and  $\text{SO}_2$  ( $0\text{--}10 \text{ mg/m}^3$ ) produced in the organic fuel combustion setup in the present study did not exceed the limits in the flue gases.

4. Burning the glycerol–fuel oil emulsion produced a nearly six-fold reduction in the content of  $\text{SO}_2$  ( $993\text{--}1074 \text{ mg/m}^3$ ) in the flue gases as well as lowered the concentration of nitric oxides ( $\text{NO}_x$ ) in the exhaust smoke ( $250\text{--}280 \text{ mg/m}^3$ ) as compared to pure heavy fuel oil. Burning the emulsion also produced smoke with a significantly lower concentration of solid particles, which averaged  $0.5 \text{ g/m}^3$  over the entire load range.

## ACKNOWLEDGEMENTS

The authors are thankful to the Lithuanian Science and Studies Foundation for Support.

Received 4 June 2008

Accepted 26 June 2008

## References

1. Directive 2003/30/EC of the European Parliament and the Council of 8 May 2003 on the promotion of the use of bio-fuels or other renewable fuels for transport. OJ L 123, 2003. P. 42–46.
2. Current Situation and Prospects for Biodiesel and Vegetable Oils as Fuels: From Niche Products to Market Players. [http://www.ufop.de/downloads/Biodieselreport\\_engl\\_070306.pdf](http://www.ufop.de/downloads/Biodieselreport_engl_070306.pdf) (2007 12).
3. European Biodiesel Board. <http://www.ebb-eu.org/stats.php> (2007 10).
4. Mittelbach M., Remschmidt M. C. Biodiesel. The comprehensive handbook. Boersendruck Ges. m. b. H, Vienna, 2004.
5. Ma F., Hanna M. A. Bioresource Technology. 1999. N 70. P. 1–15.
6. Srivastava A., Prasad R. Renew. Sust. Energ. Rev. 2000. N 4. P. 111–133.
7. Bozell J. Oleochemicals as a Feedstock for the Biorefinery: High Value Products from Fats and Oils. National Renewable Energy Laboratory. August 18, 2004.
8. Van Gerpen J. Biodiesel Production Technology. NREL/SR-510-36244, Golden, Colorado. <http://www.osti.gov/bridge> (2004 05).
9. DIPPR Project 801 Full version evaluated standard thermophysical property values. Design Institute for Physical Properties, Department of Chemical Engineering, Brigham Young University, Provo, Utah, 2005.
10. EPA “Toxicological review of acrolein”, CAS No. 107-02-8, EPA/635/R-03?003 (2003).
11. Patent No. US2007113938 “Emulsion fuel and method of preparing the same”. Publication date 2007-05-24.
12. Patent No. JP11172264 “Production of emulsion fuel”. Publication date 1999-06-29.
13. Patent No. JP2007153824 “W/O-type emulsion composition”. Publication date 2007-06-21.
14. Patent No. GB2276175 “Heavy oil fuel emulsion”. Publication date 1994-09-21.
15. Patent No. KR20020032220 “Emulsion fuel oil composition”. Publication date 2002-05-03.
16. Patent No. GB2276175 “Heavy oil fuel emulsion”. Publication date 1994-09-21.
17. Patent No. KR20020032220 “Emulsion fuel oil composition”. Publication date 2002-05-03.
18. ISO 9096:2003 Stationary source emissions – Manual determination of mass concentration matter.
19. Ullmann’s Encyclopedia of Industrial Chemistry. 7th edn. 2004 [CD-ROM]. Wiley-VCH Verlag GmbH & Co. KGaA.
20. Xu G., Ikegami M., Honma S., Takeshita Y. Burning droplets of heavy oil residual blended with diesel light oil: characterization of burning steps // Combustion Science and Technology. 2002. Vol. 174. P. 115–145.
21. Kukliauskas A., Stravinskas G., Barkauskas V. Application of differential thermal analysis in the investigation of heavy fuel oil // Chemical Technology. 2003. N 1(27).

Nerijus Striūgas, Anupras Šlančiauskas, Violeta Makarevičienė, Milda Gumbytė, Prutenis Janulis

## GLICEROLIO FRAKCIJOS PANAUDOJIMO ŠILUMOS GAMYBAI GALIMYBĖS

### Santrauka

Didėjant biodyzelino gamybos apimtims, susiduriama su gamybos metu susidarancio šalutinio produkto – glicerolio panaudojimo problemomis. Šių tyrimų tikslas buvo įvertinti techninio glicerolio (80% grynumo) ir glicerolio fazės (iki 60% grynumo) panaudojimo šilumos gamybai galimybes.

Atlikti glicerolio panaudojimo kuro emulsijų gamybai tyrimai, į emulsijų sudėtį įtraukiant mazutą, kurio tiesioginis panaudojimas ribotas dėl didelio sieros kiekio jame. Įvertintas emulsijų stabilumas, atsižvelgus į jų sudėtį. Nustatyta, kad stabilios emulsijos gali būti gautos, kai jų sudėtyje yra 27–34% glicerolio ir 27–34% mazuto. Emulsijų stabilumui padidinti tikslinga naudoti emulsiklius: riebalų rūgščių monogliceridus (optimalus kiekis 1,5–3%) ir muilus (optimalus kiekis 1,3%), kurių aptinkama biodyzelino gamybos metu atskirtoje glicerolio fazėje.

Pateikiami paruoštos stabilios emulsijos mėginio ir techninio glicerolio palyginamųjų deginimo tyrimų rezultatai ir analizė. Eksperimentinių techninio glicerolio deginimo bandymų metu visame apkrovimų intervale gautos  $\text{NO}_x$  ( $\sim 90 \text{ mg/m}^3$ ), CO ( $40\text{--}130 \text{ mg/m}^3$ ) bei  $\text{SO}_2$  ( $0\text{--}10 \text{ mg/m}^3$ ) koncentracijos šalinamuose dūmuose atitiko ES Tarybos direktyvose nurodytas leistinas išmetamųjų teršalų iš kurų

deginančių įrenginių normas. Deginant emulsiją, sieros dioksido ( $\text{SO}_2$ ) kiekis deginiuose sumažėja beveik 6 kartus, palyginti su grynu mazutu, ir siekia 993–1074  $\text{mg}/\text{m}^3$ . Mažesnės azoto oksidų ( $\text{NO}_x$ ) koncentracijos šalinamuose dūmuose (250–280  $\text{mg}/\text{m}^3$ ), gerokai sumažėjo ir kietųjų dalelių susidarymas.

**Raktažodžiai:** glicerolis, mazutas, kuro emulsijos, deginimo tyrimai, emisijos

Нерийус Стрюгас, Анупрас Шланчаускас,  
Виолета Макарявичене, Милда Гумбите, Прутянис Янулис

#### ПЕРЕРАБОТКА ГЛИЦЕРОЛЬНОЙ ФРАКЦИИ В НОВЫЙ ВИД ТОПЛИВА ДЛЯ ПРОИЗВОДСТВА ТЕПЛОВОЙ ЭНЕРГИИ

##### Резюме

С ростом производства биодизельного топлива в настоящее время возникают большие проблемы рационального использования побочного продукта глицерола. Цель данного исследования – вычислить возможность использования технического глицерола (чистота 80%) и глицерольной фракции (чистота до 60%) для производства тепловой энергии.

Рассматривается использование глицерола для производства топливной эмульсии с мазутом. В настоящее время использование мазута ограничено из-за высокого содержания в нем серы. Определено, что эмульсия стабильна за счет ее состава. Результаты показали, что более устойчивая эмульсия может быть приготовлена, когда в ее составе содержится 27–34% глицерола и 27–34% мазута. Чтобы повысить стабильность эмульсии, можно использовать эмульгаторы в глицерольной фракции, например, моноглицериды жирных кислот (оптимальная концентрация 1,5–3%) и мыло (оптимальная концентрация 1,3%).

Также представлены сравнительные результаты исследования горения стабильной эмульсии и технического глицерола. Во всех экспериментальных режимах горения технического глицерола концентрации  $\text{NO}_x$  (~90  $\text{mg}/\text{m}^3$ ),  $\text{CO}$  (40–130  $\text{mg}/\text{m}^3$ ) и  $\text{SO}_2$  (0–10  $\text{mg}/\text{m}^3$ ) в дымовых газах не превышали допустимых норм загрязнения окружающей среды. В случае горения топливной эмульсии концентрация диоксида серы достигала 993–1074  $\text{mg}/\text{m}^3$ , но это почти в шесть раз меньше, чем при сжигании серистого мазута. Кроме того, концентрации оксидов азота в дымовых газах не превышали 250–280  $\text{mg}/\text{m}^3$ .

**Ключевые слова:** глицерол, мазут, топливная эмульсия, горение, эмиссии