VILNIAUS GEDIMINO TECHNIKOS UNIVERSITETAS

APLINKOS INŽINERIJOS FAKULTETAS

APLINKOS APSAUGOS KATEDRA

Dovilė Stepanonytė

RAPSO ALIEJAUS METILO ESTERIO GAMYBOS PROCESO ŠALUTINIO PRODUKTO UTILIZACIJOS TYRIMAS

INVESTIGATION OF RAPE SEED OIL METHYL ESTER PRODUCTION AND BY – PRODUCT UTILIZATION

Baigiamasis magistro darbas

Aplinkos apsaugos vadybos ir švariosios gamybos studijų programa, valstybinis kodas 62404T103
Aplinkos inžinerijos ir kraštotvarkos mokslo kryptis

Vilnius, 2007

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Vadovas______________________ ___________ ___________
(Moksl. laipsnis, vardas, pavardė) (Parašas) (Data)

Konsultantas______________________ ___________ ___________
(Moksl. laipsnis, vardas, pavardė) (Parašas) (Data)

Konsultantas______________________ ___________ ___________
(Moksl. laipsnis, vardas, pavardė) (Parašas) (Data)

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APLINKOS INŽINERIJOS FAKULTETAS
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TVIRTINU
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(Vardas, pavardė)
2005.09.30
(Data)

Technologijos mokslo sritis

Aplinkos inžinerija ir kraštotvarka mokslo kryptis

Aplinkos inžinerija studijų kryptis

Aplinkos apsaugos vadyba ir švarioji gamyba studijų programa, valstybinis kodas ***62404T103***

BAIGIAMOJO MAGISTRO DARBO UŽDUOTIS

2005.09.23 Nr. ....

Vilnius

Studentui (ei) Dovilei Stepanonytei
(Vardas, pavardė)

Baigiamojo darbo tema: Rapso aliejaus metilo esterio gamybos proceso šalutinio produkto utilizacijos tyrimas

patvirtinta ***2007m.*** ***kovo mėn. 21*** **d. dekano įsakymu Nr.** ***139ap***

Baigiamojo darbo užbaigimo terminas 2007.m. birželio 1 d.

BAIGIAMOJO DARBO UŽDUOTIS:
Atlikti literatūrinę apžvalgą apie pasaulyje naudojamo rapso aliejaus metilo esterio gamybos proceso šalutinių produktų panaudojimą; susisteminti duomenis apie biodyzelino jo panaudojimą bei aplinkosaugines problemas jį naudojant. Atlikti eksperimentinius tyrimus įvertinant degimo produktų koncentracijas, atlikti mazuto emulsijos bandinių dispersiškumo tyrimus. Atlikti degimo produktų sklaidos modeliavimą. Išvados, rekom.

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2005.09.23
(Data)

Vilniaus Gedimino Technikos Universitetas
Aplinkos inžinerijos fakultetas
Aplinkos apsaugos katedra

ISBN ISSN
Egz. sk. 2
Data 2007

Aplinkos inžinerijos studijų programos baigiamasis magistro darbas

Pavadinimas **Rapso aliejaus metilo esterio gamybos proceso šalutinio produkto utilizacijos tyrimas**

Autorius **Dovilė Stepanonytė** Vadovas doc. dr. **Aušra Zigmontienė**

Kalba

☒ **lietuvių**
užsienio

Anotacija

Baigiamajame darbe išnagrinėtos rapso aliejaus metilo esterio (RME) gamybos proceso šalutinių produktų utilizacijos problemos, pateikti statistiniai duomenys apie biodyzelino gamybos bei susidarančių šalutinių produktų apimtis, aprašytos biodyzelino gamybos plėtros perspektyvos, savybės bei poveikis aplinkai, pagrindinės gamybos technologijos, Lietuvos bei užsienio šalių patirtis šioje srityje, apibrėžti pagrindiniai darbo tikslai ir uždaviniai. Atliktas RME gamybos proceso pagrindinio šalutinio produkto – glicerolio – utilizacijos tyrimas. Išanalizuotas vienas iš naujų galimų utilizavimo būdų - deginti glicerolį kartu su sieringu (~ 2,0 %) mazutu, siekiant sumažinti SO_2 emisijas, kurių nustatyta ribinė vertė dūmuose negali būti didesnė kaip 1700 mg/Nm^3 (pagal ES Direktyvą 1999/32EC ir LAND 43-2001 „Išmetamų teršalų ir didelių kurą deginančių įrenginių normos“).

Laboratorinėmis sąlygomis stendiniame įrenginyje paruošta mazuto-glicerolio emulsija, nustatytas optimaliausias mazuto emulgavimo glicerolių santykis (1:1), atlikti mazuto emulsijos bandinių homogeniškumo tyrimai.

Eksperimentiniai mazuto bei gautų emulsijų deginimo bandymai buvo atlikti VGTU Termoizoliacijos instituto eksperimentiniame stende bei UAB „Rietavo veterinarinė sanitarija“ termooksidaciniame katile „UMISA-CR/11,9 (13)“. Išmatuotos mazuto ir mazuto-glicerolio emulsijos CO, NO_x, SO_2 ir kietųjų dalelių emisijos bei palygintos su jų didžiausiomis leistinoms vertėmis.

Remiantis gautais rezultatais pateiktos išvados, rekomendacijos, mazuto emulsijos modifikuotos glicerolio priedu techninis reglamentas.

Darbą sudaro 6 dalys: įvadas, biodyzelino gamybos ir šalutinių produktų utilizacijos apžvalga: dabartinė situacija ir ateities perspektyvos, mazuto modifikuoto glicerolių emulsijos paruošimo ir deginimo eksperimentiniai tyrimai, oro taršos sklaidos matematinis modeliavimas, bendrosios išvados ir pasiūlymai, literatūros sąrašas.

Darbo apimtis – 136 p. teksto be priedų ir publikuotų straipsnių, 57 pav., 24 lent., 10 bibliografinių šaltinių, 6 teisės aktai, 19 mokslinių straipsnių, 35 interneto nuorodos.

Atskirai pridedami darbo priedai.

Prasminiai žodžiai: rapso aliejaus metilo esteris, transesterifikacija, šalutiniai produktai, mazuto - glicerolio emulsija, homogeniškumas, SO_2 koncentracijos.

Vilnius Gediminas Technical University
Faculty of Environmental Engineering
Department of Environmental Protection

ISBN ISSN

Copies No.
Date 2007

Environmental Engineering Master study programme master thesis
Title **Investigation of rape seed oil methyl ester production and by-product utilization**
Author **Dovilė Stepanonytė** Academic supervisor doc. dr. **Aušra Zigmontienė**

Thesis language

Lithuanian
☒ **Foreign (English)**

Annotation

The problems of rape seed methyl ester (RME) production process by-products utilization were analyzed, statistical data for the capacities of biodiesel production and by-products generation were presented, the prospects of biodiesel production expansion, properties and environmental impact, main production technologies, Lithuanian and foreign countries experience were described, the main aims and tasks of work were defined. The investigation of glycerol – major by-product of RME production process – utilization was accomplished. One of the new possible utilization methods was researched, when combusting glycerol with highly sulphurous (~ 2.0 %) heavy fuel oil to reduce SO_2 emissions, which limit value in the flue gas can not exceed 1700 mg/Nm^3 (according to EU Directive 1999/32EC and LAND 43-2001 „Norms for the exhaust of pollutants from large fuel burning equipment“).

The heavy fuel oil – glycerol emulsion was prepared in the pilot plant operating in the laboratory conditions, the most optimal ratio (1:1) for heavy fuel oil emulsification was estimated, the dispersivity investigation of heavy fuel oil - glycerol emulsion samples was performed.

The experimental heavy fuel oil and obtained emulsion combustion investigations were carried out in VGTU Institute of Thermal Insulation pilot plant and in the thermal oxidation boiler „UMISA-CR/11,9 (13)“ at JCS „Rietavo veterinarinė sanitarija“. The CO, NO_x, SO_2 and particulate matter concentration values for heavy fuel oil and heavy fuel oil – glycerol emulsion were measured and obtained values compared to their MAC values.

The conclusions, recommendations and a technological regulation for heavy fuel oil modification by glycerol additive are made according to the obtained results of this study.

Structure – 6 parts: introduction, a review of biodiesel production and by-product utilization: current situation and future prospects, experimental investigation of heavy fuel oil – glycerol emulsion formation and combustion processes, atmospheric air pollution dispersion modeling, general conclusios and recommendations, references.

Thesis consist of 136 p. text without annexes and published articles, 57 pictures, 24 tables, 10 bibliographical entries, 6 law acts, 19 scientific articles, 35 internet references.

Annexes are included.

Keywords: rape seed methyl ester, transesterification, by-products, heavy fuel oil – glycerol emulsion, homogeneity, SO_2 concentration.

CONTENT

Abbreviations and symbols 7

List of table captions 9

List of figures captions 10

Introduction 13

1. A review of biodiesel production and by-product utilization: current situation and future prospects 16
   - 1.1. A review of the situation in the world and lithuania 16
   - 1.2. Main rape methyl ester (RME) characteristics 26
   - 1.3. Advantages and drawbacks of biodiesel fuel 28
   - 1.4. Comparison of petroleum diesel and biodiesel emissions 32
   - 1.5. Biodiesel production processess 36
   - 1.6. Utilization methods for biodiesel by-products 41
   - 1.7. Processes for glycerol utilization 50
   - 1.8. Atmospheric air pollution dispersion modelling 60
   - 1.9. Conclusions 63
2. Experimental investigation of heavy fuel oil – glycerol emulsion formation and combustion processes 64
   - 2.1. Introduction 64
   - 2.2. Methodology of heavy fuel oil - glycerol emulsion preparation, combustion and evaluation of the obtained emission concentrations 65
   - 2.3. Analysis of research results 73
   - 2.4. Glycerol as sulphur modifier (plasticizer) 98
   - 2.5. Conclusions 100
3. Atmospheric air pollution dispersion modelling 102
   - 3.1. Introduction 102
   - 3.2. Methodology of air pollution dispersion simulation 102
   - 3.3. Analysis of pollution dispersion simulation results 108
   - 3.4. Conclusions 126
4. General conclusions and recommendations 127

References 130

Annexes 136

ABBREVIATIONS AND SYMBOLS

EU – European Union;
EU15 – old-time EU members;
EU25 – number of member countries in the European Union after the accession of ten new candidate countries on 1st of May 2004;
EC – European Commission;
JSC- joint stock company;
LAND- environmental protection normative documents of Lithuania
RME – rape methyl ester;
SME – soybean oil methylester;
DF – diesel fuel;
ASTM – American Society for Testing & Materials Standards;
EPA – Environmental protection agency;
B20 – 20 % biodiesel by volume, 80 % petroleum diesel by volume;
B100 – 100 % biodiesel by volume;
APR - aqueous-phase reforming
HFO – heavy fuel oil;
G – glycerol;
HFO–G – heavy fuel oil – glycerol emulsion;
LCA – life cycle assessment;
CO – carbon monoxide;
CO_2 – carbon dioxide;
NO_x – nitrogen oxide;
SO_2 – sulphur dioxide;
MAC- maximum admissible concentration;
PM – particulate matter;
PAH – polycyclic aromatic hydrocarbon;
VOC – volatile organic compound;
ppm – parts per million;
HC – hydrocarbon;
FAME – fatty acid methyl ester;
USP - United States Pharmacopeia;
FCC - Food chemicals codex;

PSA – pressure swing adsorption;

$ - American dollar;

€ - Euro;

H_2 – hydrogen;

atm – standard atmospheric pressure;

MONG – matter organic non – glycerol;

B – peak integral area;

K – constant;

λ – X-ray wavelength;

t – crystal size;

θ - Brag angle;

C – concentration of the chemical air;

Q – rate of chemical emissions;

u – wind speed in x direction;

σ_y – standard deviation in y direction;

σ_z – standard deviation in z direction;

y – distance along a horizontal axis perpendicular to the wind;

z – distance along a vertical axis;

H – effective stack height;

ΔH – plume rise as defined by Briggs equation;

x – downwind distance;

u – wind speed in x direction;

F_b – buoyancy flux;

g – acceleration due to gravity;

d – stack diameter;

V – exit velocity;

T_s – absolute gas temperature;

T_a – absolute air temperature.

LIST OF TABLE CAPTIONS

Table 1.1	European Union: Estimated biodiesel production, 2005/2006 (thous. t.)	19
Table 1.2	Meeting target quantities in 2005 according to guideline 2003/30/EC	21
Table 1.3	Average biodiesel emissions compared to conventional diesel	34
Table 1.4	Emissions of greenhouse gases (g/km)	35
Table 1.5	Chemical composition of glycerol as related to purity	45
Table 2.1	The highly sulphurous heavy fuel oil qualitative properties	69
Table 2.2	The physico – chemical properties of glycerol	70
Table 2.3	The quality indicators of glycerol	70
Table 2.4	The parameters of heavy fuel oil modification by glycerol and water mixtures	74
Table 2.5	Computer-based qualitative composition X-ray diffraction pattern analysis	80
Table 2.6	The computer-based qualitative composition X-ray diffraction pattern analysis	81
Table 2.7	The compound elements of glycerol liquid product pyrolysis	83
Table 2.8	The measured concentration of CO emission in flue gas from heavy fuel oil combustion process	85
Table 2.9	The measured concentration of NO_x emission in flue gas from heavy fuel oil combustion process	86
Table 2.10	The measured concentration of SO_2 emission in flue gas from heavy fuel oil combustion process	87
Table 2.11	The measured concentration of particulate matter emission in flue gas from heavy fuel oil combustion process	88
Table 2.12	The measured concentration of CO emission in flue gas from heavy fuel oil-glycerol emulsion combustion process	89
Table 2.13	The measured concentration of NO_x emission in flue gas from heavy fuel oil-glycerol emulsion combustion process	90
Table 2.14	The measured concentration of SO_2 emission in flue gas from heavy fuel oil-glycerol emulsion combustion process	92
Table 2.15	The measured concentration of particulate matter emission in flue gas from heavy fuel oil-glycerol emulsion combustion process	93
Table 2.16	Summary of pollutants concentrations measurement results and comparison with MAC values	95
Table 2.17	Sulphur modification with glycerol additive	98
Table 2.18	The glycerol part (%) absorbed by sulphur	99
Table 3.1	Pasquill stability classes	108

LIST OF FIGURES CAPTIONS

Fig. 1.1 Major EU biodiesel producers versus total EU production 16

Fig. 1.2 Absolute production of biodiesel 2002-2004 year 17

Fig. 1.3 Evolution of the biodiesel production in the EU-15 18

Fig. 1.4 Annual market growth projections 2001 – 2011 year 20

Fig. 1.5 JSC “Rapsoila” – the major RME producer in Lithuania 23

Fig. 1.6 Biodiesel production development in Lithuania 33

Fig. 1.7 Relative emissions: diesel and biodiesel 36

Fig. 1.8 Biodiesel production process – input and output 39

Fig. 1.9 Base catalyzed Biodiesel production process 42

Fig. 1.10 Rape seed flowchart 47

Fig. 1.11 Fluctuation of glycerol prices in Europe 55

Fig. 1.12 Overview of the production of the hydrogen from biodiesel waste 62

Fig. 1.13 ADMS 3 simulation potential 66

Fig. 2.1 The principal scheme of experimental pilot plant for modified fuel preparation 67

Fig. 2.2 The principle scheme of thermal oxidizing boiler „UMISA -CR/11,9 (13) “ 68

Fig. 2.3 Thermal oxidizing boiler „UMISA -CR/11,9 (13) “ 71

Fig. 2.4 Gas analyser TESTO 342-3 (Germany) 71

Fig. 2.5 Aspirator (Model 822) 72

Fig. 2.6 Gas detector pump ACCURO (Germany) 73

Fig. 2.7 The PH-meter WTN 330i 75

Fig. 2.8 Micropicture (x100) of freshly made heavy fuel oil-glycerol emulsion structure containing 10% of H_2O 75

Fig. 2.9 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after one month 76

Fig. 2.10 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after 3 months 76

Fig. 2.11 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after 3 months storage and mechanical activation 77

Fig. 2.12 Micropicture (x320) of heavy fuel oil M100 and water emulsion 78

Fig. 2.13 The X-ray diffraction pattern for emulsion ash, obtained in a laboratory 79

Fig. 2.14 The X-ray diffraction pattern for emulsion ash, obtained in a laboratory and treated with hydrochloric acid 79

Fig. 2.15 The X-ray diffraction pattern for ash, obtained while calcining HFO-G emulsion at 600°C for 2.5 hours and slowly cooling it 82

Fig. 2.16 The heavy fuel oil-glycerol emulsion (1:1) ash X-ray diffraction pattern 85

Fig. 2.17 CO emissions from heavy fuel oil combustion process 86

Fig. 2.18 NO_x emissions from heavy fuel oil combustion process 87

Fig. 2.19 SO_2 emissions from heavy fuel oil combustion process 88

Fig. 2.20 Particulate matter emissions from heavy fuel oil combustion process 90

Fig. 2.21 CO emissions from heavy fuel oil – glycerol emulsion combustion process 91

Fig. 2.22 NO_x emissions from heavy fuel oil – glycerol emulsion combustion process 92

Fig. 2.23 SO_2 emissions from heavy fuel oil – glycerol emulsion combustion process 93

Fig. 2.24 Particulate matter emissions from heavy fuel oil – glycerol combustion process 96

Fig. 2.25 Comparison of HFO measured concentrations to their MAC values, mg/Nm^3 97

Fig. 2.26 Comparison of HFO-G emulsion measured concentrations to their MAC values, mg/Nm^3 99

Fig. 2.27 Sulphur modification with glycerol as a plasticizer 99

Fig. 3.1 The schematic geometry of Gaussian plume model 103

Fig. 3.2 Wind effect on pollution dispersion 106

Fig. 3.3 Schematic Gaussian Plume model: side and top view 109

Fig. 3.4 Operational pollution model and dispersion parameters 109

Fig. 3.5 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (Top view) 112

Fig. 3.6 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (Side view) 113

Fig. 3.7 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (plume crossection) 114

Fig. 3.8 Operational pollution model and dispersion parameters 115

Fig. 3.9 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (Top view) 116

Fig. 3.10 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (Side view) 117

Fig. 3.11 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (plume crossection) 118

Fig. 3.12 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (Top view) 120

Fig. 3.13 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (Side view) 121

Fig. 3.14 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (plume crossection) 122

Fig. 3.15 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (Top view) 123
Fig. 3.16 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (Side view) 124
Fig. 3.17 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (plume crossection) 125

INTRODUCTION

The problem. The heavy fuel oil still is one of the most popular types of fuel in the major heat supply and industrial boiler-houses in Lithuania. In the most region centres of Lithuania, which are not connected to the natural gas network, the heavy fuel oil is the strategical fuel of a high importance. In many cities heavy fuel oil is mostly used as an alternative for natural gas.
According to the order August 31, 2001 No. 438/268/266 signed by the Ministries of Environment, Economy and Transport and Communications of Lithuanian Republic, prohibition for the heavy fuel oil with sulphur content higher than 1 % usage came into force from January 1st 2004, unles the SO_2 emission concentration level in the exhaust flue gas does not exceed value of 1 700 mg/Nm^3. Currently, the heavy fuel oil combustion MAC SO_2 values are defined in the normative document LAND 43-2001 “Norms for the exhaust of pollutants from large fuel burning equipment“. Such MAC SO_2 < 1 700 mg/Nm^3 value can be obtained if heavy fuel oil is combusted with sulphur content up to 1 % (according to the EU Directive 1999/32/EC). Neither SC „Mažeikių nafta“, nor Russia or Belarus oil refining companies produce heavy fuel oil, that would meet such requirements (here sulphur content in heavy fuel oil ~ 2.0 - 2.5 %). In such a case, heavy fuel oil with sulphur content ~ 2.2 % could be combusted in large fuel combustion equipment only if combined with at least 50-55 % of biofuel. The biodiesel, produced from rape seed, does not emit sulphur compounds during the combustion process. Only in such a case, when mixing the heavy fuel oil with biodiesel, can the SO_2 emission level 1 700 mg/Nm^3 and lower be achieved. Since the year 2008, requirements for SO_2 emission will be even more strictened (according to the principle of linear decrement 1 700 mg/Nm^3 - 400 mg/Nm^3), so the solution for this significant problem of Lithuania energetics sector must be found as soon as possible.

Also, according to the Directive of the European Parliament and of the Council 2003/30/EC, the use of biodiesel for transport is promoted. The attainable fuel quata is presented in this Directive. By 2005, the minimum share of biofuels was 2 % and should gradually rise to 5.75 % by the year 2010. With substantial increases in biodiesel output, there is inevitably proportionate increase in glycerol volumes. The main restrictive factor for biodiesel production expansion - high production costs and generated relatively large amounts of by-products. The cost of biodiesel is the main hurdle to commercialization of the product. The main means for cost minimization and profitability increment is the rational waste and by-products utilization.

The actuality of the investigation. Recently, the increase in crude oil prices, limited resources of fossil oil and environmental concerns (lowering CO_2 emissions) leads to the significant interest in biofuels. Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources.

During rape seed oil transesterification by methanol a methyl ester biodiesel – rape methyl ester (RME) - is produced. The biodiesel production generates wastestreams; however, unlike many production processes, biodiesel production also produces by-products that are of significant market value. In fact, the economic viability of today's biodiesel industry is so sensitive that the overall economic viability is highly dependent on the market price of these by-products. Glycerol is a major by-product of the biodiesel production process, obtained through the transesterification reaction, with most estimates of the by-product are as high as 10 % of the product output. High purity glycerol has many potential customers in the world marketplace, including the pharmaceutical and cosmetics manufacturers. However, biodiesel-derived glycerol is of poor quality and requires expensive refining before it is suitable for new product technologies. So, it needs to be pointed out that new niches for technically impure glycerol must be found with a view of biodiesel production cost minimization and increment of competitiveness to conventional diesel.

Taking into account USA and EU Directives (Directive 2003/30/EC of the European Parliament and the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport), promoting biodiesel production and consumption extents, it could be projected, that surplus glycerol will become even more sore point in a context of economically viable and cost-effective biodiesel production development. At the present moment glycerol surplus in a global market is significant. The expansion of biodiesel production worldwide is driving down the value of glycerol and reducing by-product revenue of biodiesel and oleochemical producers. The biodiesel production costs are higher than those of mineral diesel, therefore only efficient use of by-products could enable biodiesel compete with coventional diesel in respect of production costs. To ensure the future of this biofuel technology, the new outlets must be found for this by-product.

Lithuania, according to the EU Directive requirements, also promotes biodiesel production and consumption, thus glycerol utilization researches are also in progress as well. Recently, Lithuania with foreign associates participates in the scientific programme EUREKA for research in glycerol utilization.

Investigation objective. The objective of investigation is the rape seed oil methyl ester production by-product – glycerol utilization as related to SO_2 emission to the atmosphere lowering it to MAC <1 700 mg/Nm^3 level and economically beneficial glycerol utilization for biodiesel production cost and glycerol surplus in the market reduction.

Investigation tasks are the following:

1. To collect information from different sources and prepare a literature review for the present situation of biodiesel production and by-product utilization practice.
2. To describe the present situation in Lithuania.
3. To investigate the heavy fuel oil – glycerol emulsion preparation, its stability, homogeneity and dispersivity conditions and to obtain the most optimal solution.
4. To perform the phase composition and quantitative impurity analysis for the heavy fuel oil - glycerol emulsion ash using the X-ray diffraction pattern analysis method at VGTU Institute of Thermal Insulation.
5. To perform heavy fuel oil and prepared heavy fuel oil – glycerol emulsion combustion experiments and measure CO, NO_x, SO_2 and particulate matter emission concentrations in the exhaust flue gas at JSC „Rietavo veterinarinė sanitarija“ boiler and to compare with their MAC values.
6. To evaluate the heavy fuel oil – glycerol emulsion combustion process influence on SO_2 emission concentrations.
7. To simulate model for dispersion of pollutants under various specific conditions.

Novelty of the investigation. The recent, traditional glycerol utilization methods leads to the use of expensive distillation methods, thus the development of new, cost - effective technologies for further new novel glycerol fraction applications is needed. The new solutions would eliminate an unavoidably expensive glycerol phase processing and create conditions for more economically efficient biodiesel production. This also would strenghten biodiesel and related companies viability and competitive ability in local and foreign market. With reference to the results of this investigation the probability to use heavy fuel oil modified by glycerol additive emulsion as a fuel, with a purpose to meet the EU Directive 1999/32/EC requirements for $SO_2 < 1\ 700$ mg/Nm^3 and glycerol utilization will be evaluated.

Practical value of the research. As a result of this investigation, the technological regulations and recommendations would enable companies, which are interested in rational biodiesel production by-product glycerol utilization, and also companies, using sulphurous heavy fuel oil as a fuel to meet the EU requirements for heavy fuel oil combustion and to lower SO_2 emission levels to the admissible concentrations.

1. A REVIEW OF BIODIESEL PRODUCTION AND BY-PRODUCT UTILIZATION: CURRENT SITUATION AND FUTURE PROSPECTS

1.1. A REVIEW OF THE SITUATION IN THE WORLD AND LITHUANIA

Nowadays we have based our mobility on the unrestricted use of fossil fuel. But these resources are limited and using them often results in high environmental pollution. Substituting mineral oil diesel with biodiesel from rape-seed oil in diesel engines is one way of reducing environmental pollution. This option has now been fully researched, tested and demonstrated.

The global market for biodiesel is poised for explosive growth in the next ten years. Although Europe currently represents 90 % of global biodiesel consumption and production, the U.S. is now ramping up production at a faster rate than Europe, and Brazil is expected to surpass U.S. and European biodiesel production by the year 2015. The biodiesel market in the U.S. has a significant amount of room to grow to reach the status of its European counterparts. In Europe, biodiesel represents 2 % of total on-road transportation fuel consumption and is expected to reach 6 % by 2010. The total biodiesel being sold in the U.S. amounts to less than 1/2 of 1% of all petro-diesel on-road consumption in 2005.

As it is given in Fig. 1.1, close to 2 million tons of biodiesel were produced in 2004, mainly in Germany, France and Italy. Production increased at ~ 35 % since 2002 and if the aim of the Directive 2003/30/EC on the promotion of the use of biofuels for transport is attained, European demand will increase to around 10 million tonnes per year (note : 1 tonne biodiesel equals 1.143 litres) [1].

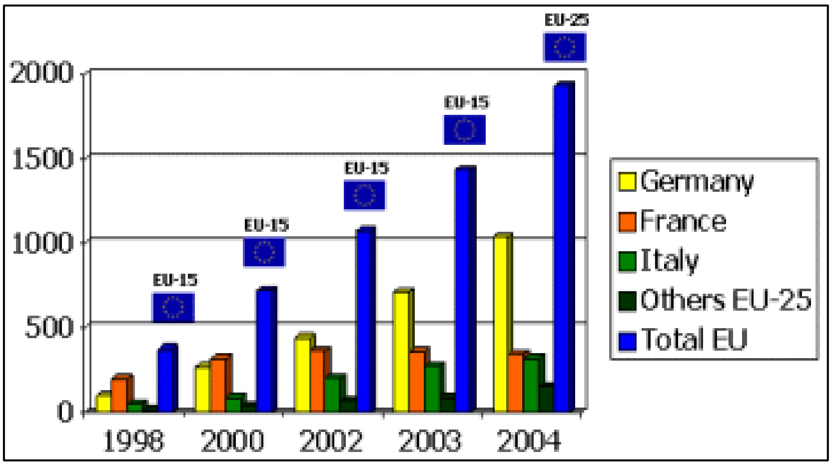


Fig. 1.1 Major EU biodiesel producers versus total EU production

It is estimated world production of biodiesel reached 3 billion litres per year in 2005/06 and could be 3.7 billion litres per year in 2006/07. Biodiesel production has been driven in the European

Union (EU) and the United States (US), however other regions are adopting biofuels at a rapid rate. The US and EU markets are supported by government legislation, which has in affect created the market for biodiesel, as it is still not as economical to produce as mineral diesel. The major biodiesel producing countries are driven by similar goals - reduced pollution, increased jobs in the rural sectors and a reduced reliance on imported mineral fuels. Each country has strong lobby groups which reflect each of these causes. Malaysia and Indonesia are gearing up to supply the global market with relatively inexpensive crude palm oil as a feedstock, and more recently plans have begun to build biodiesel plants on several sites in the Association of South East Asian Nations (ASEAN) region [1].

In other parts of the world, biodiesel is becoming increasingly important as governments react to growing petroleum import dependency and enact new alternative fuels policies and targets. Economic and environmental security concerns are giving birth to new government targets and incentives in China, India, Brazil and Europe, aimed at reducing petroleum imports and increasing the consumption and production of alternative and renewable fuels [2].

Use of biodiesel is most advanced in Europe [3]. B100 or pure biodiesel is now widely available in Germany, Italy and Austria. In Germany there are over 1000 outlets where biodiesel is cheaper than standard diesel. France, currently the largest user of biodiesel in the world, has a minimum mix of 5 % in all diesel sold, with B50 becoming more common and popular. In both Europe and the US some diesel car manufacturers have extended their warranties to cover biodiesel. Biodiesel production in Europe and the US is given in Fig. 1.2 (million gallons/year; note: 1 US gallon = 3.7854118 liters):

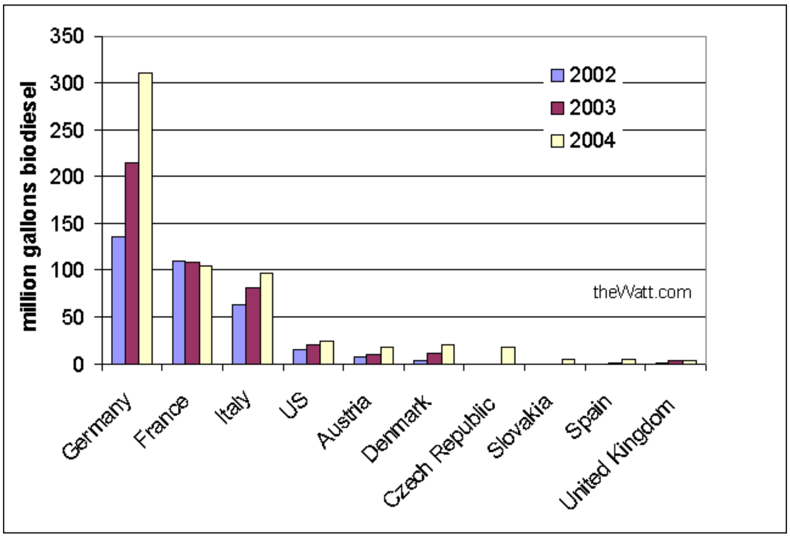


Fig. 1.2 Absolute production of biodiesel 2002-2004 year

Biodiesel production began in Austria in 1988 with a 500 t/y plant owned by a farmers' co-operative. Other plants soon followed, and the first industrial-scale biodiesel plant, with a capacity of 10.000 t/y, started up in Austria in 1991. In the following years larger plants were established all over Europe. Examples are Livorno, Italy (up to 80.000 t/y), Rouen, France (at 120.000 t/y the world's largest plant to date), Germany and Sweden. With 16 biodiesel plants, the Czech Republic is the leader in number of sites.

The EU is today the principal region in the world having developed biodiesel sector. Europe produced 1.434.000 tons of biodiesel fuel in 2003, representing an average annual increase of 34.5 %, corresponding to 26 times the amount produced in 1992. Even though there is currently a production over capacity in Europe, numerous new units should be created over the next years to meet the requirements of the European directive on biofuels. The leading European biodiesel producer is Germany, with a production of 715.000 tons. France, which was the leading biodiesel producer until 2001, produced 357.000 tons in 2003, ahead of the other European Union countries such as Italy (273. 000 tons). Evolution of the biodiesel production in the EU-15 is given in Fig. 1.3 [4]:

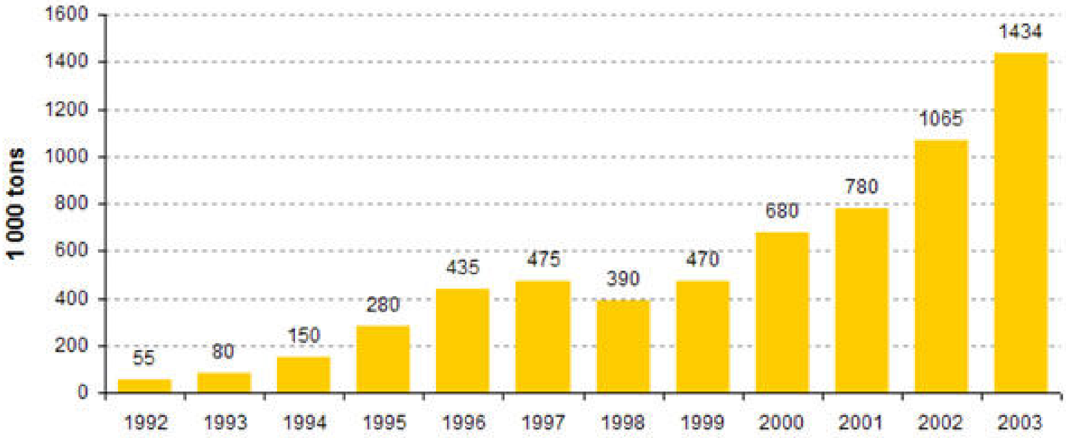
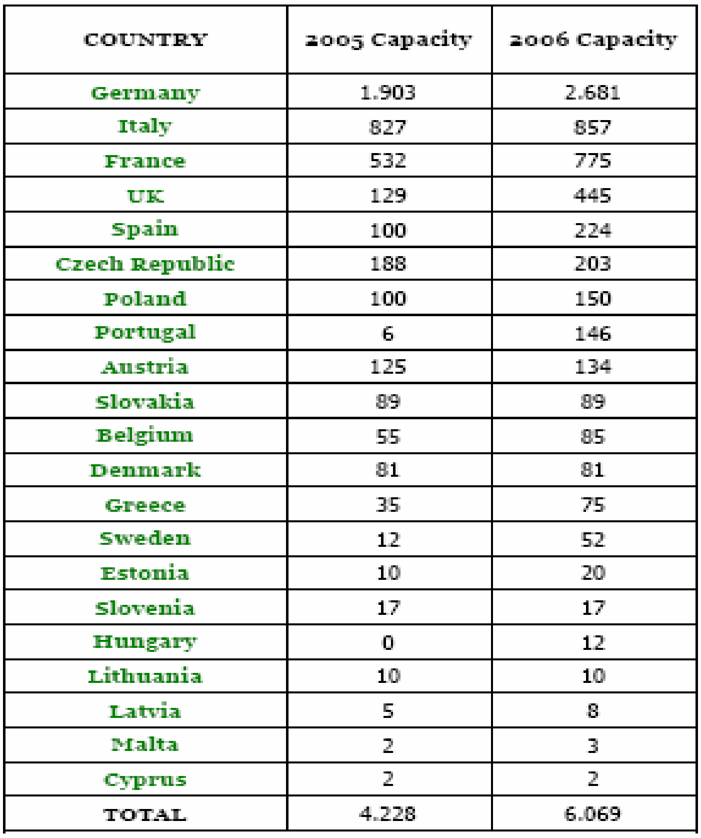


Fig. 1.3 Evolution of the biodiesel production in the EU-15

Biodiesel accounted for nearly 80 % of EU biofuel production in 2004. Production was close to 2 million tonnes compared with 1.5 million tonnes in 2003 - a 29.6 % growth in a single year. Germany produced over half of the EU's biodiesel, with production above one million tons for the first time. This can be explained by very favourable legislation that permits a total tax exemption for biofuels whether they are pure or mixed with fossil fuels. Among the new Member States, the Czech Republic is the biggest biodiesel producer [5]. Biodiesel production in Europe is growing, and is becoming an important part of the European market for rapeseed. Annual biodiesel output is now over a million tons per year and requires the input of an estimated 2.7 million tons of oilseed. Biodiesel is not cost competitive with petroleum diesel without subsidies or tax incentives except in cases where petroleum prices are high in the extreme and vegetable oil prices are low. Biodiesel has a major advantage over petroleum diesel in that it is derived from renewable sources; thus, on a net basis, fewer greenhouse gases such as carbon dioxide are emitted into the atmosphere. The political support for the production and consumption of biodiesel and renewable fuels appears to be present to expand the biodiesel industry [6].

Two factors have contributed to Europe's aggressive biodiesel industry expansion (see Table 1.1). First, in 1992, reform of the Common Agricultural Policy addressed European agricultural surpluses by idling some land used for food production through a set-aside policy. This policy, which provides a substantial subsidy to non-food crop production, stimulated the use of set-aside land for non-food purposes. In some instances the set-aside subsidy is topped up if the land is planted to raw material for biodiesel production.

Table 1.1 European Union: Estimated biodiesel production, 2005/2006 (thous. t.)



COUNTRY	2005 Capacity	2006 Capacity
Germany	1.903	2.681
Italy	827	857
France	532	775
UK	129	445
Spain	100	224
Czech Republic	188	203
Poland	100	150
Portugal	6	146
Austria	125	134
Slovakia	89	89
Belgium	55	85
Denmark	81	81
Greece	35	75
Sweden	12	52
Estonia	10	20
Slovenia	17	17
Hungary	0	12
Lithuania	10	10
Latvia	5	8
Malta	2	3
Cyprus	2	2
TOTAL	4.228	6.069

In September 2001 the Directorate – General Transport and Energy of the European Commission drafted a proposal for a Directive of the European Parliament and of the Council on the promotion of the use of bio-fuels for transport. In essence, the proposed directive aimed at increasing the use of biofuels for transport within the EU by requiring that a minimum percentage of the total transport fuels sold in each Member State is biofuels in pure or blended form. By 2005, the minimum share of biofuels should be 2 % and should gradually rise to 5.75 % by the year 2010 (these quantitative commitments set out have not been applied before 2005 in order to allow sufficient time for Member States to establish the necessary production facilities). In order to achieve this directive gave Member States the option of applying a reduced rate of excise duty to pure or blended bio-fuels. The introduction of the EU's directive has led to a large increase in biofuels production, an increase of around 100 % over the last five years.

In response to increased demand for industrial oilseeds for the manufacture of biodiesel, set-aside land planted to oilseeds for industrial purposes is estimated to have increased by 50 percent in 1995-1996 to about 0.9 million hectares. If recent increases in industrial oilseed production are maintained, the Blair House Agreement limit of 1.0 million tonnes in soybean meal equivalent could be approached and/or exceeded within the next few years. Second, high fuel taxes in European countries normally constitute 50 % or more of the retail price of diesel fuel. The majority of European governments believe that the alternative use concept for cereal grains has little economic justification and will in fact merely add to, rather than relieve, pressures on agricultural budgets.

Europe, Frost & Sullivan industry experts [7] anticipate annual market growth of up to 26 % per annum until 2011 (Fig.1.4), since the imports of vegetable oil from all over the world are on the increase and the enormous potential cultivation area for renewable raw materials in Central and Eastern European countries is increasingly being developed. ~ 11 million tons of biodiesel is projected to be produced in EU until 2010, so ~ 1.16 mln tons of glycerol will be generated then.

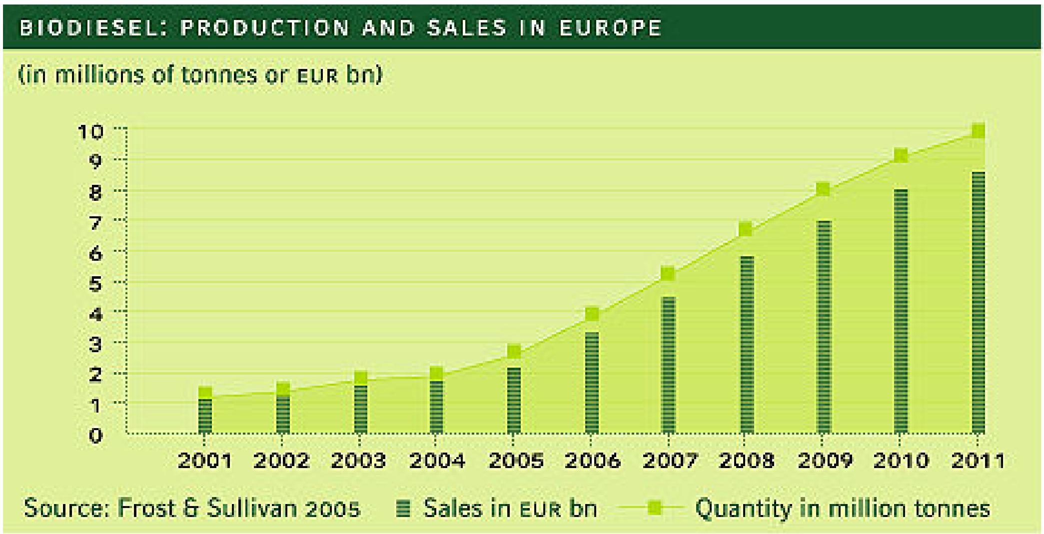


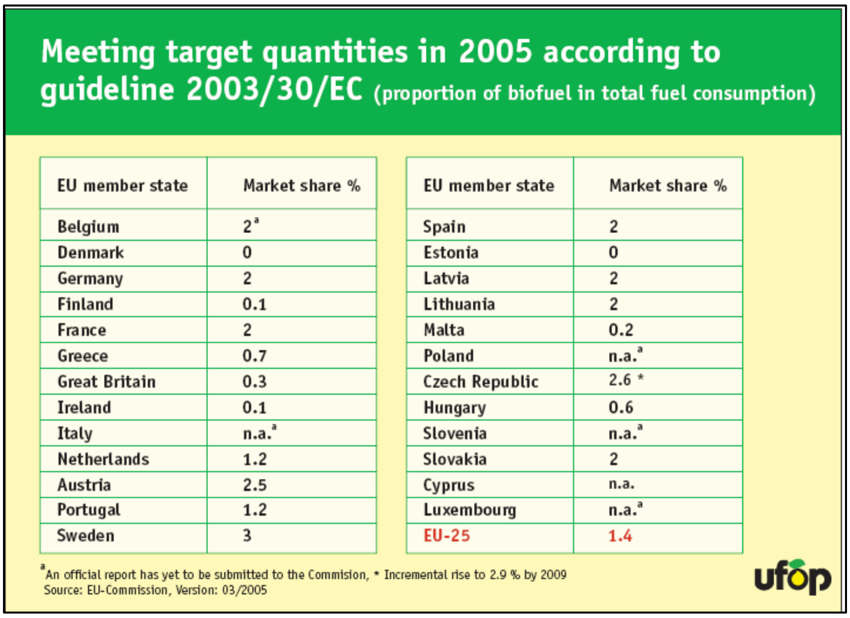
Fig. 1.4 Annual market growth projections 2001 – 2011 year

Despite strong political opposition, however, the European Parliament in February 1994 adopted a 90 % tax exemption for biodiesel. The combination of legislation supporting the use of alternative fuels, differential tax incentives and oilseed production subsidies, resulted in biodiesel being priced competitively with diesel fuel in a number of European countries. Tax incentives take the form of significantly reduced assessments or exemption from taxes normally assessed on diesel fuel.

As of 1995, western European biodiesel production capacity was over 1.1 million tonnes per year largely produced through the transesterification process. This adds over 80,000 tonnes of glycerol by-product to the market annually and has created a glut of glycerol on the market. In fact, Germany is limiting production of biodiesel using the transesterification process because of an excess supply of glycerol. One method of disposal of the excess glycerol is incineration; however this wastes a manufactured product, creates an environmental risk and results in additional costs. Germany is now focussing on biodiesel production using the cold pressed rapeseed method to avoid the excess glycerol problem. In some European countries some marketing cooperatives have produced biodiesel in a small scale through the transesterification process for their own consumption. However, utilization of the glycerol by-product remains a problem.

Several other European countries have been considering biofuels policies as part of efforts to achieve the EU biofuels target of 5.75 % of transport fuels by 2010. The proportion of biofuel in total fuel consumption in EU contries meeting the target levels set in EU Directive 2003/30/EC [8] is given in Table 1.2:

Table 1.2 Meeting target quantities in 2005 according to guideline 2003/30/EC



Meeting target quantities in 2005 according to guideline 2003/30/EC (proportion of biofuel in total fuel consumption)

EU member state	Market share %	EU member state	Market share %
Belgium	2[a]	Spain	2
Denmark	0	Estonia	0
Germany	2	Latvia	2
Finland	0.1	Lithuania	2
France	2	Malta	0.2
Greece	0.7	Poland	n.a.[a]
Great Britain	0.3	Czech Republic	2.6 *
Ireland	0.1	Hungary	0.6
Italy	n.a.[a]	Slovenia	n.a.[a]
Netherlands	1.2	Slovakia	2
Austria	2.5	Cyprus	n.a.
Portugal	1.2	Luxembourg	n.a.[a]
Sweden	3	EU-25	1.4

[a] An official report has yet to be submitted to the Commision, * Incremental rise to 2.9 % by 2009
Source: EU-Commission, Version: 03/2005

An EC Directive in 2003 provided targets for each country to meet by 2005 (2 %) and 2010 (5.75 %). Although the targets are voluntary, countries have had to submit plans for meeting targets, or justifications for why they won't. Some EU members have recently enacted biofuels promotion laws or binding targets, including Hungary, which mandates 2 % of total energy from biofuels by 2010, and the Netherlands, with a target of 2 % of transport fuels.

The current situation in Lithuania. After entering the EU, Lithuania also committed itself unconditionally to the Kyoto Protocol and various EU environmental directives. Apart from other measures, the use of biofuels is to be increased considerably. On January 18, 2007 Lithuania published an Updated National Energy Plan which emphasizes its commitment to renewable energy, both biomass and biofuel. Lithuania aims to become less dependent on the world market for its energy needs. It is currently heavily dependent on Russia, particularly for inputs for its nuclear power plant and for natural gas. There is a general concern that Russia has become an unreliable energy source, noting problems with the Russian energy supply to several of the countries in the region. In addition, the high price of oil has also generated interest in alternative energy sources.

Since the beginning of April 2006, the diesel sold in petrol stations in Lithuania has been blended with rapeseed methyl ester (RME), and petrol with ethyl alcohol (ethanol). The obligatory use of biofuel was introduced by the Law on Biofuel [9] that was passed in 2000. Of course, Lithuania cannot compete with Brazil, which has been the leader in the use of biofuel for several decades, and produces half of the world's ethyl alcohol. Neither can it compete with Germany, which produces and uses the largest amount of biodiesel in Europe, at about two billion litres a year. EU standards allow for the blending of up to 5 % of products of biological origin with fuel. In such cases, special notice is not required at the point of sale. In most countries, a much larger percentage of products of biological origin is allowed. For example, in America, the blend standard is 10 % and in Brazil as much as 90 %.

Mažeikių Nafta and Lukoil Baltija are still the largest companies which blend fuel with bio-additives. The latter, which sells oil products, was the first to blend RME with diesel fuel, and ethyl alcohol with petrol. It began to sell biofuels of both types, biodiesel and 92e5 petrol, in its petrol stations a few years ago. Biodiesel price is similar to petrodiesel costs or even higher.

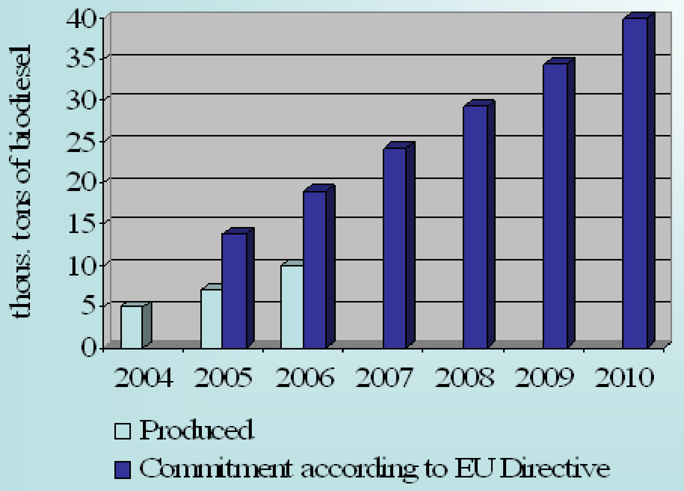
There are ten companies in Lithuania which plan to produce or are already producing biological additives for fuel. While some are waiting for support from EU funds, or trying to decide on sale prices, or looking for suppliers of the raw material, others can barely keep up with the market and increase their production. JSC „Rapsoila“, which is located in the Mažeikiai region, near the border with Latvia, belongs to the latter group. The picture of major Lithuanian rape seed methyl ester producer JSC "Rapsoila" is given in Fig. 1.5:

Fig. 1.5 JSC “Rapsoila” – the major RME producer in Lithuania

Four years ago it was the first company in Lithuania which began to produce biofuel. For the last few years, its factory has been processing 30,000 tonnes of rapeseed, and out of the pressed oil it has obtained 10.000 tonnes of RME each year [10]. It aims to increase production capacity to the 30.000 tones of biodiesel in 2007. The company buys both rapeseed oil and rapeseed from farmers and other companies. JSC „Rapsoila“ has a quality certificate, which testifies that the RME it produces corresponds to the European standard. The biodiesel producton by-product rapeseed oilcake is becoming more popular among cattle breeders. The company used to export a large amount of it, but now they can hardly keep up with the demand of the local market. Rapsoila makes biofuel only out of locally grown rapeseed. The company sells most of production to Mažeikių Nafta and Lukoil Baltija, and some to the Statoil chain of petrol stations. Last year, though, when the demand for RME was not high, they sold 65 % of their production to Germany, as the demand there exceeded the rate of production. Now biodiesel costs the same as traditional diesel. It is predicted, that if the demand does not exceed supply, the price will not rise. Though an ecological product should cost more, like, for instance, ecological food products, but biofuel prices should be competitive to conventional fuel to remain competitive and marketable. As the biodiesel in petrol stations is now blended, anyone can use biofuel. However, a few years ago, when biofuel was still making its way into the market, promotion campaigns were very necessary. Mažeikių Autotransporto Ūkis was one of the first to use the biodiesel made by Rapsoila. Four of the company’s buses filled their petrol tanks with pure RME, and 20 others used RME mixed with traditional diesel. Vilnius city also participated in the biodiesel promotion campaign. In 2004, more than half (136) vehicles of Vilniaus Autobusai filled their tanks with ecologically clean Rapsoila fuel.

The obligatory consumption for Lithuania of the 2 % biofuel, in accordance with the EU directive, amounted to 20.000 tonnes in 2006 [11]. Of this, RME is 14,000 tonnes, and bio-ethanol 6.000. This target is quite easy for Rapsoila alone to achieve. It has been producing most of the RME so far. The second 'veteran' in the production of bio-additives is the Stumbras distillery. The company's operation in Šilutė has been going for three years now, and manufactures about 10.000 tonnes of bioethanol a year.

Biodiesel production capacities and perspectives in Lithuania are reflected by Fig. 1.6.



Source: Lithuanian energy institute

Fig. 1.6 Biodiesel production development in Lithuania

According to the Ministry of Agriculture, ~ 24.000 tonnes of RME will be needed in 2007, and ~ 29.000 tonnes in 2008. ~ 7.000 tons of biodiesel was produced in 2005 along with ~ 742 tons of glycerol generated. Moreover, according to the commitments to EU, at least ~ 40.000 tons of biodiesel should be supplied to the market in 2010, and this would lead to 4.000 tons of glycerol. Accordingly, the current situation shows that the production capacity is quite enough for the manufacture of the necessary quantity of biofuel. In addition, there is a real flurry on the biofuel market. As long as oil prices remain at around fifty dollars a barrel or even higher, the manufacture of biofuel will have great potential. Currently oil prices are about seventy dollars a barrel or higher, so the business is very profitable. That's why many people are investing in factories in order to get a share of the market.

What concerns biodiesel by-products utilization practices in Lithuania, the similar problems are observed. Recently, the rape meal has found its utilization niche, though glycerol utilization question remains under a big question-mark. Currently, the largest biodiesel producer JSC "Rapsoila" deposits surplus glycerol in the repositories and is expect for the potential customers along with novel niches for glycerol utilization.

Arvi, a new Marijampolė-based company producing biodiesel, is opened. With investment exceeding 23 million litas, the company appeared on the premises of “Arvi Cukrus”, in Vilkaviškis. The projected capacity is 12.000 tonnes per year. It will produce biodiesel from rape grown by local farmers, and lard to be supplied by “Rietavo Veterinarinė Sanitarija”, a company also owned by Arvi. “Arvi Cukrus” has signed numerous agreements with local farmers on buying up rapeseed. Half of the fuel manufactured will be used for company transport, and the rest will be sold. The Joniškis-based company “Šiaurės Vilkas” is also making great efforts to enter the biofuel market. It is marketing rape, wheat and barley both at home and abroad. In 2005, the company acquired the bankrupt oil producer “Obelių Aliejus” in an auction, and set up “SV Obeliai”, a special company for manufacturing biofuel. To start the new business, it took out a three million euro loan (10.4 mln Lt), and expects to receive 3.5 million litas more from EU structural funds [12]. At the moment, the projected production capacity is 6.000 tonnes a year, but the company has ambitious plans for next year.

The farmers who grow rape and sell the seed earn about 2.100 litas per hectare. If they sell their own pressed oil, oilcake and rape straw, with subsidies from the state, they can get over 3.200 litas per hectare. The cost price of biofuel is about a third higher than that of oil products. Therefore, without state support, the business would make a loss. Biodiesel and bioethanol are made from rapeseed and grain respectively, and the manufacture of the fuel should be subsidised in order to make it affordable for the customers. It is estimated that a tonne of biodiesel would require a 450-litas subsidy, and a tonne of bioethanol about 200 litas. According to the Biofuel Association, the aggregate total of subsidies for biofuels would amount to 14.1 million litas this year, including 9.1 million litas for biodiesel and 5 million litas for bioethanol. In 2007, the projected subsidies for the acquisition of grain should amount to 9.12 million litas, and for rapeseed 24 million litas. In 2008, it should be 12.54 million litas and 36.8 million litas respectively. In 2007, manufacturers of bioethanol will be compensated 114 litas per tonne for the acquisition of grain, and manufacturers of RME, 160 litas per tonne for the acquisition of rapeseed. In 2007, the need for rapeseed will reach 600,000 tonnes. In 2006, farmers harvested only 239.000. So, the farmers should significantly increase productivity. According to experts, the quantity of rapeseed grown in Lithuania is enough for one medium-size plant. Average EU biodiesel plants process from 200.000 to 400.000 tonnes a year. This kind of capacity allows them to remain competitive.

The development of the biofuel market is a strategic objective for the country, leading us to independence from Russia in energy terms. Needless to say, this business will contribute to the creation of job opportunities in rural and urban areas, increase farmers’ earnings, and provide an opportunity to choose an ecological and quite inexpensive fuel.

1.2. MAIN RAPE METHYL ESTER (RME) CHARACTERISTICS

Tackling climate change presents a major challenge to society to find ways of cooperating and innovating to make possible the big cuts in carbon emissions that are necessary. Biofuels from crops offer not just the potential for significant carbon reductions from transport, but other environmental benefits as well.

"The use of vegetable oil as a fuel may today be rather insignificant, but such products can become very important over time such as petroleum and coal-tar-products today." Even though these perceptions may sound new today, they were written down in the year of 1912 by Rudolf Diesel in a patent specification. It took about 80 years until vegetable oil actually played a role as a fuel [13].

In any case it is a high-tech product that contributes a great deal to the reduction of noxious exhaust fumes and thereby represents an important relief to the environment. Biodiesel is the name of a clean burning alternative fuel produced from domestic renewable resources [14]. Biodiesel is produced from any fat or oil through a refinery process called transesterification. Biodiesel can be used directly as a fuel or blended with petrodiesel. The most common blend being 20 % biodiesel by volume with 80 %, petroleum diesel represented as BD20. Its physical and chemical properties as it relates to operation of diesel engines are similar to petroleum based diesel fuel. Biodiesel is clean, environmentally friendly, burns completely, easily biodegradable, and emits less pollutions than diesel oil when used in diesel engines.

In Europe the use of rapeseed oil fuels in diesel engines has been intensively investigated since the beginning of the on-going energy crisis. In the beginning, the emphasis was placed on the technical possibilities associated with the use of rapeseed oil as a fuel. However, research has shown that pure rapeseed oil can only be used in specially designed engines. Research that followed indicated that rapeseed oil methyl ester (RME) was a suitable replacement for petroleum diesel fuel (DF). After this discovery, research has focused on the engine exhaust emissions that result when fueling with both unmodified rapeseed oil and RME. In the USA research has focused on soybean oil methylester (SME). Nowadays both RME and SME are called biodiesel. Initially, environmentally relevant research concentrates on the federally regulated hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO) exhaust gas emissions. In addition, a series of current publications compare the environmentally important but nonregulated polycyclic aromatic hydrocarbons (PAH), aldehydes, and ketones and in some cases, the aromatic compounds.

Rape methyl ester (hereinafter referred to as RME) is the rape methyl ester that is produced from the rape-oil by the esterification and that is intended for the diesel engines. Usually the mix of the traditional diesel fuel and RME, which is called biodiesel, is used for engines. The optimum mix of biodiesel fuel is when the composition of mix is 35 % of RME and 65 % of traditional diesel fuel. As the producers of RME, "Rapsoila" JSC, claims the ratio of RME may be increased up to 50 percent. Biodiesel improves the lubrication of the engine. If the biodiesel fuel is used, the smokiness is reduced by 60 % in comparison to the mineral diesel fuel; due to this fact, while executing the technical inspection of the vehicles in accordance to LAND 15-96, the vehicles, which technical condition do not allow their exploitation, if the traditional mineral diesel fuels are used, will be possible to exploit while using the biodiesel fuel. RME is characterized for the bigger amount of oxygen in comparison to diesel fuel (10.8%); due to this fact it burns much better in the engine. The bio raw materials are neutral in regard to emissions of CO_2 [15].

The temperature of the combustion of RME is higher than 1200°C whereas the temperature of the combustion of the diesel is only about 550°C. In regard to fire prevention, the RME is more suitable for stationary engines that work indoors and for the engines of the vehicles that carry people, fuel, dangerous materials and etc. The cetene number of diesel fuel is not less than 51 (the minimum limit during the winter season is 48), and the cetene number of RME is 51. So these fuels are very similar. The bigger the cetene number, the more quickly the fuel is inflamed and it is more easy to start the engine that is very important during winter season.

The density is also very important characteristic of fuel. It helps to decide on the chemical and fractional composition, the viscosity and the calorific value of the fuel. The density of the diesel is 0.82-0.845 g/cm^3, and the density of RME is 0,84-0,89 g/cm^3, if the temperature is 150°C. The density of RME is less dependable on the temperature. Due to the higher density of RME, a smaller quantity of RME is used while going the same distance.

The kinematic viscosity of diesel fuel in the temperature of 400°C is 4.5mm^2/s; the kinematic viscosity of RME in the same temperature is 3.5-5.0 mm^2/s. In regard to these facts, the better qualities belong to the diesel fuel because it better filtrates through cleaning filters, its fluidity is better. However, the more viscous fuel has better lubricating and sealing qualities. The ash-content increases not only the quantity of slag, but also it increases the abrasion of cylinder. Due to these facts, the ash-content should not be higher than 0.01 %. Yet, the ash-content of RME is 0.02 %. However, the ashes of RME are of biological nature and are not characterized by the abrasive qualities.

Biodiesel dissolves the deposits that accumulate in the tanks of fuel, the housings of filters and pipelines during the longer period of time. The rapidly increased quantity of contamination may block the filters of fuel system and disorder the work of entire supply system. It is particularly relevant, if the fuel is kept in the casual unclear tanks or if infiltrated fuel is poured to the tanks.

Due to this reason it is recommended to clean the entire supply system, to change the filtrating elements before the usage of biodiesel.

The biodiesel slightly changes rubber parts. However, the research that has been carried out in the Czech Republic showed that the negative effects are not so intense if the mix of 30 % of RME and 70 % of mineral diesel is used; this mix may be used in the usual engines without changing their construction and exploitation requirements [16].

1.3. ADVANTAGES AND DRAWBACKS OF BIODIESEL FUEL

Key benefits of Biodiesel [17]:

- Similar physical and chemical properties to petroleum diesel.
- For each unit of energy input, biodiesel creates 3 or more energy units.
- Engine performance is virtually the same as petroleum diesel. Higher cetane value than conventional diesel, means reduced knocking and smoother running engine.
- It can be used in almost any diesel with little or no engine modification.
- Non-toxic, biodegradable and essentially free of sulphur and carcinogenic benzene. No danger from oil spills and safer to handle.
- Safe storage is possible due to the higher flash point of biodiesel. This reduces risk of fire in transport, storage and delivery of biodiesel.
- Produces a significantly improved emissions profile because it contains virtually no sulphur or carcinogenic benzene.
- Markedly improves combustion and makes for a significantly cleaner burn because biodiesel supplies additional oxygen (contains 11 % oxygen by weight vs. diesel has 0 % oxygen). Biodiesel have higher oxygen content which ensures complete combustion of hydrocarbon.
- Mixes readily with petroleum diesel, making it a very effective fuel additive. In a 20 % blend with diesel, emissions are significantly reduced.
- Improved lubricity of the fuel means there is less need for maintenance of injectors and injector pumps.
- Cleans fuel system instead of leaving deposits like normal diesel does.
- Quality is assured by ASTM standards.

Socio-Economic benefits of Biodiesel use:

- Expansion of farming capacities.
- Creates new production jobs and a new industry.
- Insurance against oil embargos.

- Reduces dependency on foreign oil.

Environmental benefits of Biodiesel use:

- It's a renewable energy source – inexhaustible energy source.
- It reduces the emission of particulate matter by 40 %, carbon monoxide by 44 %, unburnt hydrocarbon by 68 %, polycyclic aromatic hydro-carbons by 80 %, carcinogenic nitrated PAHs by 90 % on an average compared to petrodiesel.
- Sulphur emissions are essentially eliminated with pure biodiesel. The exhaust emissions of sulphur oxides and sulphates (major components of acid rain) from biodiesel are essentially eliminated compared to diesel.
- Free of carcinogenic benzene and other carcinogenic emissions are reduced.
- It is safe to handle as it is non toxic and biodegradable.
- Does not increase life cycle carbon (CO_2) in the atmosphere helping stop global warming. Decreases fossil fuel based CO_2 by 78 %.
- Reduces hydrocarbon (HC), carbon monoxide (CO), particulate (PM_{10}) emissions and flue gas.

One of the major selling points of biodiesel is that is *environmentally friendly*. Biodiesel has fewer emissions than standard diesel, is biodegradable, and is a renewable source of energy.

Emissions control is central to the biodiesel argument, especially in legislation matters. Sulphur and its related compounds contribute to the formation of acid rain; carbon monoxide is a widely recognized toxin; and carbon dioxide contributes to the greenhouse effect. There are also some lesser known compounds that cause concern, such as polycyclic aromatic hydrocarbons (PAHs), ring-shaped compounds that have been linked to the formation of certain types of cancer. Particulate matter (PM) has negative health effects, and unburned hydrocarbons contribute to the formation of smog and ozone.

Biodiesel does *reduce hazardous emissions*. Of the current biofuels, biodiesel is the only one to have successfully completed emissions testing in accordance with the Clean Air Act. Biodiesel has similar properties to petroleum diesel fuel and can be blended with petroleum diesel fuel at any ratio [18]. In addition, B100 (pure biodiesel) can *reduce CO_2 emissions* by 78 % and lower the carcinogenic properties of diesel fuel by 94 %.

Another feature of biodiesel is that it is *biodegradable*, meaning that it can decompose as the result of natural agents such as bacteria. According to the EPA (Environmental Protection Agency), biodiesel degrades at a rate four times faster than conventional diesel fuel. This way, in the event of a spill, the cleanup would be easier and the aftermath would not be as frightening. This would also hold true for biodiesel blends. The high environment friendliness of biodiesel is being highlighted by its classification as water hazardous class 1, meaning that biodiesel is being classified a not very hazardous to water. The traditional diesel is classified as water hazardous class 2. The reason results in a higher biological degradability of biodiesel. Within 21 days biodiesel is biologically degradable by 98 %. As a comparison: Mineral diesel reaches a biological degradability of only 70 %.

Biodiesel could also *lower dependence on imported oil* and increase our energy security.

Biodiesel also contributes to an *engine's lubricity*, or its ease of movement. Biodiesel acts as a solvent, which helps to loosen deposits and other gunk from the insides of an engine that could potentially cause clogs. Since pure biodiesel leaves no deposits of its own, this results in increased engine life. It is estimated that a biodiesel blend of just 1 % could increase fuel lubricity by as much as 65 %.

Biodiesel is also safer. It is *non-toxic* (about 10 times less toxic than table salt) and has a higher flashpoint than conventional diesel. Because it burns at a higher temperature, it is less likely to accidentally combust. This makes movement and storage regulations easier to accommodate.

Esterified biomass oils are suitable for application in diesel engines as their viscosity, density, and cetane number are similar to those of diesel [19]. (RME) indicates a higher cetane number for RME compared to regular diesel. This results in a good ignition quality, which means higher engine efficiency and a better prospect for emission reduction. RME density is slightly higher than of diesel, compensating for the reduced energy content of RME to some extent as per volume LCV are closer. This lower value is due to the much higher oxygen content of RME compared to diesel. Because vehicles using RME have, on an energy basis, the same fuel consumption as those running on diesel fuel, this lower energy content leads to larger fuel consumption. Biodiesel can be easily used in existing diesel engine in its pure form or in any blending ratio. Unlike ethanol though, the use of biodiesel in pure form requires min or engine adaptation as it is not compatible with some types of synthetic and natural rubbers. Biodiesel properties are related to the oil they come from. RME and SME present better freezing point properties than palm oil methyl ester for instance.

Biodiesel have similar properties than diesel. However they shown better lubricity, no aromatic or sulphur contaminant and higher cetane number which allow lower emissions of most of the pollutants common with petroleum products. US Environment Protection Agency (EPA) reported that the potential for emission reduction of a fuel is almost linear to its biodiesel concentration, with the exception of NO_x. One of the major advantages to compare to diesel is its ability to reduce SO_x emissions. Sulphur which increase lubricant properties of diesel can be replaced by a small quantity of biodiesel. However, this may require high concentrations of biodiesel depending on the goal sought after.

Biodiesel is non-toxic, biodegradable, and especially beneficial for use in urban, enclosed, or environmentally sensitive areas. It has even been used for crude oil clean-up. A 5% blend eliminates microbiological contamination in fossil diesel.

Drawbacks of Biodiesel [20]:

- Cost of biodiesel production is curently high.
- Disadvantages of using biodiesel produced from agricultural crops involve additional land use, as land area is taken up and various agricultural inputs with their environmental effects are inevitable.
- Solidification and thus clogging of the system at lower temperatures persists. It requires special anti freezing agents.
- Biodiesel has high viscosity during fuel injection.
- Pure biodiesel reduces the fuel economy and power by 10 %.
- In the first weeks of using biodiesel, the fuel system is being cleaned so there may be a few fuel filter changes to be made.
- Biodiesel is less suitable for use in low temperatures. Cloud point and gel point are higher – can be solved by using anti-gelling agents.
- Engines prior 1993 that are going to use 100 % biodiesel should change their rubber seals with VitronTM or other non-rubber seals (a blend of up to 35 % biodiesel can be used with no changes).
- NO_x emissions are not reduced. Interested parties are developing fuel formulation, fuel additive, and engine operational strategies to eliminate it. Transportation & storage of biodiesel require special management. Some properties of biodiesel make it undesirable for use at high concentrations. For example, pure biodiesel doesn't flow well at low temperatures, which can cause problems for customers with outdoor storage tanks in colder climates. A related disadvantage is that biodiesel, because of its nature, can’t be transported in pipelines. It has to be transported by truck or rail, which increases the cost.
- There have been a few concerns regarding biodiesel’s impact on engine durability.

One of the problems with the fuel itself is the increase in NO_x in biodiesel emissions. Often, in diesel fuel manufacturing, when you decrease the amount of particulate matter in the emissions, there is a corresponding increase in nitrogen oxides, which contribute to smog formation. Though some of this can be addressed by adjusting the engine itself, that's not always feasible. There are technologies being researched to reduce NO_x amounts in biodiesel emissions. Nitrogen oxide emissions from biodiesel blends could possibly be reduced by blending with kerosene or Fischer-Tropsch diesel.

Another problem is biodiesel's *behavior as a solvent*. Though this property is helpful, it's kind of a double-edged sword. Some older diesel vehicles (such as cars made before 1992) may experience clogging with higher concentrations of biodiesel. Because of its ability to loosen deposits built up in the engine (which may be there from old diesel fuel), biodiesel can cause the fuel filter to become jammed with the newly freed deposits. Biodiesel manufacturers suggest changing the fuel pump shortly after switching to high-concentration biodiesel blends. Components within these older fuel systems may also become degraded. In addition to deposits within the fuel system, biodiesel also breaks down rubber components. Some parts in the older systems, such as fuel lines and fuel pump seals, may become broken down due to their rubber or rubber-like composition. This is usually remedied by replacing such components. Though many manufacturers have included biodiesel in their warranties, potential for problems could still exist.

Also, in some engines, there can be slight decrease in fuel economy and power. On average, there is about a *10 % reduction in power*. In other words, it takes about 1.1 liters of biodiesel to equal 1 liter of standard diesel.

The major drawbacks to biodiesel are connected to the bigger picture, namely the market and associated logistics. Of these, the most important is *cost*. This all depends on variables such as the feedstock used and market conditions.

The other, perhaps more important issue is that of amount *and availability*. Though biodiesel isn't necessarily produced in countries, it can be made available in all of them. There are three major ways to get biodiesel, with each particular method better suited for certain types of customers. Biodiesel can be purchased directly from the supplier, from a petroleum distributor, or from public pumps. This production is flexible, and can be increased or decreased as needed

1.4. COMPARISON OF PETROLEUM DIESEL AND BIODIESEL EMISSIONS

Biodiesel is the only alternative fuel to have fully completed the health effects testing requirements of the Clean Air Act. The use of biodiesel in a conventional diesel engine results in substantial reduction of unburnt hydrocarbons, CO and PM compared to emissions from diesel fuel.

In addition, the exhaust emissions of sulphur oxides and sulphates (major component of acid rain) from biodiesel are essentially eliminated compared to diesel (Fig. 1.7) [21]:

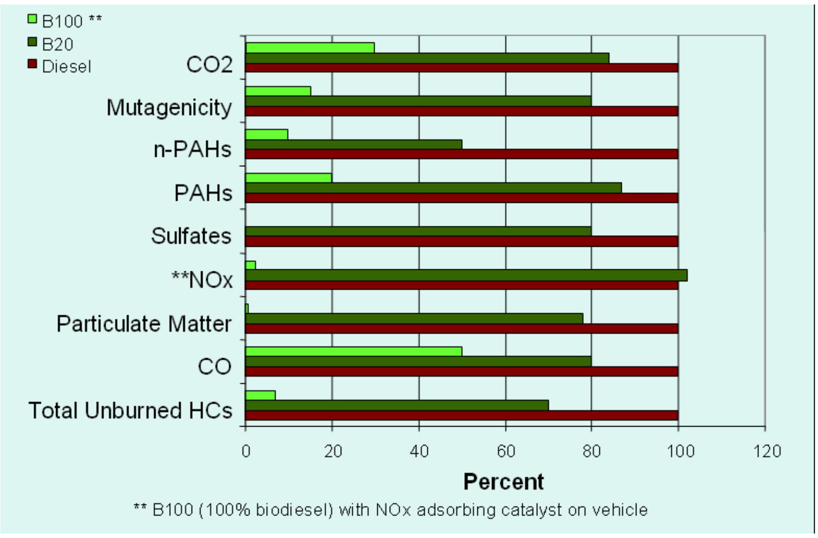


Fig. 1.7 Relative emissions: diesel and biodiesel

Compared with conventional diesel fuel, diesel–biodiesel blends showed lower carbon monoxide (CO), and smoke emissions but higher oxides of nitrogen (NO_x) emission.

It becomes obvious that by use of RME the cancerogenic danger is significantly lower compared to diesel engines. On the other hand, the aldehyde emissions of biodiesel induce disadvantages for this alternative fuel.

The benefit of using biodiesel is proportionate to the blend level of biodiesel used. Substituting B100 for petroleum diesel in vehicles reduces the life cycle consumption of petroleum by 95 %. A 20 % blend of biodiesel and petroleum diesel (B20) causes the life cycle consumption of petroleum to drop 19 %.

Biodiesel decreases the solid carbon fraction of particulate matter (since the oxygen in the fuel enables more complete combustion to CO_2), eliminates the sulphur fraction (as there is no sulphur in the fuel), while the soluble or hydrogen fraction stays the same or is increased.

The most common blend rate is 20 % biodiesel, 80 % petroleum diesel. This mixture is referred to as B20. Pure or neat biodiesel is called B100 [22]. Emission results for pure biodiesel (B100) and mixed biodiesel (B20-20 % biodiesel and 80 % petrodiesel) compared to conventional diesel are given in Table 1.3 [23]:

Table 1.3 Average biodiesel emissions compared to conventional diesel

Emissions	B100	B20
Regulated Emissions		
Total Unburned Hydrocarbons	-93%	-30%
Carbon Monoxide	-50%	-20%
Particulate Matter	-30%	-22%
NO_x	+13%	+2%
Non-Regulated Emissions		
Sulphates	-100%	-20%*
Polycyclic Aromatic Hydrocarbons	-80%	-13%
NPAH (Nitrated PAHs)**	-90%	-50%***
Ozone Potential of Speciated HC	-50%	-10%
Life-Cycle Emissions		
Carbon Dioxide (LCA)	-80%	
Sulphur Dioxide (LCA)	-100%	

*Estimated from B100 results. **Average reduction across all compounds measured.
***2-nitroflourine results were within test method variability.

Of the major exhaust pollutants, both unburned hydrocarbons and nitrogen oxides are ozone or smog forming precursors. The use of biodiesel results in a substantial reduction of unburnt hydrocarbons, carbon monoxide and particulate matter. Emissions of nitrogen oxides are either slightly reduced or slightly increased depending on the duty cycle of the engine and testing methods used. Based on engine testing, using the most stringent emissions testing protocols required by EPA for certification of fuels or fuel additives in the US, the overall ozone forming potential of the speciated hydrocarbon emissions from biodiesel was nearly 50 percent less than that measured for diesel fuel [24].

The life-cycle production and use of biodiesel produces approximately 80 % less carbon dioxide and almost 100 % less sulphur dioxide compared to conventional diesel. From Table 1.3 it is clear that biodiesel gives a distinct emission benefit almost for all regulated and non-regulated pollutants when compared to conventional diesel fuel but emissions of NO_x appear to increase from biodiesel. NO_x increases with the increase in concentration of biodiesel in the mixture of biodiesel and petrodiesel. This increase in NO_x may be due to the high temperature generated in the fairly complete combustion process on account of adequate presence of oxygen in the fuel. This increase in NO_x emissions may be neutralized by the efficient use of NO_x control technologies, which fits better with almost nil sulphur biodiesel than conventional diesel containing sulphur.

The study on mechanism of soot formation from diesel as well as biodiesel (RSME) indicates reduction in total particulate matter. When the engine is operated on RSME, soot emissions (insolubles) are dramatically reduced, but the proportion of emissions composed of fuel derived hydrocarbons (fuel solubles), condensed on the soot, is much higher. This implies that the RSME may not burn to completion as readily as diesel fuel. Since concern over particulates arises partly from the potential harmful effects of the soluble fraction, it might be suspected that emissions from RSME would be more harmful however data shows no tendency for the mutagenicity of exhaust gas to increase for a vehicle running on 20 % RSME and 80 % diesel blends.

Comparative emissions of greenhouse gases for diesel and biodiesel in various stagers of life cycle are depicted in Table 1.4:

Table 1.4 Emissions of greenhouse gases (g/km)

	Diesel		**Biodiesel**
Extraction	15.84	Fertiliser Production	15
Transport	2.74	Fertiliser Application	10
Refining	13.63	Agricultural Machinery*	25
Distribution	0.95	Oil Production	3
Vehicle Operation	245	Processing Straw**	1
		Processing Gas	17
		Transport	5
		Vehicle Operation	0
Total	278.16	Total (Straw Processing)	59
		Total (Gas Processing)	75

*Assumed mineral diesel oil used. ** Emissions of straw include those from transporting straw.

As it can be seen from Table 1.4, the emissions of greenhouse gases during the production of diesel are about 32 g/km. These are hardly a half of the emissions from producing biodiesel even when straw rather than electricity is used to fire the processing. However, this difference is far outweighed by the emissions of CO_2 during the combustion of the diesel itself (245 g/km).

1.5. BIODIESEL PRODUCTION PROCESSES

Biodiesel, which is produced from plant and animal-based feedstock, represents an alternative to petroleum-based diesel fuel. This fully renewable resource can be produced from cultivated high oil-yielding plants that are energetically charged from energy derived from the sun and absorbed carbon dioxide. Animal-based products (fats and oils) are energetically charged from plants, which also means that they are also ultimately energetically charged from the sun and composed of absorbed atmospheric carbon dioxide because animals directly use plants and thus indirectly use these primary energy and carbon sources. Chemically speaking, biodiesel is a mixture of mono-alkyl ester of fatty acids obtained from extracted plant oils and/or collected animal fats [25].

The starting substances for biodiesel are traditionally plants. In Europe countries mainly rapeseed oil is being used. Biodiesel produced from rape seed is known as Rape Methyl Ester – RME. The biodiesel production process input and output are given in Fig. 1.8.

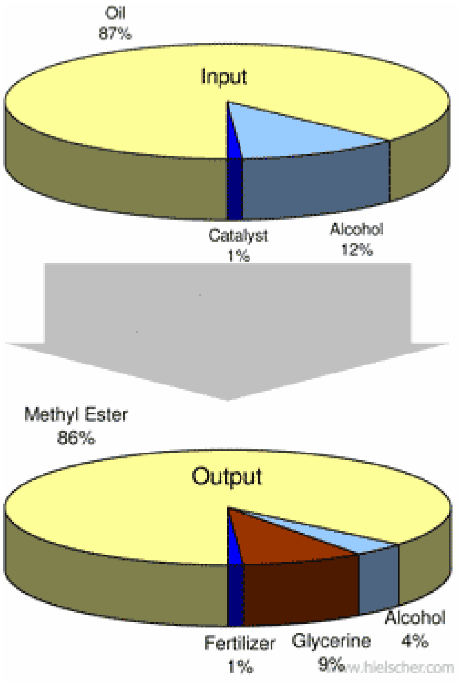


Fig. 1.8 Biodiesel production process – input and output

There are three primary ways to make biodiesel [26]:

- Base catalyzed transesterification of the oil;
- Direct acid catalyzed transesterification of the oil;
- Conversion of the oil to its fatty acids and then to biodiesel.

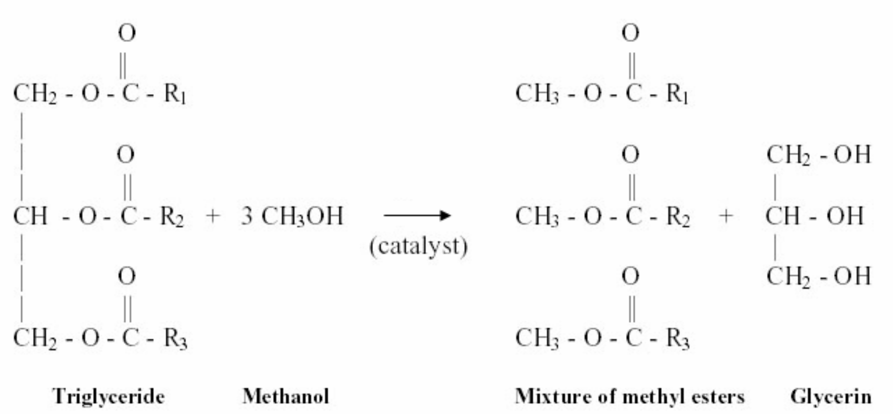
However, the base-catalyzed, methyl-transesterification of soybean or rapeseed oil has been the predominant production technique used for biodiesel production. The monoesters commonly known as biodiesel are usually produced through the transesterification of vegetable oils or animal fats. Both oils and fats are triglycerides or fatty esters of glycerol. During this process, the oil (previously extracted prior to production) is reacted with a primary alcohol (methanol [CH3OH]) and a base (sodium hydroxide, aka. caustic [NaOH]) to form the fatty acid mono alkyl ester (in this production case, a fatty acid methyl ester which is often referred to as FAME). The tansesterification reaction is affected by molar ratio of glycerides to alcohol, catalysts, reaction temperature, reaction time and free fatty acids and water content of oils or fats [27].

Molecules having three fatty acid chains are referred to as triglycerides. Raw triglyceride vegetable oils have properties similar to those of petroleum-based diesel fuels and can be used as a direct replacement without engine modification for a limited operating duration. Long-term diesel operation on raw vegetable oils causes numerous problems including injector coking, contamination of lubrication oil, engine deposits, and increased emissions. These problems are primarily the result of the high viscosity of the triglyceride oils as compared to petroleum-based diesel fuels. Increased viscosity adversely affects fuel injection duration, pressure, and atomization. The increased injection line pressure can lead to advanced injection timing, increasing combustion pressures and temperatures, and increased NO_x formation in the exhaust [28 - 30].

Therefore, the fatty acid composition of the feedstock plays a vital role in determining the feedstock's suitability for biodiesel production. It is important to note that the FAME is 100% biodiesel. When directly used as fuel without blending with petroleum diesel, the pure biodiesel is often referred to as “neat” biodiesel. However, most often, biodiesel within the general marketplace is sold as a petroleum diesel/biodiesel blend. These blends are compositionally identified within the marketplace using the “B” designation, which defines the volumetric biodiesel composition of the blend by placing the percentage composition immediately after the letters “B”. For example, a 20% biodiesel/ 80% petroleum diesel is designated as a B20 blend. Therefore, the biodiesel reaches the European norm E DIN 51606 and is thus approved as a fuel for all motor vehicles.

The transesterification process is one useful method of reducing the high viscosity of triglyceride oils. In this process, the long fatty acid chains are removed from the glyceride molecule by reacting with alcohol and a catalyst. Common catalysts are potassium hydroxide, sodium hydroxide, and sodium methoxide. The reaction produces fatty monoesters and free glycerol. Any remaining unreacted monoglycerides, diglycerides, or triglycerides make up the bonded portion of the remaining glycerol in the fuel. Together, the free and bonded glycerols make up the total glycerol percentage remaining. This total glycerol percentage is used to determine the completion of the reaction.

The transesterification process is given in the 1.1 equation, where R_1, R_2, and R_3 represent long hydrocarbon chains:



(1.1)

The transesterification reaction is similar to saponification, which is used to produce soap from fatty acids. A stoichiometric material balance yields the following simplified equation [31]:

$$\text{Oil or Fat (1000 kg)} + \text{Methanol (107.5 kg)} = \text{Methyl ester (1004.5 kg)} + \text{Glycerol (103 kg)} \quad (1.2)$$

This reaction reduces the molecular weight of the triglycerides by 60 % when the methyl ester is formed. Additionally, viscosity is reduced eightfold and volatility increases [32].

After reacting, two phases are formed, the glycerol and ethanol/alcohol phases, because glycerol has a higher specific gravity and is immiscible in the biodiesel phase. A static gravity settling vessel is often used to separate these phases; however, a centrifuge separator can also be used. Once the glycerol phase is separated, the alcohol is then removed from the biodiesel using distillation or flash evaporation. With most processes, the biodiesel is cleaned using one to several water washes. Outside of reagent purity, the key factors impacting the production of biodiesel in terms of quality, rate, and efficiency include temperature, mixing, catalyst type/concentration, and alcohol to ester ratio [32]. The glycerol is collected and can be sold as an industrial feedstock to other processes or refined for sale within the pharmaceutical industry. The biodiesel and alcohol are separated allowing recycle of the alcohol within the plant. The biodiesel collected undergoes further processing for cleanup, consisting of water cleanup, distillation, drying, and filtration.

The base catalyzed reaction is currently the most used process in biodiesel production. Steps of biodiesel production are presented in Fig. 1.9 [33]:

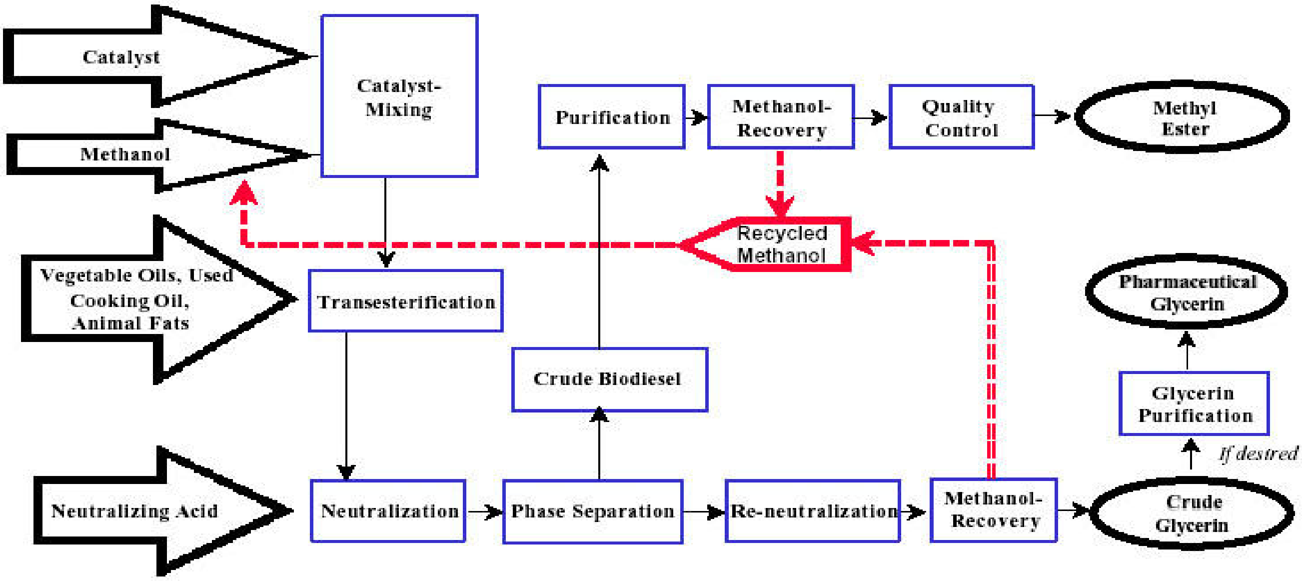


Fig. 1.9 Base catalyzed Biodiesel production process

Catalyst Mixing: The catalyst is sodium hydroxide or potassium hydroxide and it dissolves in the alcohol.

Transesterification: Transesterification, where the pretreated triglycerides are reacted with methanol to form the raw methyl esters and glycerol. There are two basic steps: the reaction process followed by separation of the methyl ester and glycerol streams. In most technologies, these two steps are undertaken twice to push the transesterification closer to completion by reducing the concentration of glycerol in the second stage. The reaction is also pushed closer to completion by using an excess of methanol. The system is closed for preventing alcohol loss. Processes are generally designed to a high level of conversion, and methyl ester purity (>98 %), as lower conversion rates result in increased levels of mono- and di-glycerides, causing processing problems with emulsion formation and low temperature hazing problems with the biodiesel itself as these compounds have higher melting points (and viscosity) than the methyl ester.

Neutralization: Sometime the product from the transesterification has acid, thus, there is a need of neutralization to make solution to neutral.

Phase Separation: The product from the transesterification is glycerol and biodiesel. The glycerol is much denser than biodiesel. They can be gravity separated and the glycerol drawn off the bottom of the setting vessel.

Purification: Biodiesel from phase separation is not pure. It can be purified by washing gently with warm water to remove residual catalyst or soaps and dried. Glycerol purification, removing methanol for recycling to the transesterification process. Further impurities, such as catalyst, tallow and methyl ester, are carried in the glycerol and may be removed to produce a higher grade of glycerol.

Methanol Recovery: The alcohol is removed from separation and it is recovered using distillation equipment and is re-used. Methyl ester purification, which removes the excess methanol, catalyst and glycerol carried from the transesterification process. Methanol removed is recycled to the transesterification process.

Quality control: The finish biodiesel must be analyzed using sophisticated analytical equipment to ensure it needs ASTM specifications.

The most important aspects of biodiesel production to ensure trouble free operation in diesel engines are [34]:

- Complete Reaction
- Removal of Glycerol
- Removal of Catalyst
- Removal of Alcohol
- Absence of Free Fatty Acids

The type and concentration of fatty acids in a feedstock are directly related to several key properties in the resulting biodiesel. Conventional diesel fuel consists of long-chain, unbranched hydrocarbons. One of the major reasons biodiesel is a suitable substitute for conventional diesel is the fact that biodiesel consists of long, unbranched chains of fatty acids. One of the most important characteristics of any diesel fuel is its cetane number, which is a measure of the ignition quality of a diesel fuel. The ignition quality is directly related to the ignition delay of the fuel, and the shorter the ignition delay time, the higher the cetane number. Therefore, a high cetane number indicates good ignition quality. Long-chain, unbranched, saturated hydrocarbons have high cetane numbers while branched hydrocarbons and aromatic compounds have low cetane numbers. However, too high or too low of a cetane number can result in incomplete combustion in both cases. Most engine manufacturers recommend a cetane number between 40 and 50 [35]. If a feedstock is mainly composed of fatty acids that are saturated, then the cetane number of the biodiesel derived from that feedstock could be too high. Likewise, if a feedstock is mainly composed of fatty acids that are highly unsaturated, then the cetane number could end up being too low. Two other important properties are cloud point and heat of combustion. Cloud point is the temperature at which a fuel becomes cloudy due to the formation of wax crystals, and these crystals can clog fuel lines and filters [35]. The heat of combustion is the amount of heat that is released when a certain amount of a material burns. Both cloud point and heat of combustion are directly related to the level of saturation and the number of carbons in a fatty acid. In general, as a fatty acid becomes more saturated or if the number of carbons in a fatty acid chain increase, then cloud point and heat of combustion increase.

1.6. UTILIZATION METHODS FOR BIODIESEL BY-PRODUCTS

Like most other production processes, biodiesel production generates wastestreams; however, unlike many production processes, biodiesel production also makes by-products that are of significant market value. In fact, the economic viability of today's biodiesel industry is so sensitive that the overall economic viability is highly dependent the market price of these byproducts. The by-products will become more and more important in the future as biodiesel production increases. The amount and value of the co-products play a critical role in the seed oil prices as the price of oilseeds, cake and oil are intrinsically bound together.

This chapter presents a listing of the major chemicals/products used within the biodiesel process. Also, included in this chapter are by-products, both value-added and waste, that are produced. [36].

SEED MEAL

Seed meal is the other by-product of the process and can be a valuable livestock feed, depending on the seed type. In fact, the meal product portion of the operation can be more profitable than the biodiesel production, since the fuel is a commodity feeding into a very competitive market. The crushing of rape seed produces rape seed oil that can be sold to the food market and/or sold to the biofuel market where it is converted into biodiesel. The meal remaining after the oil has been extracted can be sold to the livestock industry as feedstuff (rape seed meal) and/or can be used as a soil amendment or fertiliser (Fig. 1.10) [37]:

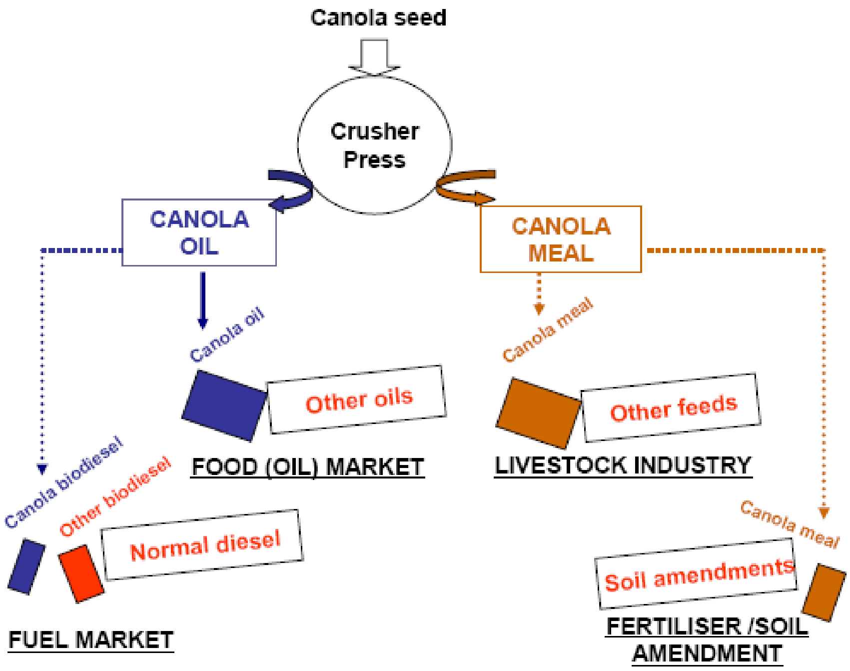


Fig. 1.10 Rape seed flowchart

As well, the residual meal left after pressing the oil from rapeseed contains both valuable proteins and toxic chemicals.The toxic chemicals are removed to yield a meal with nearly 40 percent better-balanced proteins. This protein-rich meal can improve the nutrition of animal feed and increase its economic production. The isolated toxic chemicals may be used as a soil fumigant or to selectively kill pests or unwanted weeds. In the testing, such chemicals have killed dreaded slugs, yet are pet-friendly [38].

The forage production seems the best way for rapeseed meal utilization. Thus the larger biodiesel production plants should organize forage for cattle, hogs and fowl forage, when adding corn and vitamin enriched mineral premixes to the meal. Since forage is twofold expensive than rapeseed meal, such production would be the cost-effective one [29]. Approximately 90-93 % of dry matter, 10-20 % fat, 26-31 % protein is left in the residual meal after mechanical rapeseed crushing. The irreversible amino acids are found in the rape proteins, and fat acids in the adipose [30].

Industrial rapeseed meal and canola meal could be used as a fertiliser and soil amendment. Rapeseed meal is a good organic fertiliser with responsible amounts of nitrogen, phosphorus and sulphur. In the longer term, rape seed meal could be used as a source of specific proteins that could be the raw material for the production of several products with industrial applications. These include soil amendments, soil fertilisers, bio-polymers, surfactants and adhesives [37].

LECITHIN

Lecithin is used widely in foods as an emulsifier, stabilizer, and antioxidant. Its chemical name is phosphatidylcholine, which identifies its major components of choline, phosphoric acid, glycerol, and fatty acids. Lecithin is separated from soybean oil by the addition of water and centrifuging. It is purified prior to use as a food additive.

SOLVENTS

To first remove the oil from the seeds, they must undergo some sort of extraction process. This can take place via either pressure extraction or solvent extraction. The extraction of oil by expeller, sometimes called a screw press, is a physical process. The oil is squeezed from the heated seeds. However, most conventional processors in the U.S. use solvent extraction. In that process a solvent, usually hexane is used to leach the oil from the seeds. In pressure extraction the only products are oil, meal, and trace amounts of water. However, in solvent extraction, the extraction fluid must be separated from the raw oil. After a distillation step, the solvent can then be recycled in the system and used again.

ALCOHOL

Methanol is one of the two main reactants in the biodiesel process. As with any reaction, the efficiency is not 100% and not all of the alcohol will go to produce biodiesel and glycerol.

This excess alcohol vapor can be recaptured and recycled back to the feed to be used again in the main process. Maintaining an efficient recycle stream can lead to reduced process costs by reducing the amount of methanol wasted in the process. By recycling, the excess alcohol is no longer a waste.

ACID OR BASE

During transesterification, an acid or base is used as a catalyst for the reaction. By definition, a catalyst is not used up in the reaction and therefore should be recycled. Such is the case in the biodiesel process. The acid or base can be reused after a separation step. Most large scale biodiesel operations use base catalyzed reactions due to their favorable economics. Low temperature, low pressure, and high conversion make the base catalyzed reaction far more feasible. The most common bases used are sodium and potassium hydroxide, and are usually mixed with the methanol before reaction.

Erudic acid is a by-product to biodiesel production, valuable in making more than 200 industrial products such as pharmaceuticals, plastics, cosmetics, ink, and photographic and recording materials.

SOAP

When water builds up in the system, soap can form as a product. While soap can be sold as a commodity, it takes away from more profitable products. Because of this, the process should be set up in such a way that minimizes the production of water.

WATER

Very little water is associated with this process. Minute amounts of water may be present in the rape seeds before oil extraction, but this water should be dealt with before it enters the biodiesel process. Due to the water that can get into the process after pressing the seeds, soap can form in the system. This soap combines with the glycerol and makes it difficult to separate. It is common for crude oil to be degummed prior to caustic refining. Usually oil refiners add acid to the soap stock to form acid oil that can be sold to fatty acid processors. If the soap stock has not been degummed prior to caustic refining, then an acid oil water emulsion will form which will be a problem. Caustic refining of degummed oil in a self cleaning centrifuge will minimize the waste disposal problems. The only other water associated with the process is in the heating unit. Steam is used to heat the process, but it condenses in its own loop and is not a waste water issue. Additionally, management of the wash waters must be considered.

GLYCEROL

During biodiesel production, vegetable oil is mixed at high speed with alcohol, resulting in two layers of fluid - the top one is usable biodiesel, the lower is glycerol. This impure glycerol has little economic value and is too costly to purify into a useable product. It's too condensed to dispose of directly, so one current use is mixing it with organic waste for composting. The value of biodiesel by-products must be increased, to reduce the cost of biodiesel itself.

Glycerol is a major by-product of the biodiesel fuel production process, gained through the tranesterification reaction, with most estimates of the byproduct as high as 10 % of the product output. Approximately one litre of biomass oil plus 10 % of methanol are needed to make 1 litre of biodiesel and 350 g of glycerol.

Separation of glycerol from biodiesel is relatively simple. Centrifuging after the reaction is finished or even gravitational settling are both sufficient at accomplishing a good separation, depending on how fast the separation is to be completed and the purity of glycerol desired.

The resulting raw glycerol from this esterification process is contaminated with alcohols and inorganic salts. Currently, biodiesel producers are purifying the glycerol so that it is acceptable as either food-grade or pharmaceutical grade. Most (97 %) of the glycerol used today is a highly refined product (97 %+ purity). Glycerols of three different purities (low, medium, high) reflected different stages of the same process of rapeseed oil methyl ester production [39]. The most pronounced variations among purities were the concentrations of water, glycerol, phosphorus and methanol (Table 1.5):

Table 1.5 Chemical composition of glycerol as related to purity

	Purity of glycerol		
	Low	Medium	High
Water, %	26.8	1.1	2.5
Composition of the dry matter[1], %			
Glycerol	63.3	85.3	99.8
Ether extract	0.71	0.44	n.a.[2]
P	1.05	2.36	n.a.
K	2.20	2.33	n.a.
Na	0.11	0.09	n.a.
Pb	0.0003	0.0002	n.a.
Methanol	26.7	0.04	n.a.
[1] Concentrations of cadmium, mercury and arsenic were below the detection limit.			
[2] not analysed.			

Glycerol of different purities can be included in mixed diets for ruminants up to 10 % of the dry matter as a substitute for rapidly fermentable starch sources, e. g., wheat or tapioca, without negatively affecting ruminal environment, ruminal nutrient turnover and whole-tract digestibilities of organic matter constituents. When fed with a low-starch concentrate, pure glycerol at dietary inclusion levels up to 20 % had no effect or positive effects on nutrient digestibilities. When included in diets containing high-starch concentrates, glycerol reduced cell-wall digestibilities but had no obvious effect on whole-tract organic matter digestibilities. Chemical as well as physical pellet quality variables were not affected greatly. The preserving effect on concentrate pellets of the glucogenic substance glycerol must be emphasized.

Glycerol is an excellent feed constituent, even when included in an impure form as derived from biodiesel production. Glycerol may serve as an ingredient both of pelleted concentrates and of total mixed rations. In pelleted concentrates, the contribution to the hygienic quality of the feedstuff might be of special interest. Economic assessment will be decisive of a wider use of glycerol as a dietary ingredient for ruminants.

Glycerol in its pure form, is a sweet-tasting, clear, colorless, odorless, viscous liquid. It is completely soluble in water and alcohols, slightly soluble in many other common solvents and insoluble in hydrocarbons. Liquid glycerol boils at 290°C under normal atmospheric pressure. Its specific gravity is 1.26 and its molecular weight is 92.09 [40]. It is a relatively stable compound and is considered flammable. Until after World War II, nearly all commercial glycerol was produced as a by-product in the manufacture of soap or from the hydrolysis of fats and oils. Today, substantial amounts of synthetic glycerol are prepared from propylene. Crude glycerol is purified to make various grades, such as dynamite grade, yellow distilled and chemically pure glycerol. Only the highest grades of glycerol are used in foods and medicines.

The glycerol product is categorized as follows [41]:

1. Crude (75 - 90 % glycerol);
2. Refined:
    - 99.5 % technical grade;
    - 96 % USP (vegetable – based);
    - 99.5 % USP (tallow – based);
    - 99.5 % USP (vegetable – based);
    - 99.5 % USP/FCC – Kosher;
    - 99.7 % USP/FCC – Kosher.
3. Kosher.

Glycerol (1,2,3 propanetriol) is an unavoidable by-product of producing fatty acid products and fuels. Most (97 %) of the glycerol used today is a highly refined product (97 %+ purity). Purification costs are high ($400 per ton) and glycerol prices range between $0.60 and $0.90 per pound. As a result of its high price, most glycerol product markets are small and fragmented. Crude glycerol (50 % to 90 % glycerol by weight) sells at a discount to USP prices, depending on the glycerol content of the product, the amount and type of contaminants present, and supply and demand balances. Biodiesel producers receive between 5 and 15 cents/lb for crude glycerol (50 % glycerol) and 80 % to 88 % refined sells for between 30 and 40 cents/lb. [42].

Small increases in fatty acid consumption for fuels and products can increase world glycerol production significantly. The expansion of biodiesel in recent years has had major impact on glycerol prices. In fact, regardless of United States B2 biodiesel policy, world production of biodiesel is likely to increase in S. America, Australia, Southeast Asia, Asia, the former USSR, Africa, and elsewhere. Biodiesel production from local soy and palm oils can be cost effective in many countries with high petroleum prices or poor balance of payment positions due to petroleum imports (in United States dollars).

The potential future output of glycerol is expected to increase as biodiesel plants come on line, and the output will greatly outpace demand. Biodiesel production has already had a significant impact on the price of refined glycerol, as Fig. 1.11 shows [42]:

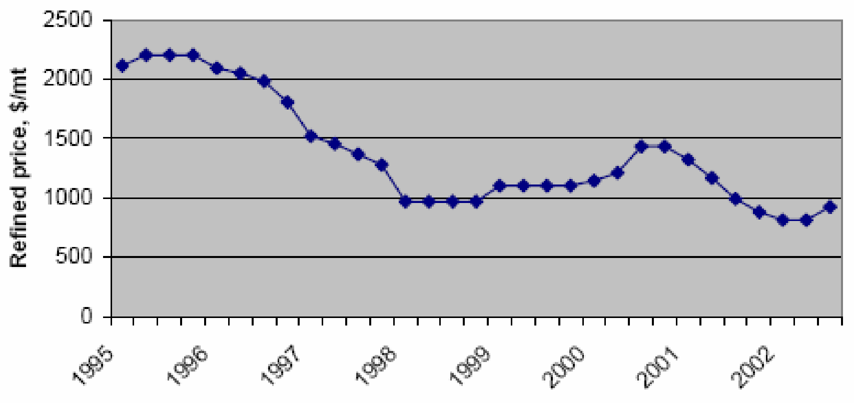


Fig. 1.11 Fluctuation of glycerol prices in Europe

At current glycerol market prices, glycerol credit reduces biodiesel cost in the range of 0.05 to 0.1 US$/l of biodiesel in the EU. A large biodiesel expansion would flood the international market with glycerol. Therefore the development of new applications for glycerol would allow a rapid growth of the biodiesel industry.

The refined glycerol market is more complex to penetrate than the crude glycerol market. This is because, for crude glycerol, a small number of refineries represent the entire potential customer base. In contrast, refined glycerol can be sold to hundreds of different companies.

Biodiesel production is much more economical if you have a good market for the glycerol. However, with the coming growth in biodiesel production, pressure will be put on glycerole prices and finding markets for non-kosher or non-halal glycerol may become increasingly difficult. The glycerol market is not that big by chemical industry standards, and the additional glycerol being produced by the biodiesel industry ruined that market. In 2005, glycerol has been as much as €500 per tonne cheaper than competing petrochemicalderived glycols, even though demand in 2006 was up 5 % since the beginning of the year. It is not clear how much of the increased demand is a result of glycerole replacing petrochemical-based raw materials, In September 2005, the price of glycerol had fallen to €450 per tonne, compared with a peak of over €1000 two years ago forcing the closure of many fatty acids producting plants and glycerol refineries [43].

Glycerol literally has thousands of uses. However, those uses are in constant flux as new technologies are adapted. Here is an overview of the most common uses [44]:

Foods and Beverages

Glycerol is used to moisten, sweeten and preserve foods and drinks. It is used for meat casings and the remainder finding application in many different areas, such as emulsifiers,humectants, heat transfer media, flavors and colors, sweeteners, edible plasticizers (i. e., raisins saturated with glycerol remain soft when mixed with cereals. Certain glycerol esters, such as glycerol mono and distearate, are used for reduced fat foods. Polyglycerols find use as emulsifiers. Primary competition in this market segment is again sorbitol. Examples: soft drinks, candies, cakes, casings for meats and cheese, dry pet foods. As an intermediate, glycerol also is used in margarine, salad dressings, frozen desserts and food coatings.

Drugs

Glycerol is one of the most widely used ingredients in drugs and pharmaceuticals. Glycerol is used to increase smoothness and lubrication, and in the production of gel caps. Uses include: capsules, suppositories, ear infection remedies, anesthetics, cough remedies, lozenges, gargles, as an emollient for skin medications and as a vehicle for antibiotics and antiseptics.

Cosmetics and Toiletries

Because glycerol is nontoxic, non-irritating and odorless, it is used as a moisturizing agent (or humectant) and emollient (softening agent) for cosmetics and toiletries, including: toothpaste, skin creams and lotions, pre-shaving lotions, deodorants, make up, lipstick and mascara.

Tobacco

Glycerol keeps tobacco moist and soft to prevent breaking and crumbling during processing; it also adds flavor to chewing and pipe tobaccos. Glycerol also is used to manufacture cigarette filter tips.

Paper and Printing

Glycerol is used to soften and reduce shrinkage during paper manufacturing. Related uses: grease-proof paper, food wrappers and to manufacture printing ink.

Textiles

Glycerol is used to size and soften yarn and fabric and to lubricate many kinds of fibers in spinning, knitting and weaving operations.

The agricultural sprays

It can be used of as an adjuvant with humectant properties increasing herbicide activity in low humidity conditions. Used as a spreader or wetting agent – a material that increases the area that a droplet of a given volume of spray mixture will cover on a target. Used as an antifoaming agent in micronised wettable sulphur. This enables the product to be mixed in a tank effectively and sprayed on evenly.

Surface coatings

It can be used in the manufacture of alkyd resins; this is an important component of surface coatings.

Electrical and electronics

It can be widely employed in manufacturing electrolytes for electrolytic condensers, which are used in radios and neon lights, and in processes for electrodeposition and treatment of metals.

Cryoprotectant

It can be used as a cryoprotectant is a substance that is used to protect biological tissue from freezing damage (damage due to ice formation). Glycerol has been used for decades by cryobiologists, those biologist specialists in the effects of low temperatures on organisms, to reduce ice formation in cattle sperm and embryos that are cold-preserved in liquid nitrogen.

Other common uses

Glycerol has also found use in the production of other materials. The explosives industry, production of polyether polyols (foams for furniture, car seating, carpet underlay, packaging) and alkyd resins (coatings), both of which are large volume markets that could offer an opportunity to expand glycerol’s utility. Glycerol also is used as a plasticizer, humectant, lubricant, and in textiles, photography, gas drying, and production of electrolytic capacitors. Examples:

- As a lubricant for food processing machinery;
- To manufacture resin coatings;
- To add flexibility to rubber and plastic;
- As a building block in manufacturing flexible foams;
- To manufacture dynamite; and
- To create a component used in radios and neon lights.

The profitable glycerol market is very important to maintaining sound economics in the biodiesel process. While biodiesel is the primary product of the process, prospective buyers must also be found for the secondary product, glycerol. Industrial chemicals such as CP glycerol, USP glycerol, and dynamite glycerol are all potential markets for high-grade glycerol. The market for glycerol has been volatile in the past. Extensive biodiesel production could flood the glycerol market and lower the glycerol price.

The expansion of biodiesel production worldwide is driving down the value of glycerol and reducing by-product revenue of biodiesel and oleochemical producers. Further expansion of the biodiesel industry will produce as much as one billions pounds of glycerol and reduce its price to a point where it may become a useful platform chemical. However, biodiesel-derived glycerol is poor quality and requires expensive refining before it is suitable for new product technologies. Glycerol refining technology is relatively mature and requires significant economies of scale to be economical.

The potential research avenues are:

- Produce products from crude glycerol in situ followed by product separation;
- Improve biodiesel technology to produce higher quality glycerol;
- Develop glycerol-refining technology suitable for small biodiesel producers.

Of these options, the one that can simultaneously reduce biodiesel production costs, glycerol refining costs, and increase by-product revenues is the second option above. A new technology that eliminates mobile catalysts and replaces them with fixed catalysts or a catalyst-free technology will achieve that goal. The target markets for glycerol coproducts must be large, as future supplies from a biodiesel driven industry will create billions of pounds of glycerol. There are three directions that research could focus on:

- develope new market uses for crude (unrefined) glycerol
- develope new chemistry or products that are chemical derivatives of purified glycerol
- develope new chemistry or products from crude glycerol in situ.

Fuel uses for glycerol are attractive from a large market perspective but should be avoided unless there is compelling evidence that 1) the glycerol does not cause long term engine damage as seen in previous research studies, 2) the price structure of the resulting compound can be supported by the fuel market.

Glycerol has a tradition of volatile price movements. Moreover, the market is currently undergoing radical changes driven by very large supplies of glycerol from biodiesel production. Researchers and industry looking at new uses for glycerol needs to attract larger funds and a lot of investment money before it can start to replace petrochemicals as a source of raw materials for the production of many chemicals. Eventually glycerol will replace ethylene glycol in anti-freeze, propylene glycol in animal feeds and other petrol derived chemicals in coatings. A lengthy period of high oil prices is what the fledgling sector needs to establish itself as a new force in chemicals.

1.7. PROCESSES FOR GLYCEROL UTILIZATION

As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetables oils has also been generated in a large quantity. Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics, and many other industries, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers. Many research projects and studies have been conducted and innovative utilizations of the crude glycerol are under investigations [45]. It will be beneficial to the research community as well as biodiesel industry in understanding the progress of glycerol for value-added applications and for reference in manipulating their own integrated plans for sustainable and profitable biodiesel production. This section summarizes the currently available studies and possible ways on the utilizations of crude glycerol generated from biodiesel industry [46].

Hydrogen or syn gas production from glycerol using pyrolysis and steam gasification processes

Hydrogen is considered as a novel fuel for the twenty-first century, mainly due to its environmentally benign character. At present, hydrogen is produced entirely from fossil fuels such as natural gas, naphtha, and coal. In such cases, however, the same amount of carbon dioxide is released during the production of hydrogen as that formed by direct combustion of those fuels. Biomass is an attractive alternative to fossil feedstocks because it has essentially zero CO_2 impact. It is well reported that pure glycerol is an excellent source of hydrogen [47].

Glycerol, a by-product from production of biodiesel process, has an ability to produce value added products using three possible processes namely *pyrolysis, steam gasification and catalytic steam reforming.*

Glycerol is a potential feedstock, for hydrogen production because one mole of glycerol can produce up to four moles of hydrogen [48]. Hydrogen (H_2) is mostly used in refinery hydrotreating operations, ammonia production and fuel cells [49]. When glycerol is cracked at high temperature to produce hydrogen, it is possible to get carbon monoxide as one of the gaseous products. Formation of syn gas (H_2+CO) in the ratio of H_2/CO equal to 2:1 could be used as a feedstock in Fischer Tropsch synthesis to produce long chain hydrocarbon (-CH_2-; green diesel) [50]. Gases which are produced from thermal cracking of glycerol would have medium heating value and can be used as a fuel gas. Therefore, it was proposed to produce value added products such as hydrogen or syn gas and medium heating value gases from glycerol using fixed bed reactor without a catalyst. Non-catalytic processes such as pyrolysis and steam gasification are technologies that can produce value-added products such as hydrogen and syn gas from glycerol. Pyrolysis is the high temperature thermal cracking process of organic liquids or solids in the absence of oxygen [51]. Steam gasification produces gaseous fuel with higher hydrogen content than the pyrolytic process in the presence of oxygen and it reduces the diluting effect of nitrogen, used as a carrier gas in the pyrolysis, in the produced gas [52].

The pyrolysis process yields liquid fuels at low temperatures (400 to 600°C) and gaseous products at high temperatures (>750°C). Gasification is a process related to pyrolysis, but the major difference between is that gasification achieved in the presence of oxygen, in the form of air, pure oxygen or steam. Value added products such as hydrogen or syn gas is produced from pyrolysis of glycerol in a fixed bed reactor [50]. The pyrolysis of glycerol can be carried out in two ways; pyrolysis with and without any carrier gas (nitrogen). It is found that the complete conversion of glycerol occurred at 700°C. The gaseous product essentially consisted of syn gas (H_2/CO ratio: 1.77). After carried out steam gasification of glycerol the syn gas can be further converted to hydrogen by water-gas shift reaction and can be used as a fuel for fuel cells. Also, syn gas could be converted to green diesel using the Fischer-Tropsch reaction.

Catalytic treatment of glycerol

Catalytic steam reforming of organic compounds is one of the processes used to produce hydrogen. Catalyst is mainly used to increase the reaction rate and to increase the selectivity of hydrogen. Steam reforming reactions of any oxygenated organic compounds such as glycerol and acetaldehyde proceeds according to the following equation 1.3 [53]:

$$C_nH_mO_k + (n\text{-}k)\ H_2O\ nCO + [(n+m/2\text{-}k)]\ H_2 \tag{1.3}$$

Because of the excess steam used in the process, carbon monoxide further undergoes the water gas shift reaction to produce CO_2 and H_2. Research has been also carried out to produce hydrogen from biomass-derived oxygenated compounds such as methanol, glycerol and ethylene glycol using catalytic aqueous phase reforming reactions [54].

The optimum conditions to produce maximum gas yield (71 wt %), volume of gas (1.32 L/g of glycerol), syn gas composition (93 mol %) and minimum amount of char (8.1 wt %) and liquid (21.9 wt %) in pyrolysis of glycerol process were at 800°C, 50mL/min of nitrogen and quartz packing with the particle diameter 0.21-0.35mm. Glycerol was completely converted to gas which was mostly syn gas of 93 mol % (mole ratio of H /CO is 2) and a small amount of char when 50:50 weight ratio of steam to glycerol was used with the quartz packing of particle diameter of 0.21-0.35mm at 800°C. The addition of steam enhanced the gasification of glycerol process to produce large volume of gas and hydrogen yield. The crude glycerol was completely gasified into gaseous product when the steam to crude glycerol weight ratio of 50:50 was used at 800°C with quartz packing having particle diameter of 0.21-0.35mm. The gas product yield and synthesis gas production was 91.1 wt % and 79 mol % respectively. There was no significant change in the product gas composition for the steam gasification synthetic mixture and crude glycerol. Net energy recovered from pyrolysis and steam gasification processes were 111.7 kJ/mole of glycerol fed and 117 kJ/ mole of glycerol, respectively. The studies show that there is a strong potential for making syn gas, methane, ethylene, and high-heating value gas from the pyrolysis of glycerol. Overall conclusion from this research is that a waste by-product glycerol from biodiesel production can be completed converted to gaseous products such as hydrogen or syn gas and medium heating value gas in the range of 21MJ/m^3- 13.9 MJ/m [48].

It was also suggested that the steam reforming of biomass derived oxydegenated hydrocarbon such as glycerol, sorbitol and ethylene glycol using nickel based steam reforming catalyst could maximize the production of hydrogen. They also suggested that the robustness of a nickel based catalyst guarantee this operation over thousands of hours.

From this review, it is clear that glycerol has an ability to produce value added products using three possible processes namely pyrolysis, steam gasification and catalytic steam reforming. Very few researchers are working in the chemistry of gasification of glycerol .The results obtained by Chaudhari and Bakhshi showed that there is no liquid product in pyrolysis of glycerol process at 700^{o}C. This result was in contrast with those obtained by Stein and Antal who reported that pyrolysis process produced liquid products consisting of acrolein and acetaldehyde. Also, the results indicated that glycerol pyrolysis and steam gasification could lead to high quality hydrogen production. Thus, pyrolysis and steam gasification of glycerol processes should be revisited to understand the chemistry of the reactions and process parameters such as temperature, carrier gas flow rate and packing material. In addition, steam to glycerol weight ratio should be tuned to maximise the yield of hydrogen or syn gas. Therefore, it was proposed that detailed pyrolysis and steam gasification studies would be carried out for both pure glycerol and crude glycerol to produce value-added products.

Hydrogen generation from glycerol using aqueous - phase reforming (process)

Investigation on the technical and economic feasibility of generating hydrogen from biomass derived glycerol utilizing Virent Energy System’s (Virent) aqueous-phase reforming (APR) process is provided [55]. Virent has developed the novel APR process and has shown that it is effective for generating hydrogen from aqueous solutions of glycerol. The key breakthrough of the APR process is hydrogen can be generated from oxygenated hydrocarbons such as glucose, sorbitol, glycerol, and ethylene glycol via liquid-phase reforming. The APR process is a simple one-step reforming process that can generate easily purified hydrogen and as such is especially cost effective.

APR process is a unique and innovative pathway to biofuel and bioproduct production. This catalytic route is superior to high temperature thermochemical or fermentation pathways. It is simple, thermally efficient, and entirely scalable for small distributed or large centralized production. Unlike time-consuming fermentation, this robust and fast process does not depend on living microbes or enzymes. The simplicity of the process results in low capital and operating costs. The process uses a simple reactor system at relatively low temperatures and pressures and, once it is operating, no additional energy inputs are needed. As a platform technology, the BioForming process can reliably convert many types of sugars into many different fuels and chemicals.

The APR process:

1) generates hydrogen without the need to volatilize water, which represents a major energy saving;

2) occurs at temperatures and pressures where the water-gas shifts reaction is favorable, making it possible to generate hydrogen with low amounts of CO in a single chemical reactor;

3) occurs at pressures (typically 15 to 50 bars) where the hydrogen-rich effluent can be effectively purified using pressure swing adsorption technology;

4) takes place at low temperatures that minimize undesirable decomposition reactions typically encountered when carbohydrates are heated to elevated temperatures; and

5) utilizes agricultural derived feedstocks.

Virent is investigating using low-value raw glycerol streams as feedstock to Virent's novel aqueous-phase reforming (APR) process to generate hydrogen. The resulting hydrogen can be purified and utilized as a renewable chemical reagent necessary to produce ammonia, methanol and hydrogenated food oils as well as a fuel for current internal combustion engines and future hydrogen fuel cells.

The overall concept for this proposed method of hydrogen generation from biomass is to utilize raw glycerol. This raw glycerol can be mixed with water and the resulting aqueous solution can be fed to the APR process that generates hydrogen in a single reactor. The effluent gas from the APR process can be purified to produce high purity hydrogen. A schematic of the process is given in Fig. 1.12:

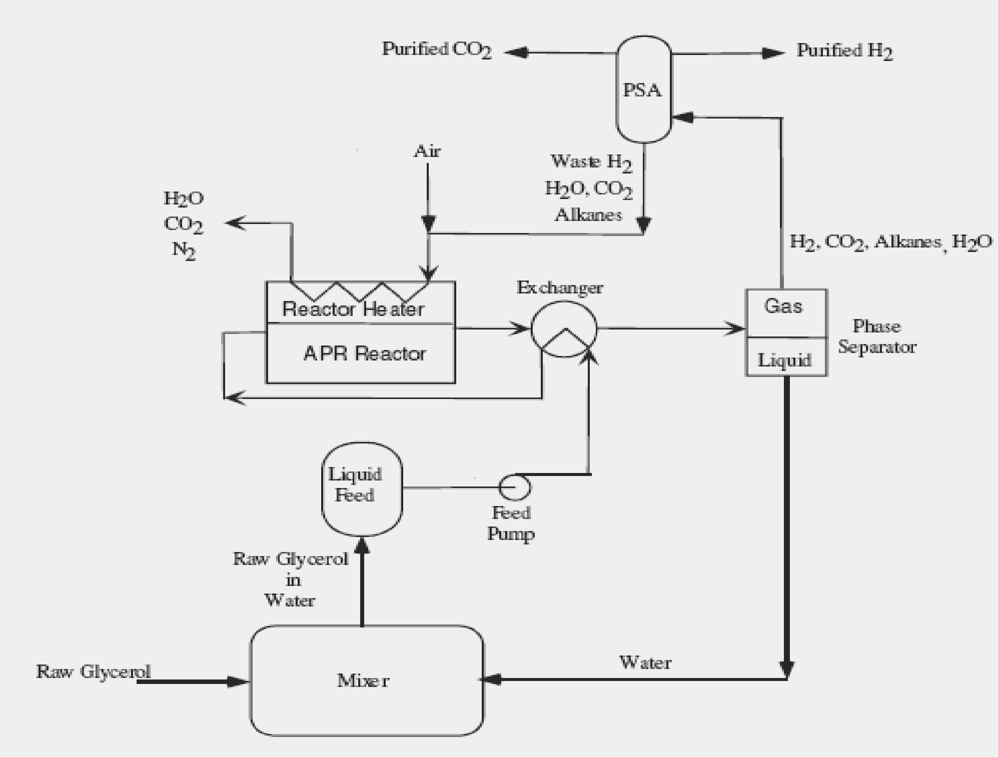


Fig. 1.12 Overview of the production of the hydrogen from biodiesel waste

Aqueous-Phase Reforming Process - Virent’s novel APR process generates hydrogen by reacting a carbohydrate, in this case glycerol, with water to form carbon dioxide and hydrogen as follows:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7\ H_2 \qquad (1.4)$$

This reforming reaction takes place over a catalyst in a single reactor at temperatures between 200 and 250°C and at pressures above the bubble point of water (16 and 40 bar, respectively). The reforming reaction is endothermic and requires heat input. This heat can be supplied by combustion of product hydrogen as shown in Fig. 1.12. Since the APR process runs at low temperature, an alternative method of providing process energy will be to utilize waste heat streams from other associated processes. Thermal efficiencies of the process can be maintained via proper heat exchange (i.e. preheating feed to the reactor by exchanging with the reactor effluent, see). Alkanes such as methane, ethane, and propane are also formed in low concentrations in the APR reactor. The alkane formation is an exothermic process, and while alkane formation lowers the hydrogen yield, the formation of these compounds provides heat for the endothermic hydrogen generation process. These alkanes can be separated from the APR effluent and combusted to provide the necessary process heat.

Gas Purification - the non-condensable gas stream leaving the APR contains predominately CO_2 and H_2. Hydrogen can easily be purified from this gas stream utilizing pressure swing adsorption (PSA) technology. Importantly, the gas stream that exits the APR is at desired feed pressures for the PSA unit (between 16 and 40 bar). Accordingly, the PSA unit does not need an expensive and energy consuming compressor to provide the necessary feed pressure. This results lower capital costs and increased system energy efficiency. Another important feature is that the PSA technology will generate a waste hydrogen stream (typically 10 to 20 % of the feed) due to the pressure swing and purging cycles. This waste stream would also contain the alkanes produced in the APR process. Combustion of the waste hydrogen and alkanes would provide much of the necessary processing heat for the reactor.

Gas Utilization –the gas stream leaving the APR could be utilized directly as a high energy fuel gas to power internal combustion engines, gas-fired turbines, and solid oxide fuel cells. The high temperature waste heat from such devices could be recycled back to provide the necessary process heat for the APR process. In such a configuration, the APR process could generate a fuel gas stream that contains over 100 % of the heating value of the feed glycerol. In addition to fuel, purified hydrogen from the waste stream could be used as a chemical reactant for hydrogenation reactions. It also is possible to efficiently purify the CO_2 from the high-pressure effluent stream of the APR process. This purified CO_2 could be used either as a chemical or sequestered making the process of generating hydrogen from corn a consumer of the greenhouse gas CO_2.

Finally, the waste stream could provide a starting reactant for the production of biodiesel. Hydrogen and CO_2 reacted over a catalyst of copper and zinc is converted to methanol by the reaction:

$$6H_2 + 2CO_2 \rightarrow 2CH_3OH + 2\ H_2O \qquad (1.5)$$

Providing this starting material for biodiesel production from the waste stream can represent a large reduction in material costs. Laboratory proof-of-concept measurements have shown it is possible to generate hydrogen in high yields via the conversion of glucose in the liquid-phase [56]. In particular, the selectivity for H_2 production decreased in the order: Ethylene glycol > Glycerol > Sorbitol > Glucose. Subsequent investigations have shown that a variety of catalyst compositions are active for the generation of hydrogen via the aqueous-phase reforming of oxygenated compounds.

Glycerol combustion

The glycerol by-product burns well, but unless it's properly combusted at high temperatures it will release toxic acrolein fumes, which mainly form at between 200 and 300°C. Using the by-product in a burner to preheat the vegetable oil for biodiesel processing would be an elegant solution, if it worked well enough. It's an elusive goal. Complete and clean combustion of the by-product requires a burning temperature in excess of 1000°C. And perhaps preheating and atomisation as well with the sort of low-tech burners backyard brewers have made so far, what happens instead is that the burner might burn for long enough to pre-heat the oil, but then it gets gunged up with sticky black stuff that won't burn (mostly soap) and it goes out. If you want more heat you have to clean it out and start it up again. Another disadvantage is that it's not a clean burn; it smokes, especially towards the end of the burn when it's trying to combust the soap [57].

Glycerol vacuum distilation

Vacuum distillation is a simple and efficient process to recover glycerol from crude glycerol with high contents of salt and MONG (matter organic non-glycerol). On average, 141.8 g glycerol was recovered from 1 kg glycerol residue, leaving 142.6 g distilled bottom. The distilled bottom comprised mainly salt, high boiling MONG and some glycerol. The crude glycerol was distilled at 120^{o}C - 126^{o}C and 4.0 x 10-1 - 4.0 x 10-2 mbar pressure to produce 96.6% glycerol. The optimum pH for the distillation was < 5 in which foaming was obviated [58].

New chemical modifications of glycerol

There is a tremendous potential to develop a variety of new processes and product lines from glycerol, taking advantage of its unique structure and properties. Glycerol is a nontoxic, edible, biodegradable compound. These characteristics provide important environmental benefits to new platform products. Most products are based on unmodified glycerol or simple modifications to the glycerol molecule. More complex chemistry was hindered by its high cost. Lower cost glycerol could open significant markets in polymers, ethers, and other compounds.

From a technical standpoint, glycerol's multifunctional structure can be exploited by several different means. It is clear that a very large number of products and product classes could, in principle, be derived from glycerol [59].

Selective oxidation of Glycerol. Glycerol's structure lends itself to catalytic oxidative processes using inexpensive oxidizing agents such as air, oxygen, hydrogen peroxide, or bleach. Combining these inexpensive oxidizing agents with an inexpensive source of glycerol will allow the production of a number of new derivatives. A few research groups have investigated this technology, but their focus has been limited to a small number of catalysts, leaving a number of questions of selectivity and yield unanswered.

Glycerol carbonates as a new solvent and product. Glycerol carbonate is a relatively new material in the chemical industry, but one that could offer some interesting opportunities, as it can be prepared directly and in high yield from glycerol. Glycerol carbonate has been investigated as a novel component of gas separation membranes, polyurethane foams, as a surfactant component, as a new solvent for several types of materials, as a component in coatings, as a potential component of the paint industry, as a nonvolatile reactive solvent, and as a component of detergents. As glycerol becomes less expensive, the use of glycerol carbonate in applications occupied by currently cheaper carbonates should be investigated. Dimethyl carbonate is being positioned as a green replacement for phosgene in the production of polycarbonates and polyurethanes. Inexpensive glycerol carbonate could serve as a source of new polymeric materials for this industry. Glycerol carbonate can be prepared by very simple processes, such as the direct reaction of glycerol with urea, or the treatment of glycerol with ethylene or propylene carbonate. Direct production of glycerol carbonate from glycerol and carbon dioxide under supercritical conditions has also been reported.

Glycerol as a component of new polymers. Glycerol has traditionally played a role in the production of several types of polymers, some of which are available commercially. Selective etherification reactions can convert glycerol into polyglycerol esters, which have been suggested for use as biodegradable surfactants and lubricants and as replacements for conventional poly (oxoethylene) nonionic surfactants.

Polyglycerol and polyglycerol methacrylates are used as treatments for wood to improve its stability. This application would compete with the more widely used polyethyleneglycols. However, glycerol based polymers offer additional benefits including lower amounts of leachability into the environment. As the cost of glycerol decreases, processes to manufacture polyglycerols through modification of its structure become more affordable, and would lead to new optimized wood treatments. More recently, significant attention is being given to preparation and properties of new, more highly branched polymers. Glycerol’s multifunctional structure is well suited for the production of these new types of polymers. In addition, glycerol has been used with lactic acid to prepare branched polylactide polymers. More generally, branched polymers exhibit a wide range of new properties that could be exploited in useful marketplace products.

A number of more specific product application areas have been suggested for branched polymers. Many of these could be very high value applications, such as use in sensors, personal care products, or organic conductors. Other applications in larger volume markets have been suggested, and branched polymers could find utility as polyester polyols, surfactants, coatings, and alkyd resins, new solvents, and polyurethanes.

New highly branched polymers have been made using glycidol as a starting monomer. The resulting structure is a branched polyether polyol, but is frequently referred to as a polyglycerol. Glycidol is a high value component in the production of a number of polymers, including epoxy resins and polyurethanes. Glycidol has been conventionally synthesized from epichlorohydrin, which in turn is derived from the chlorination of allyl alcohol. More recently the high yield preparation of glycidol from glycerol carbonate, and thus, from glycerol, has been reported, making it likely that low cost glycerol could be used to produce low cost glycidol and its family of products. Small scale production of these highly branched glycidol polymers has been commercialized in Europe by Hyperpolymers (Germany).

Using glycerol as a starting material for the production of other small molecules also offers a new opportunity. Glycidol has the advantage of being a current commercial, albeit specialty product. Lowering its cost by producing low cost glycerol presents new opportunities to further expand of the glycerol product family. For example, extensive work has been carried out on catalytic transformations of epoxides. Should the cost of glycerol, and thus, the cost of glycidol drop, it will become important to investigate the ability of these processes to convert glycidol into a source of alcohols and other epoxide derivatives.

Co-polymers and blends of glycerol with citric acid, lactic acid, and starch were prepared by condensation reactions. These materials were shown to have potential in coating applications.

Biochemical transformations**.** Glycerol can also serve as a feedstock in biochemical transformations [59]. Glycerol has been investigated for the fermentative production of 1,3 propanediol, one of the primary components of DuPont’s Sonora (1,3 PDO and terephthalic acid), a polymer being investigated for use in textiles and carpeting. This is by no means a new process. Fermentation of glycerol to PDO was described as early as 1881. Simple economic evaluation indicates that biochemical PDO production would be more economical than chemical PPO production. A primary question for this application area is the proper choice of biochemical feedstock. Current prices of glycerol imply that an alternate fermentative route from glucose would give cheaper 1,3-PDO. A considerable effort has been carried out to improve biochemical PDO production. It was reported that minimizing the amount of methyl glyoxal and glycerol-3-phosphate produced during fermentation using engineered E. Coli improves the conversion of glycerol to PDO by removing these two enzyme inhibitors.

As glycerol prices fall, industrial/government partnerships to develop new products and identify large market uses provides mutual benefits. There is a specific expertise in the development of new catalytic oxidations based on novel polyoxometallate catalysts, and the use of simple radical based oxidations of polyols, which have been examined as new types of nylons. As their cost drops, these intermediates can be considered as components of new polyfunctional, glycerol derived polymers, such as polyesters and nylons. Other selective oxidation products may find applicability as structural analogs of polylactic acid.

Glycerol in UV filters. Glycerol esters were developed that exhibit strong absorption in the ultraviolet region. Such compounds serve as organic UV filters for personnel care formulations [60].

1.8. ATMOSPHERIC AIR POLLUTION DISPERSION MODELLING

Atmospheric dispersion modeling is the mathematical simulation of how air pollutants disperse in the ambient atmosphere. It is performed with computer programs that solve the mathematical equations and algorithms which simulate the pollutant dispersion. The dispersion models are used to estimate or to predict the downwind concentration of air pollutants emitted from sources such as industrial plants and vehicular traffic. The models serve to assist in the design of effective control strategies to reduce emissions of harmful air pollutants [61].

The dispersion models require the input of data which includes:

- Meteorological conditions such as wind speed and direction, the amount of atmospheric turbulence (as characterized by what is called the "stability class"), the ambient air temperature and the height to the bottom of any inversion aloft that may be present.
- Emissions parameters such as source location and height, source vent stack diameter and exit velocity, exit temperature and mass flow rate.
- Terrain elevations at the source location and at the receptor location.
- The location, height and width of any obstructions (such as buildings or other structures) in the path of the emitted gaseous plume.

Many of the modern, advanced dispersion modeling programs include a pre-processor module for the input of meteorological and other data, and many also include a post-processor module for graphing the output data and/or plotting the area impacted by the air pollutants on maps.

There are five types of air pollution dispersion models, as well as some hybrids of the five types:

Box model assumes the airshed (i.e., a given volume of atmospheric air in a geographical region) is in the shape of a box. It also assumes that the air pollutants inside the box are homogeneously distributed and uses that assumption to estimate the average pollutant concentrations anywhere within the airshed.

Gaussian model assumes that the air pollutant dispersion has a Gaussian distribution, meaning that the pollutant distribution has a normal probability distribution. Gaussian models are most often used for predicting the dispersion of continuous, buoyant air pollution plumes originating from ground-level or elevated sources. Gaussian models may also be used for predicting the dispersion of non-continuous air pollution plumes (called *puff models*).

Lagrangian dispersion model mathematically follows pollution plume parcels (also called particles) as they move in the atmosphere and model the motion of the parcels as a random walk process. The Lagrangian model then calculates the air pollution dispersion by computing the statistics of the trajectories of a large number of the pollution plume parcels.

Eulerian dispersions model is similar to a Lagrangian model in that it also tracks the movement of a large number of pollution plume parcels as they move from their initial location. The most important difference between the two models is that the Eulerian model uses a fixed three-dimensional Cartesian grid as a frame of reference rather than a moving frame of reference.

Dense gas models simulate the dispersion of dense gas pollution plumes (i.e., pollution plumes that are heavier than air).

Any method, which is permissive to measure, to calculate or forecast air pollution level could be applied for air quality estimation. There are three main air quality estimation methods [62]:

1. Air pollution measurements.
2. Inventory of pollutants emitted from pollution source.
3. Pollutants dispersion modeling.

Many computer based programmes could be applied for pollution dispersion simulation, hereinafter are given some of them:

AERMOD atmospheric dispersion modeling system is an integrated system that includes three modules: (1) A steady-state dispersion model designed for short-range (up to 50 km) dispersion of air pollutant emissions from stationary industrial sources.

(2) A meteorological data preprocessor (AERMET) that accepts surface meteorological data, upper air soundings, and optionally, data from on-site instrument towers. It then calculates atmospheric parameters needed by the dispersion model, such as atmospheric turbulence characteristics, mixing heights, friction velocity, Monin-Obukov length and surface heat flux.

(3) A terrain preprocessor (AERMAP) whose main purpose is to provide a physical relationship between terrain features and the behavior of air pollution plumes. It generates location and height data for each receptor location.

AERMOD also includes PRIME (Plume Rise Model Enhancements) which is an algorithm for modeling the effects of downwash created by the pollution plume flowing over nearby buildings.

ADMS 3 (Atmospheric Dispersion Modelling System) is an advanced atmospheric pollution dispersion model for calculating concentrations of atmospheric pollutants emitted both continuously from point, line, volume and area sources, and intermittently from point sources (Fig. 1.13)

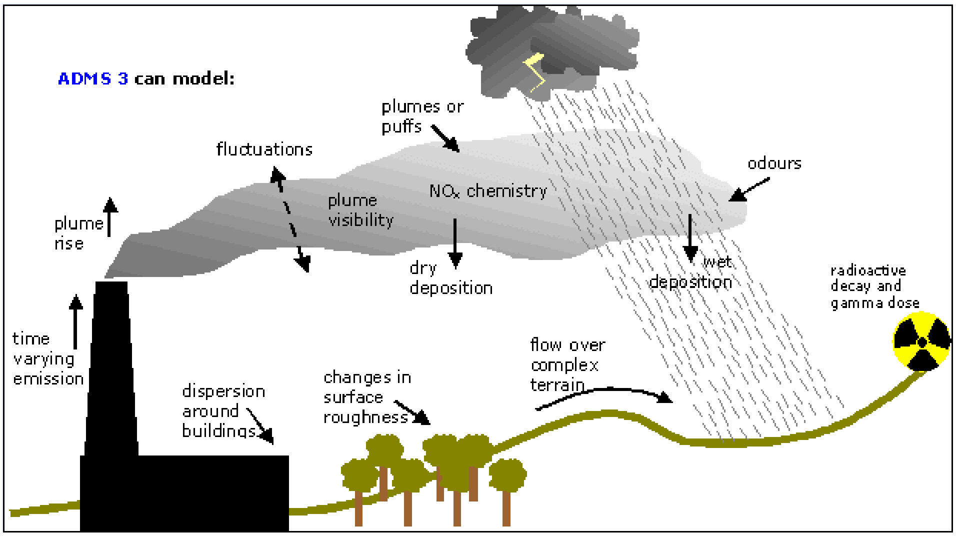


Fig. 1.13 ADMS 3 simulation potential

The model includes algorithms which take into account: downwash effects of nearby buildings within the path of the dispersing pollution plume; effects of complex terrain; effects of coastline locations; wet deposition, gravitational settling and dry deposition; short term fluctuations in pollutant concentration; chemical reactions; radioactive decay and gamma-dose; pollution plume rise as a function of distance; jets and directional releases; averaging time ranging from very short to annual; and condensed plume visibility. The system also includes a meteorological data input preprocessor.

ISC3 (Industrial Source Complex) model is a popular steady-state Gaussian plume model which can be used to assess pollutant concentrations from a wide variety of sources associated with an industrial complex. This model can account for the following: (1) Point, area, line, and volume sources, (2) Settling and dry deposition of particles, (3) Downwash, (4) Separation of point sources, (5) Limited terrain adjustment.

1.9. CONCLUSIONS

1. Recently, the increase in crude oil prices, limited resources of fossil oil and environmental concerns (lowering CO_2 emissions) leads to the significant interest in biofuels. Biodiesel has become more attractive recently because of its environmental benefits and due to the fact that it is made from renewable resources.
2. Europe is the leader in biodiesel production. Rape seeds are the main raw material for biodiesel production in Europe. The largest producers – Germany, France and Italy.
3. EU Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport provided voluntary targets for each country that minimum share of biofuels should be 2 % by 2005 and should gradually rise to 5.75 % by the year 2010.
4. Biodiesel is environmentally friendly. It reduces the emission of particulate matter by 40 %, carbon monoxide by 44 %, unburnt hydro carbon by 68 %, polycyclic aromatic hydrocarbons by 80 %, carcinogenic nitrated PAHs by 90 % on an average compared to petrodiesel. The exhaust emissions of sulphur oxides and sulphates from biodiesel are essentially eliminated compared to diesel. One of the problems with the fuel itself is the increase in NO_x in biodiesel emissions.
5. Transesterification is the reaction of a fat or oil with an alcohol to form simpler esters and glycerol – the main by-product in biodiesel production process (about 10 % based on biodiesel). Other by-products may be seed meal, lecithin, solvents, alcohol, acid/base, soap, water.
6. High purity glycerol has many potential customers in the world marketplace, including the pharmaceutical and cosmetics manufacturers as well as several others. The glycerol produced by transesterification is only about 50 – 80 % pure. So, it needs to be pointed that new niches for technically impure glycerol must be found with a view of biodiesel production cost minimization and increment of competitiveness to conventional diesel. Recently used procesess for impure glycerol utilization are syn gas or hydrogen production through gycerol pyrolysis, vaccum distilation, new chemical modifications and etc.
7. The main limiting factors for biodiesel production expansion – high production costs and generated relatively large amounts of by-products. The biodiesel production costs are higher than those of mineral diesel, therefore only efficient use of by-products, especially glycerol, could enable biodiesel to compete with coventional diesel in respect of production costs. To ensure the future of this biofuel technology, new outlets must be found for this by-product.
8. Many computer based programs could be applied for air pollution dispersion simulation, thus it is particularly important to choose the most suitable to achieve objectives established for simulation.

2. EXPERIMENTAL INVESTIGATION OF HEAVY FUEL OIL – GLYCEROL EMULSION FORMATION AND COMBUSTION PROCESSES

2.1. INTRODUCTION

One of the most perspective raw materials for the biodiesel production in Lithuania is oily rape seed. The main by-product of biodiesel production process – glycerol - amounts 10-12 % from all amount of biodiesel produced.

The *object* of this research is to verify the possibility of rapeseed oil methyl ester production by-product - glycerol usage to lower SO_2 emission level into the atmosphere from boiler-houses combustion processes. According to norm LAND 43-2001 “Norms for the exhaust of pollutants from large fuel burning equipment“ [62], SO_2 emission level can not exceed MAC value of 1 700 mg/Nm^3. Neither SC „Mažeikių nafta“, nor Russia or Belarus oil refining companies produce heavy fuel oil, that would meet such requirements (here sulphur content in heavy fuel oil ~ 2.0 - 2.5 % by mass). In such a case, heavy fuel oil in Lithuania could be combusted in large fuel combustion equipment only if combined with at least 50 % of biofuel. The biodiesel, produced from rape seed, does not emit sulphur compounds during combustion process. Only in this case, when mixing heavy fuel oil with biodiesel, SO_2 emission level 1 700 mg/Nm^3 and lower could be achieved.

The research *aim* was to investigate the heavy fuel oil – glycerol emulsion formation conditions and its combustion impact on the environment. A technology was developed based on the research investigation for modifying the higher density biodiesel fuel by-product from rapeseed oil – technical glycerol to obtain a stable heavy fuel oil emulsion modified with it (50 % heavy fuel oil + 50 % glycerol). Laboratory and pilot plant experiments allowed us to optimize the emulsion composition containing < 10 % water. A technological specification for heavy fuel oil-glycerol emulsion was prepared on the bases of combustion experiments carried out at JSC „Rietavo veterinarinė sanitarija”.

So, the aim of this section “Experimental investigation of heavy fuel oil – glycerol emulsion formation and combustion processes” is methodology description, experiment accomplishement, evaluation of experimental investigation results and presentation of conclusions for the heavy fuel oil – glycerol emulsion formation conditions and evaluation of the obtained emissions during combustion process.

2.2. METHODOLOGY OF HEAVY FUEL OIL - GLYCEROL EMULSION PREPARATION, COMBUSTION AND EVALUATION OF THE OBTAINED EMISSION CONCENTRATIONS

The experiment was started from the preparation of heavy fuel oil-glycerol emulsion sample and initial incineration experiments. Heavy fuel oil with additives were modified by using a ultrasonic dispergator ”UZDN-2T“ (Russia) and laboratory shaker „Chirana“ (Czechia) in laboratory conditions. The other samples were prepared in the pilot plant system using rotary-pulsation machine “RPA”. The laboratory modified heavy fuel oil samples were incinerated by dripping it into a porcelain plate heated to 850°C, and the pilot experiment was accomplished in the experimental furnace, when incinerating in 750-950°C temperature.

The quantitative impurity analysis was performed using photocalorimetric and atomic absorption spectroscopy methods.Using the X-ray examination method, the raw material and ash phase composition were investigated. The analysis was performed using difractometer “DRON-2“ (Russia). The roentgen tube voltage U=30 kV, anode current I_a=8 mA (Cu anode, Ni filter, goniometer gaps 0,5:1,0:0,5 mm). Speed of sample rotation 1° min^{-1}.

All X-ray diffraction patterns were recorded in the room temperature and identified, comparing with a standard data. The integral peak area B measured by radians (rad). The relative variation of crystal size is evaluated by Laue formula:

$$B=\frac{K\lambda}{t\cos\theta} \qquad (2.1)$$

Here:
B – peak integral area (peak semiarea), rad;
K – constant;
λ - X-ray wavelength, nm;
t – crystal size;
θ - Brag angle;

The thermographic investigations were performed using derivatograph „Q-1500 D“ (Hungary) in the temperature interval 20-1000°C. The temperature raising rate was 10°C/min. The gas medium in the heating furnace – air.

The detail quantitative composition of inorganic matter observed by the emissive spectral analysis method, using laser microanalyser „LMA-10“ (Germany). The sample under investigation was attached to the carbon electrodes and excited by electric spark. Before the investigation carbon electrodes were mechanically polished and sweeped by electric spark 15 times each, to be spectrally clean.

The dispersivity of heavy fuel oil emulsion samples was investigated by optical method, using „MPSU-104“ and MIN-8“ microscopes (Russia). The qualitative composition of gas was investigated by a method of molecular spectral analysis in an infrared area of spectrum, using spectrometer „Specord M-80“ (Germany). The samples were collected into ciuvette of 100 ml volume with KBr panes. The dust concentration in a flue gas is observed using weight method.

During the pilot plant investigation, analysis of combustion gases was performed using standard chemical methods, which are operative in pollution estimation in the flue gas. The scheme of pilot plant investigations for emulsion preparation and combustion experiments are presented in Fig. 2.1. The experimental investigations of heavy fuel oil emulsification and modification by variuous additives ratios and combustion of prepared emulsions were performed in the pilot plant (Fig. 2.1) at VGTU Institute of Thermal Insulation.

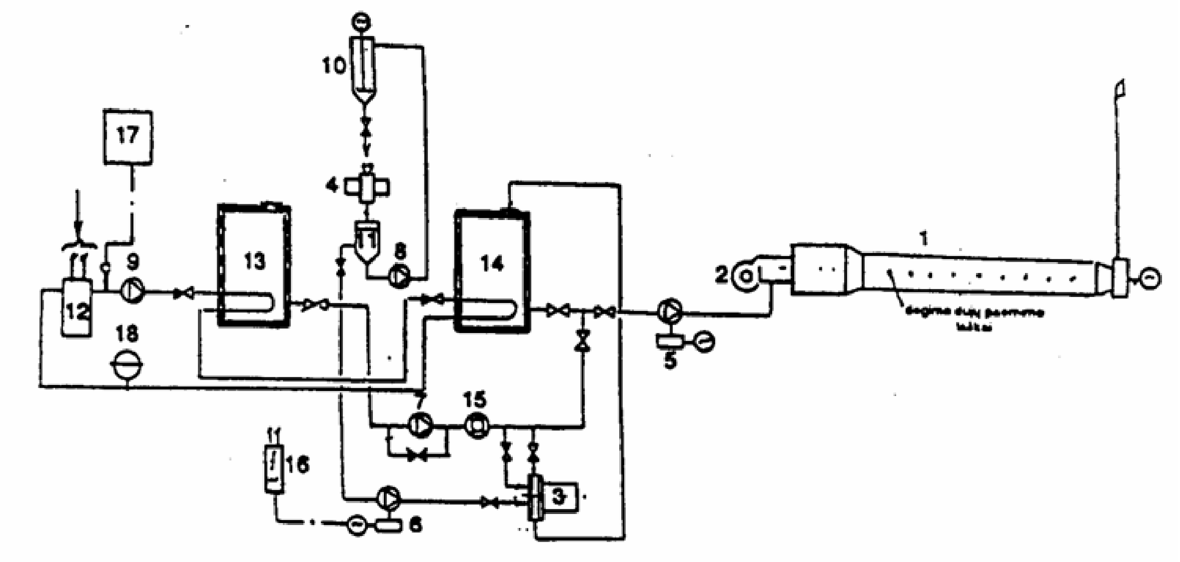
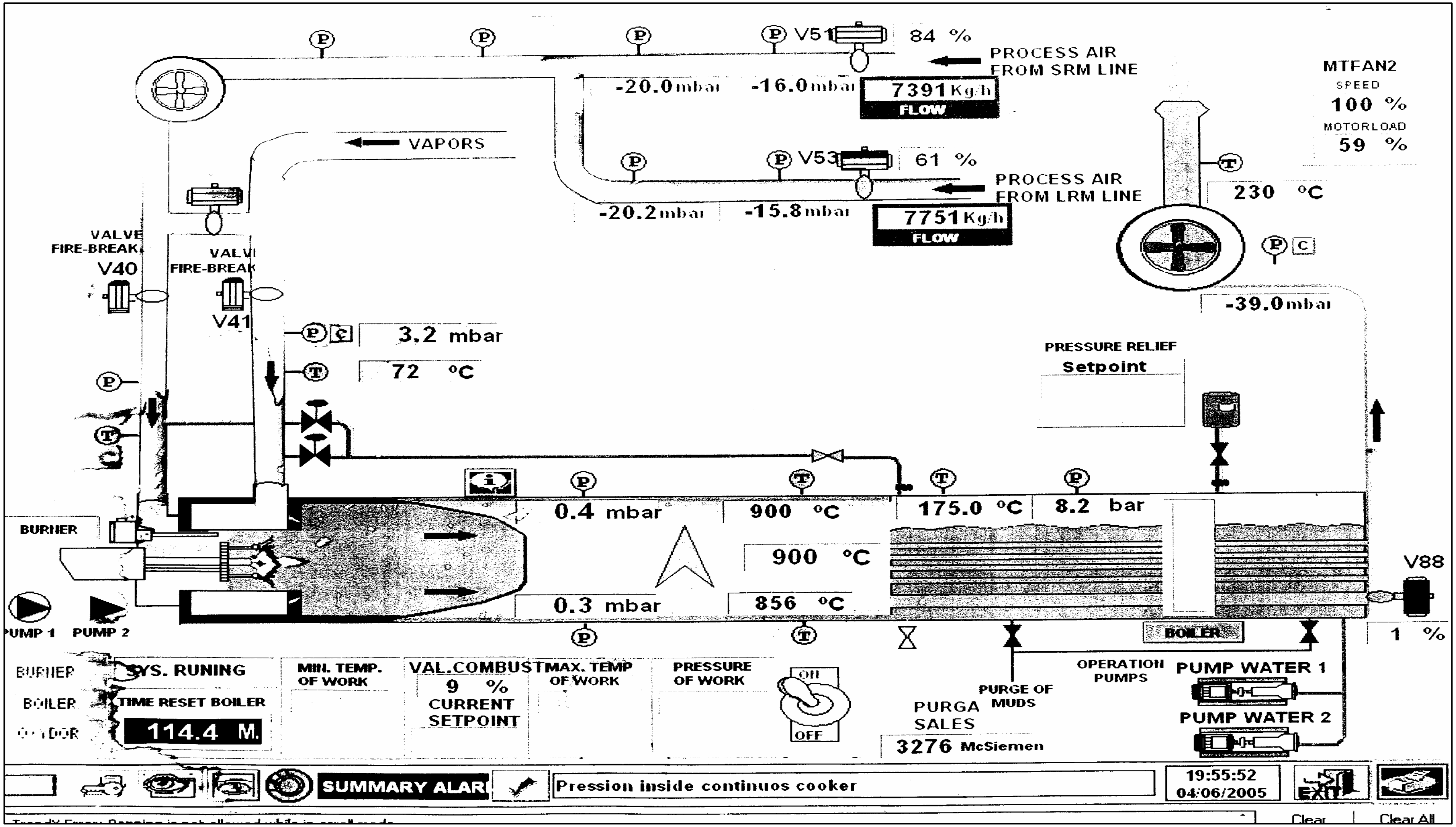


Fig. 2.1 The principal scheme of experimental pilot plant for modified fuel preparation and combustion: 1 - tubular chamber for modified fuel combustion; 2 – universal burner KG-70 for liquid fuel; 3 - emulsificator ER-2T; 4 - disintegrator DIA-01; 5 – modified fuel pump; 6 – $MgO+H_2O$ suspension pump-batcher; 7 - heavy fuel oil pump; 8 – circulation pump; 9 – hot water circulation pump; 10 - $MgO+H_2O$ suspension mixer; 11 – interim container; 12 – water heater; 13- heavy fuel oil container; 14 – modified fuel container; 15 – heavy fuel oil register; 16 – frequency changer; 17 – operating box; 18 – expansion vessel.

The heavy fuel oil-glycerol emulsion combustion experiments and measurements were carried out in the thermal oxidation boiler for meat-bone flour and technical fat combustion at the JSC “Rietavo veterinarinė sanitarija“. The principle scheme of boiler is given in Fig. 2.2



Pression inside continuos cooker

Fig. 2.2 The principle scheme of thermal oxidizing boiler „UMISA -CR/11,9 (13) “

The thermal oxidizer system is an equipment system that uses heat to destroy organic compounds by oxidizing them at high temperature. It is an effective mean against many compounds that can be oxidized by heat, including the odorous compounds. The picture of thermal oxidizing boiler, where the combustion experiments were carried out is given in Fig. 2.3, as it follows:

Fig. 2.3 Thermal oxidizing boiler „UMISA -CR/11,9 (13) "

The thermal boiler is characterized by the following technical data and features:

- **Boiler type**: pyrotubular one pass steam boiler for the heat recovery of exhaust fumes, equipped with all of the safety devices related to pressure and water level;
- **Trademark and model**: UMISA -CR/11,9 (13);
- **Steam output**: 11.900 kg/h;
- **Heat input**: 10.571 kW;
- **Design pressure:** 13 bar;
- **Design temperature:** min 200°C;
- **Fluids:** water/saturated steam;
- **Weight:** 60.000 kg;
- **Thermal oxidation conditions:**
  - Max temperature in oxidation chamber: 950°C;
  - Normal temperature in oxidation chamber: 850°C;
  - Exposure time: 2 sec up to 850°C;
  - Fuel type: heavy fuel/technical fat;

- **Parameters of oxidation chamber:**
  - Internal diameter: 2800 mm;
  - Length: 9700 mm;
  - Chamber volume: 60m^3.

The oxidation chamber is made within the fire-resistant layer inside. The gas enters the oxidation chamber through the tube. A special projected burner is mounted in this chamber, which supplies heat energy necessary for the oxidation process proceeding according to a precisely indicated temperature conditions.

Some main aspects of thermal oxidizer system operation are as follows:

- Thermal oxidator oxidizes steam along with ambient air and/or treated air;
- Water is evaporated in rendering process and lateron injected to the oxidator for neutralization.
- Steam and combustable air in high temperature passes from burner in gas form; these gases are released to the combined steam-boiler, and accumulated gas is used as heat for steam production, which is spent again for the rendering process.
- Gases used for boiler heating are released through the smokestack as clean air;
- The hot gases from the combustion chamber are maintained in high temperature for 2 seconds in a retention chamber to assure complete oxidation of the odorous compounds.

The characteristics of materials – heavy fuel oil and glycerol- used for modified fuel preparation are estimated and described. The qualitative properties of heavy fuel oil used for preparation of heavy fuel oil-glycerol emulsion, certificated by SC “Mažeikių nafta“ are given in Table 2.1.

Table 2.1 The highly sulphurous heavy fuel oil qualitative properties

No.	Qualitative properties	Norm	Test methods
1.	Relative viscosity, degrees vR, at 80°C,max kinematic viscosity, m^2/s (cSt)	16.0	GOST 6258
	Kinematic viscosity, m^2/s (cSt)	118.0	GOST 33
2.	Ash, wt. %, max	0.14	GOST 1461
3.	Sediments, wt. %, max	1.0	GOST 6370
4.	Water, wt. %, max	1.0	GOST 2477
5.	Alkali, acid content soluble in water	not found	GOST 6307
6.	Sulphur, wt. %, max	3.5	ASTM D 4294
7.	Flash point, °C, min	110	ASTM D 92
8.	Pour point, °C, max	25	ASTM D 97
9.	Net heat of combustion, kJ/kg (kcal/kg), min	39900 (9530)	GOST 21261
10.	Density, at 20°C, kg/m^3	no norm*	GOST 3900

*only for fuel oil export

The major by-product of biodiesel production process – glycerol, used in these experimental researches, was produced in JSC "Rapsoila". The physico – chemical properties of glycerol, used for the experimental researches, are given in Table 2.2 and glycerol quality indicators in Table 2.3.

Table 2.2 The physico – chemical properties of glycerol

No.	Indicators	Properties
1.	Agregate state (solid, liquid, gaseous)	Liquid
2.	Sensual properties (color, smell)	Russet color, syrup type liquid, gentle oil smell
3.	Flammability	Flammmable
4.	Solubility	Soluble in water, ethanol, acetic, dimethylformamyde
5.	Boiling temperature, °C	290°C
6.	Melting temperature, °C	20°C
7.	Density, kg/m^3	1.26 kg/m^3
8.	Flash temperature, °C	177°C
9.	Self ignition temperature, °C	393°C
10.	Reactivity	Non-reactive
11.	Explosivity	Non-explosive
12.	Stability	Stable in normal conditions
13.	Hydroscopic properties	Has hydroscopic properties

Table 2.3 The quality indicators of glycerol

No.	Quality indicators	Investigation method	Standard	In fact
1	Ash, wt %, max	EN ISO 6245	0.14	0.085
2	Water, wt%, max	ISO 3733	1.0	7.5
3	Sulphur, wt%,max	DIN EN ISO 20884	25000	381
4	Flash point, °C, max	DIN EN ISO 3679	110	109
5	Kinematic viscosity, °C, max	LST EN ISO 3105	50.0	15.2
6	Density, at 15°C, kg/m3	LST EN ISO 3675	adjusting	1260
7	Net heat of combustion, MJ/kg, max	ASTM D 240	39.5	12.2

Glycerol (1,2,3-propanetriol, glycerine) pure chemical compound, $CH_2OHCHOHCH_2OH$, is a clear, hygroscopic liquid with a melting point above 18.17°C. Glycerol is completely soluble in water and alcohol; it is slightly soluble in ether, ethyl acetate, dioxane, and insoluble in hydrocarbons. Glycerol, the simplest trihydric alcohol, forms esters, ethers, halides, amines, aldehydes and acrolein. As an alcohol, glycerol also has the ability to form salts. On oxidation, glycerol yields a variety of products depending upon reaction conditions.

The heavy fuel oil-glycerol combustion process was carried out in the thermal oxidizer boiler and then the obtained concentrations of CO, SO_2, NO_x and particulate matter were measured using the following instruments.

GAS ANALYSER TESTO 342-3

The gas analyser is used to measure NO_x, CO and O_2 concentrations (mg/m^3) in the flue gas from the heavy fuel oil-glycerol emulsion combustion. For these measurements the gas analyser TESTO 342-3 (Germany) is applied. For the beginning, the device is calibrating automatically for 1 minute, and then measurements are carried out. The readings are displayed constantly on the display for as long as the pump is running. The measurements are carried out and data for the investigations collected in a special place for the collection of emissions near the roof in JSC “Rietavo veterinarinė sanitarija“. The gas analyser tip is placed in the flue gas flow and the air was sucked. The concentrations of measured gas are presented automatically in gas analyser screen. The gas analyser tip is kept in a flue gas for 1-2 minutes, untill stable temperature is reached. The gas analyser TESTO 342-3 is presented in Fig. 2.4.

Fig. 2.4 Gas analyser TESTO 342-3 (Germany)

ASPIRATOR 822

The concentrations of particulate matter in the flue gas are measured using device - aspirator (Model 822) and weight method. The aspirator is presented in the Fig. 2.5.

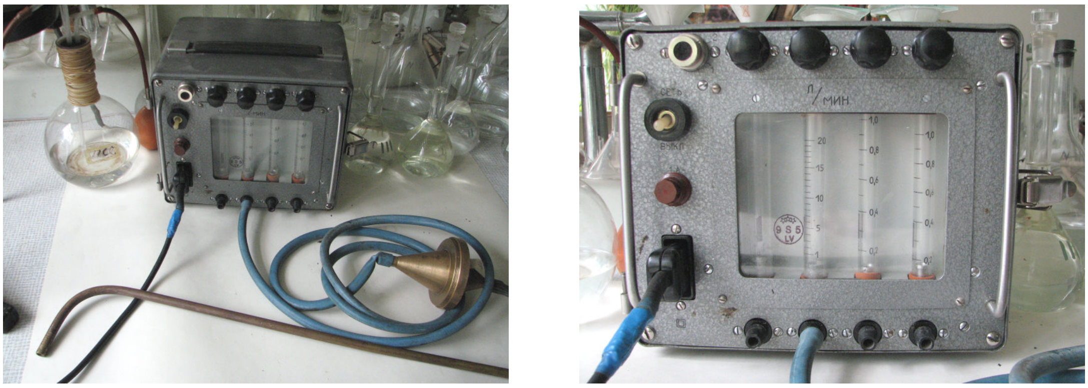


Fig. 2.5 Aspirator (Model 822)

The aim is to estimate exhaust emissions amount, velocity and time-exposure measured in l/min. At the beginning, the filter of aspirator is dessicated in the exicator above the concentrated sulphuric acid solution and then cooled for ~ 2 hours, measured its weight and then is placed to the device. Then the aspirator's measurement probe is placed in the chminey – exhaust source of pollutants and kept there for some time period, while air pass through the filter. This time period depends on the dust amount – the more dust the longer suction duration. Then filter is pulled out, dessicated in an exicator, cooled and its weight is measured. The filter weight increment is a measure of particulate matter concentration in the investigated flue gas (weight method).

GAS DETECTOR PUMP ACCURO

The gas detector pump ACCURO (Germany) is used for the determination of SO_2 concentrations in the flue gas. The gas detector pump is presented in Fig. 2.6.

Fig. 2.6 Gas detector pump ACCURO (Germany)

An appropriate tube for measurement is selected and the tip is inserted in the pump. The pump is squeezed 10 times (~ 1minute), it means that 1 l of air is pumped. The measurements are carried out using indicator tubes, which changes their color at a presencce of certain gas. The indicator tube is calibrated so the results can be taken easilly directly from the tube scale. The indicator scale is expressed in ppm (parts per million) and can be converted to mg through the transfer coefficient 2.93.

PH METER WTN 330i

The glycerol pH value (hydrogen ion concentration in a substance) is estimated using pH meter WTN 330i, which is presented in Fig. 2.7:

Fig. 2.7 The PH-meter WTN 330i

The pH meter tip is submerged into the vessel filled with glycerol and kept untill a stable value on pH meter screen automatically is displayed. Contrary to expectations, the measurement results showed that the investigated glycerol is acidic, because measured pH value is 4.49. So, the conclusions can be drawn, that this glycerol was treated by phosphoric acid in order to remove caustic hydroxide additives.

2.3. ANALYSIS OF RESEARCH RESULTS

Stable heavy fuel oil – glycerol emulsion preparation

The preparation of the heavy fuel oil-glycerol emulsion was provided and its structure was investigated through the alternation of quantities of the additives.

With a purpose to obtain a stable emulsion through heavy fuel oil modification by glycerol and water additives in various ratios and temperatures were accomplished. The purpose was to investigate the structure of prepared emulsion, the best mass ratio, taking heavy fuel oil, glycerol and water percentage contents into account, to find the most stable and suitable for further combustion experiments, to investigate duration of stable emulsion structure. During the experiments, some prepared emulsions were stable for some months, some of them disintegrated throughout few hours after emulsion preparation due to the aggregation process. If the emlsions were not homogenous, water begins to segregate and the emulsion collapses. The obtained results of emulsion preparation and its stability investigation are given in Table 2.4.

Table 2.4 The parameters of heavy fuel oil modification by glycerol and water mixtures

No.	**Mass ratio, %**			**Emulsification temperature, °C**	**Stability**	**Results of emulsion combustion in pilot plant burner**
	Heavy fuel oil	Glycerol	Water			
1	40	30	30	50	Not stable	Nonflammable
2	40	30	30	70	Not stable	Nonflammable
3	40	30	30	90	Stable	Nonflammable
4	40	40	20	50	Not stable	Nonflammable
5	40	40	20	60	Not stable	Nonflammable
6	40	40	20	70	Stable	Nonflammable
7	**50**	**40**	**10**	**50**	**Stable**	**Flammable**
8	50	40	10	60	Stable	Flammable
9	50	40	10	70	Stable	Flammable

As it can be seen from data in Table 2.4, the heavy fuel oil – glycerol emulsion with 10 % H_2O is combustible. The higher % water mass ratio in heavy fuel modification by glycerol process is not possible, because it reduces stability and flammability properties of this emulsion. It is also estimated, that it is enough to preheat to 50°C to ensure smooth heavy fuel oil and glycerol emulsification process. It is not recommended to heat more than 90°C, since it can cause emulsion degradation. The experiment was carried out by the following emulsification order of priority. So, the process is recomended to be proceeded as follows:

1. heavy fuel oil is preheated up to 90°C;
2. glycerol with water (moisture content <10 %) is added, the temperature of mixture decreases till 50-60°C;
3. afterwards, mixture is emulsificated by adding ~ 0.5 % of emulsol using emulsification pump, the process is continued for a 5-10 minutes period.
4. finally, the obtained mixture is prepared for combustion.

The obtained mixture is flammable. The caloric content ~ 7800 - 8500 kcal/kg. The emulsion was prepared at the experimental base of VGTU Institute of Thermal Insulation (total – 1 tonne) and then delivered to JSC "Rietavo veterinarinė sanitarija“ for the industrial combustion investigation in its boiler. In this investigation the emulsion of 7th structural composition (see Table 2.4) was found to be operational.

Results of stable emulsions abstraction

The experiments were carried out according to the methodology, provided in section 2.2. Here the results of microscopic investigation of emulsion stability and ash, gained from modified heavy fuel oil emulsion combustion, X-ray diffraction patterns are presented. The objective was to find out the microstructures stability and homogeneity treshholds of the prepared emulsion. So, the micropictures of these emulsions were made. As it can be seen from data in Fig. 2.8, the freshly made emulsion has a minor ~ 10 μm droplet size structure and if it is stored at ambient temperature the structure changes only slightly.

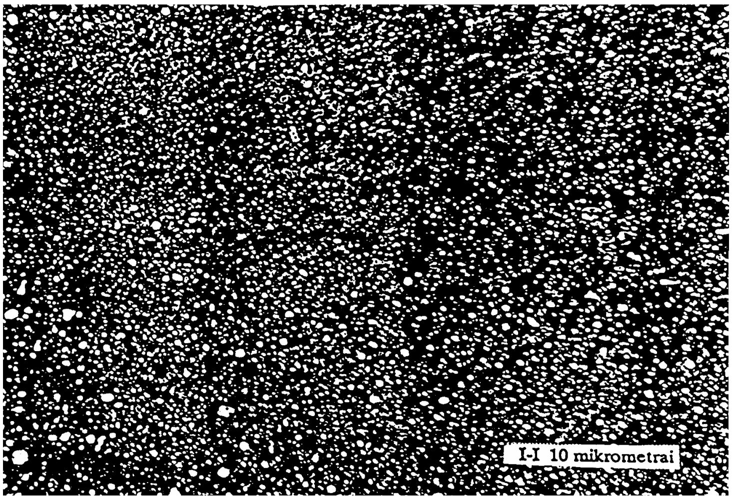


Fig. 2.8 Micropicture (x100) of freshly made heavy fuel oil-glycerol emulsion structure containing 10% of H_2O

As the the emulsion micropictures after 1 month (Fig. 2.9) and after 3 months (Fig. 2.10) shows, a tendency of increase in the heavy fuel oil droplet massiveness.

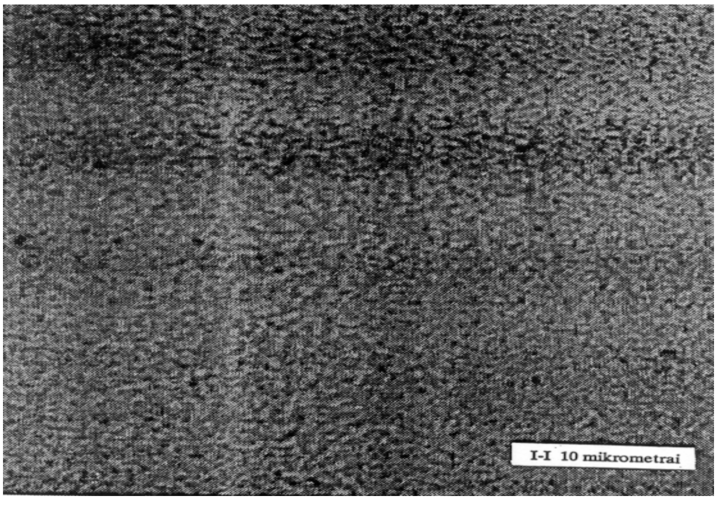


Fig. 2.9 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after one month

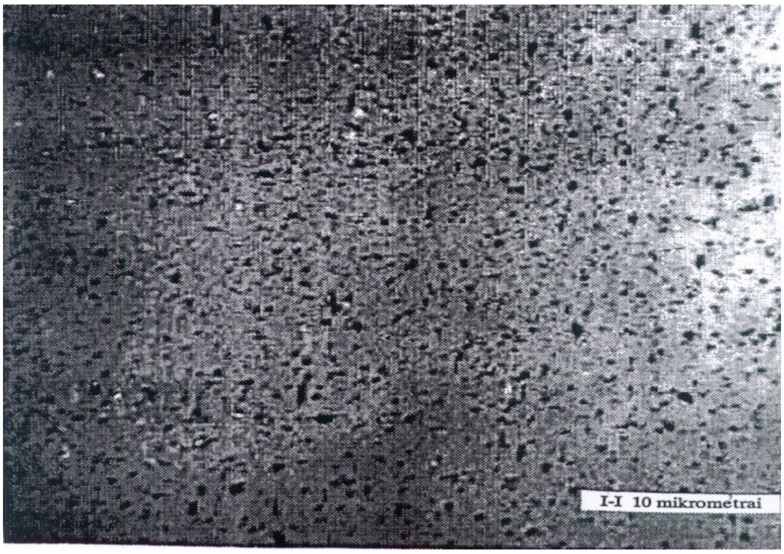


Fig. 2.10 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after 3 months

As we compare the micropictures of freshly made emulsion and after some time, we can draw a conclusion, that the emulsion stability is dependent on time. After some period an aggregation process starts to proceed, and emulsion stability is reduced. The emulsion particles start to combine and mixture looses its homogeneity.

Some prepared emulsions remain stable for weeks or even months, others loose their stability even throughout few hours. However, the emulsion's structure returns to its initial state after passing through the fuel supply pump (Fig. 2.11).

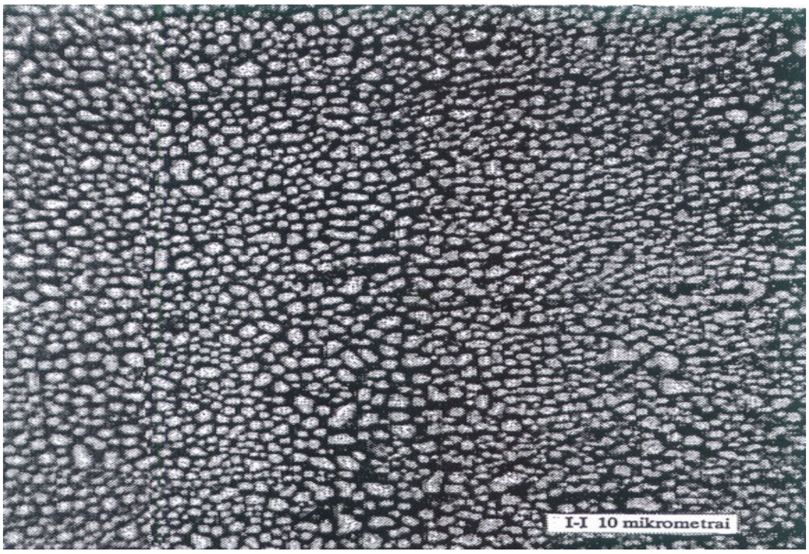


Fig. 2.11 Micropicture (x100) of heavy fuel oil-glycerol emulsion structure after 3 months storage and mechanical activation

For the purpose of comparison, the micropicture of heavy fuel oil with 10 % of H_2O emulsion without additives was also prepared (Fig. 2.12).

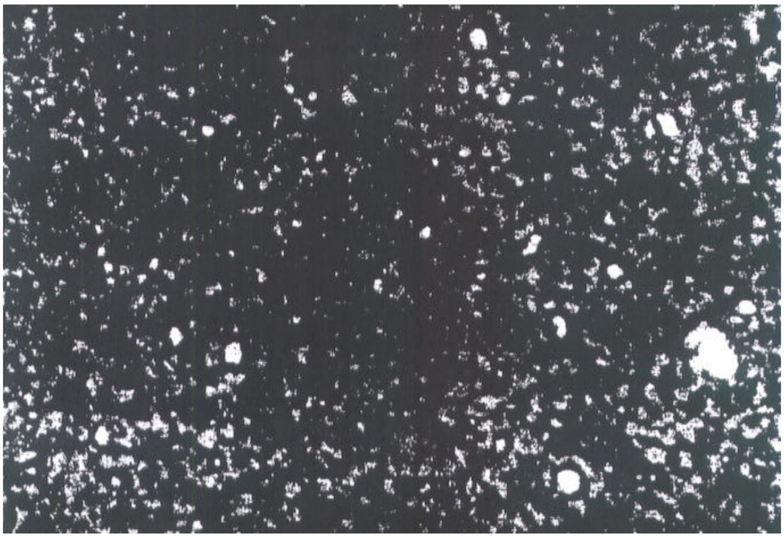


Fig. 2.12 Micropicture (x320) of heavy fuel oil M100 and water emulsion

The homogeneity and stable structure plays a significant role during the combustion process. This parameter is controlled by variables such as the temperature, mechanical agitation, physical properties of compounds, the age of emulsion and etc. When emulsion is stored for some period of time, it looses its homogeneity, water separates from the mixture and emulsion starts to disintegrate. One of the reasons, that heavy fuel oil modified by glycerol is in an emulsion, means that heavy fuel oil and glycerol are not soluble in each other. This leads to the emulsion disintegration in the time scale. The heavy fuel oil-gycerol emulsion incinerates more efficiently in a case of stable and homogenous emulsion structure. The natural tendency of oil and water to separate when mixed must therefore be compensated for by addition of further components to the formulation to aid in keeping the components of the dispersion together. Typically, maintenance of a stable dispersion requires the addition of substantial amounts of emulsion stabilizers and/or emulsifiers. In this case FAIRY, TERGITOL NP9, FELOSAN RG were used as emulsifiers).

Water, present in the glycerol (moisture content <10 %) lowers combustion temperature but improves combustion process due to the oxygen presence in water. When the fuel is in emulsion structure, it has some important advantages in comparison with pure heavy fuel oil combustion. The emulsion is preheated to 65-70°C and is easily supplied to the burner, while pure heavy fuel oil must be preheated to the 90°C before combustion process.

The other factor, which plays important role in the stability of emulsion structure – glycerol purity. During transesterification process, an acid or base is used as a catalyst for the reaction. It is important to use as pure glycerol as possible (~ 85 % purity), without fatty acids and other additives.

Heavy fuel oil-glycerol emulsion ash analysis (combustion in laboratory conditions)

In further experimental researches heavy fuel oil-glycerol emulsion was combusted in laboratory conditions. The purpose of this investigation was to estimate the crystalline structure of obtained ash samples and impurities, present in the emulsion. Using the X-ray examination method ash phasic composition and additives, present in the emulsion, was investigated.

Heavy fuel oil mixture (1:1) (100 g) with water was combusted in a muffle furnace at 850°C for various periods of time. In order to avoid foaming, the temperature was gradually increased, untill reached temperature 850°C. Keeping the samples at a temperature of 850°C for 2.5 hours, a friable, black color residue was obtained, in which unburnt carbon was observed. Further, heating for 2.5 hours at a temperature 850°C, gave a new, and similar to the glass-like melt, which was semi-soluble in water.

Its X-ray diffraction pattern indicated (Fig. 2.13), that it was a soluble sodium salt with a slight potassium salt impurity.

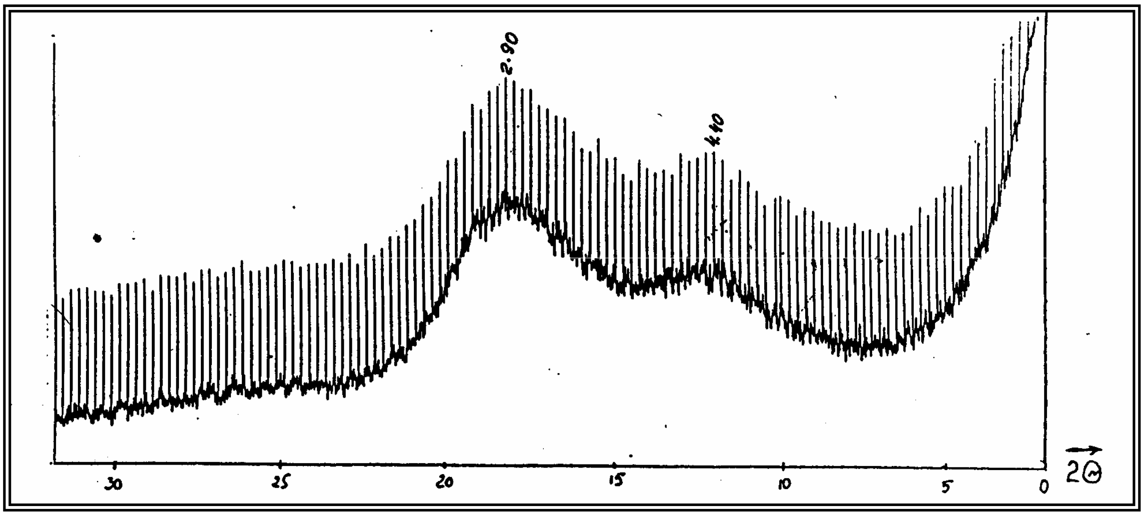


Fig. 2.13 The X-ray diffraction pattern for emulsion ash, obtained in a laboratory

The X-ray diffraction pattern given in Fig. 2.14 represents the situation, when melt was treated with hydrochloric acid. The peaks are recorded and their values are evaluated according to the specialized atlas [63], where the peak values for various chemical compounds are presented. The obtained peak values are expressed as numbers, which are compared to values given in the atlas for the inorganic phases diffraction data sets, and then ash impurities are identified.

Here clearly NaCl peaks can be observed. The observed trace of Na indicates about the catalyst, used in the transesterification process, during the biodiesel production. In this case, the base added was a single reagent NaOH. Also, we can draw a conclusion, that glycerol used for heavy fuel oil-glycerol emulsion properation was insufficiently purified.

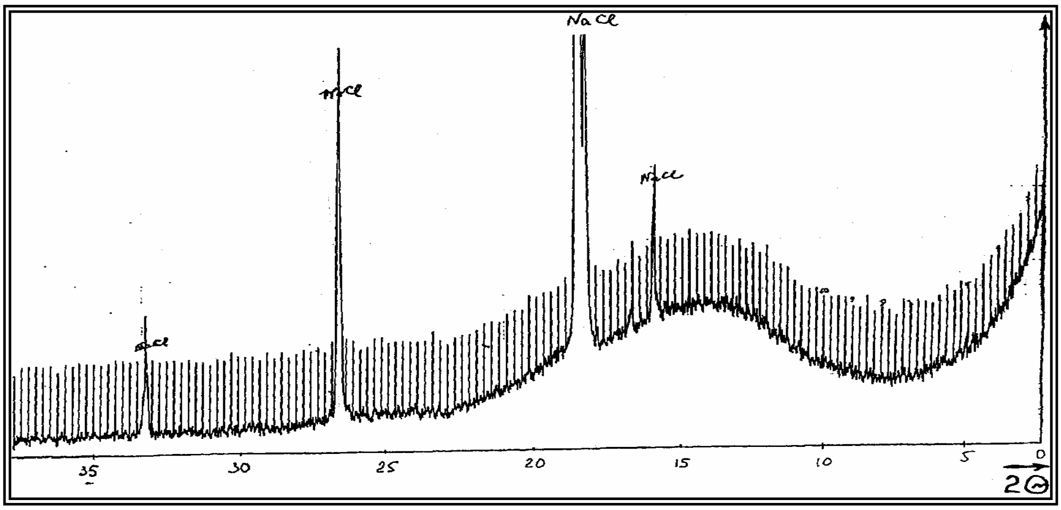


Fig. 2.14 The X-ray diffraction pattern for emulsion ash, obtained in a laboratory and treated with hydrochloric acid

During ash, obtained from emulsion combustion at 600°C for 2.5 hours and slowly cooling till room temperature investigation, it was determined, that the ash crystallizes (Fig. 2.15)

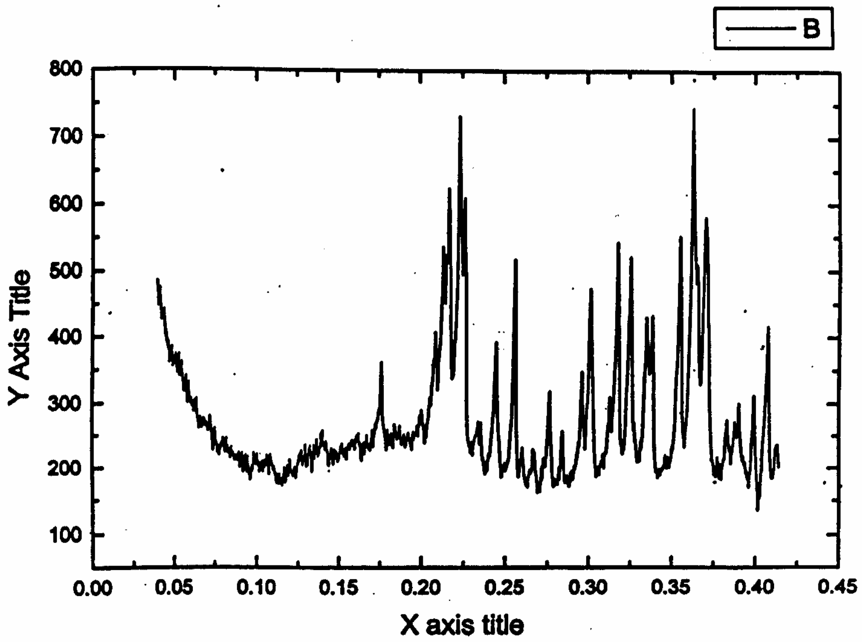


Fig. 2.15 The X-ray diffraction pattern for ash, obtained while calcining HFO-G emulsion at 600°C for 2.5 hours and slowly cooling it

As it can be seen form data in Fig. 2.15 many peak values were obtained, after the ash X-ray diffraction pattern analysis was performed. Further, operating with a computer-based programme PDWin for the identification of crystalline materials, the peaks obtained in the X-ray examination were evaluated and cards match results identified. The computer-based program assigns a possible material to each peak value. PDWin package is used for automation of the powdered radiograms processing and for identification various crystallographic and physical problems of polycrystallic materials [64]. The obtained results of computer-based examination are given in Table 2.5 and Table 2.6.

Table 2.5 Computer-based qualitative composition X-ray diffraction pattern analysis

Sample	**Phases**		
	10-179	**25-1191**	**46-1983**
4.7836	4.78	4.762	4.8
4.6806	4.67	4.691	
4.6415			4.64
4.604	4.6		
4.4726	4.47		
4.4148		4.42	4.42
4.0817	4.07		
3.8983			3.91
3.6124	3.62		3.61
3.5104			3.5
3.3178			3.31
3.1922	3.19		
3.1619		3.16	
3.1452	3.13	3.139	
3.0717	3.07		
2.981	2.981		
2.8169	2.814		
2.7552	2.755		
2.7386	2.74	2.736	
2.6995	2.708	2.695	
2.5019	2.501		
2.4553	2.455		2.456
	4.27	2.59	5.08
	4.05	2.545	4.15
	3.83		3.72
	2.682		2.852
	2.673		2.597
	2.64		2.514

The computer-based composition qualitative X-ray diffraction pattern qualitative analysis was performed according to the following factors:

- comparison range : $\Delta\Theta° = 0.2$;
- number of lines for search = 5 (of 7);
- suitable cards (after Search) – 1142;
- Match filters: g = 0.7, T = 0.5.

Table 2.6 The computer-based qualitative composition X-ray diffraction pattern analysis

#JCPDS	g	T	Chemical formula	Name
1-282	0.851	0.700	(NH4) 2 Cr O4	Ammonium Chromium Ox
1-294	0.869	0.625	C6 H12 N2 04	Ammonium Succinate
1-303	0.818	0.545	C7 H9 N O2	Ammonium Benzoate
1-319	0.748	0.615	C12 H10 Fe O8 S2	Iron Phenosulfonate
1-359	0.768	0.625	V2 O5	Vanadium Oxide
1-434	0.799	0.615	C2 H7 N O2	Ammonium Acetate
1-526	0.749	0.667	H2 Se O3	Selenium Acid Oxide
1-781	0.822	0.600	Mg (H2 P O4) 2	Magnesium Hydrogen P
1-807	0.953	0.833	K2 W O4*2 H2 O	Potassium Tungsten O
1-905	0.710	0.500	Na2 H As O3	Sodium Hydrogen Arse
1-1139	0.756	0.600	K2 C2 O4*H2 O	Potassium Oxalate Hy
2-68	0.900	0.750	Ca O*2 Si O2 * 2 H2	Okenite
2-130	0.829	0.833	Ca C2 O4 * H2 O	Calcium Oxalate Hydr
2-392	0.727	0.750	Ca3 Al10 O18	Calcium Aluminum Oxi
2-551	0.750	0.667	K2 Ca5 (S O4) 6*H	Potassium Calcium Su
2-610	1.000	1.000	Ag8 Ge S6	Argyrodite
2-1304	1.000	1.000	Cu5 Fe S4	Bornite
3-29	0.900	0.750	Ca Si2 O5 * 2 H2 O	Okenite
3-76	0.899	0.615	C4 H4 Ca O4O * H2 O	Cslcium glycolate
3-157	0.726	0.600	C6 H12 O6	SGA-D-Galsctose

As it can be seen from data given in the Table 2.6, the computer – based qualitative match results analysis gives the most probable chemical compounds that may be present in the ash. The match filters g and T indicates the accuracy of a result. The best match result for g and T match filters is 1. However, in this case, the match results wih unit value 1 indicates the compounds, which can hardly represent any of components that may be present in the heavy fuel oil-glycerol emulsion. After the computer-based qualitative X-ray diffraction pattern analysis (Table 2.5 and Table 2.6) and match results in the phases 10-179 ($Na_5P_3O_{10}$), 25-1191 ($BaFe_2O_4$) and 46-1983

($C_6H_8O_6$) it was estimated, that compound of the following composition – $Na_5P_3O_{10}$ - crystallizes in this case.

Heavy fuel oil-glycerol emulsion ash analysis (combustion in thermal oxidizer system)

The heavy fuel oil-glycerol emulsion (1:1) with 10% of water was also incinerated in the thermal oxidizing boiler in JSC "Rietavo veterinarinė sanitarija". During the combustion process the exhausted ash was captured and investigated. As it can be seen from Fig. 2.16, the ash X-ray analysis indicated presence of Na and K compounds, but due to the small peaks they are not significant.

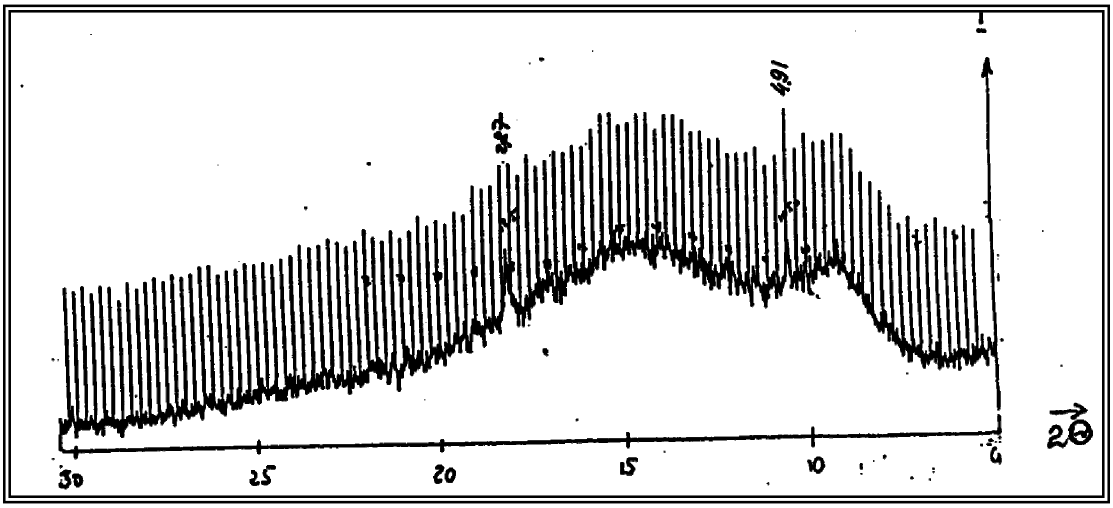


Fig. 2.16 The heavy fuel oil-glycerol emulsion (1:1) ash X-ray diffraction pattern

The observed traces of Na and K indicate about the catalyst, used in the transesterification process, during the biodiesel production. In this case, the base added as a single reagent was NaOH or KOH. Also, we can draw a conclusion, that glycerol used for heavy fuel oil-glycerol emulsion preparation was of relatively high purity, thus the X – ray diffraction indicates non-significant peaks due to the small amounts of additives.

2.3.1 The crude glycerol pyrolysis and obtained products analysis

According to the information, proposed in literature and with reference to worldwide experimental researches results, it is known that glycerol pyrolysis process gives various combustion products. The objective of this section was to identify the compounds, especially hazardous substances, that are formed during glycerol pyrolysis process, to determine the dependency of obtained chemical compounds formation temperature and to estimate temperature necessary for the complete combustion of these compounds.

The investigation of crude glycerol pyrolysis was performed in a laboratory of a JSC “Rapsoila”. Glycerol 50 ml per minute was injected to the heated quartz tube, filled-up with 3-4 mm quartz bits. The obtained liquid was analysed using LKM-8 chromotograph and flame ionization detector. The column was filled-up with adsorbent „Nukol“ (L=15, ∅ - 0,53 mm). The adsorbent “Nukol” is the aluminium oxide with a capability to adsorb substances in a compound and then comparing with a standard to identify those substances. Helium was used as a carrier gas. Water and hydrogen from hydrogen generator was used for the ignition of flame ionization detector. The injector and detector temperatures were 250°C and 330°C respectively. The methanol estimation was performed in the following way – the initial temperature 30°C, time-exposure – 5 min. Temperature rise speed 50°C/min, final temperature - 190°C. Data for glycerol are the following- the initial temperature 120°C, temperature rise speed 8°C/min, final temperature - 190°C. The obtained results are given in the Table 2.7.

Table 2.7 The compound elements of glycerol liquid product pyrolysis

Pyrolysis at 650°C	**Pyrolysis at 750°C**	**Pyrolysis at 800°C**
Formaldehyde	Formaldehyde	Formaldehyde
Acetaldehyde	Acetaldehyde	Acetone
Propanol	Propanol	Methanol
Acetone	Acetone	Ethanol
Acetic	Acetic	Water (97 wt %)
Acroleine	Acroleine	Acetic
Methanol	Methanol	
Ethanol	Ethanol	
Water(38 wt %)	Water (74 wt %)	
Alilacohol		
Propanolic acid	Propanolic acid	
Glycerol	Glycerol	

As we can see from data given in the Table 2.7, increasing pyrolysis temperature from 650°C till 800°C, in a liquid phase (condensate) number of chemical compounds (components) decreases from 62 % at 650°C till 3 % at 800°C. So, we can draw a conclusion, that increasing temperature and extending duration of glycerol combustion, we can obtain CO_2 and H_2O, and thus avoid some undesirable chemical compounds. In this experiment, the maximum reached temeperature was 800°C. It is insufficient for the complete combustion of chemical compounds, formed durng glycerol pyrolysis. So, it follows that the temperature should be increased up to 1000°C to obtain complete combustion of glycerol.

Results of industrial investigations carried out during the heavy fuel oil-glycerol emulsion combustion in the JSC "Rietavo veterinarinė sanitarija" thermal oxidizing boiler „UMISA - CR/11,9 (13) "

An experimental investigation was carried out in a thermal oxidizer boiler in Rietavas city organic waste utilization plant in order to evaluate the emissions released during combustion of two different fuels, heavy fuel oil (HFO) with high content of sulphur (~ 2 %) and heavy fuel oil - glycerol emulsion.

In this section, the analysis of experimental investigations of those fuels combustion and released air pollutants - CO, NO_x, SO_2 and particulate matter concentrations in flue gas measurements according to the methodology described in section 2.2 were carried out. The measured and recorded data are given in tables and diagrams presented hereinafter. The flue gas measurements were conducted by an independent audit company – JSC "Pramoninis servisas" and VGTU Institute of Thermal Insulation project team. The experimental emission concentrations are compared to the concentration MAC values given in the normative regulations or derived (for HFO-G emulsion).

The results for the direct measurements of combustion flue gas represents the mean of ~ 8-10 measurements conducted in the flue gas flow for each pollutant, except for particulate matter – few measurements were carried out since each measurement requires conditionally much time to obtain each concentration value of this pollutant. The concentration averages are taken into account to minimize imprecise view from random high values obtained in some measurements. So the mean values are used generally to minimize the effect of the high values, which are observed occasionally, due to some restrictions in combustion process, since an emission of the pollutants from combustion source is dependent on characteristics of the boilers, fuel and operational conditions, including temperature, pressure, feed rate, etc [65].

Emissions from heavy fuel oil combustion mainly depend on the following parameters: (1) grade of the fuel and sulphur content; (2) composition of the fuel; (3) type of boiler; (4) size of boiler; (5) firing and loading practices used; (6) level of equipment maintenance, etc.

To evaluate emissions under comparable conditions, the results were normalized at 3 % oxygen. Foremost, the initial investigations for heavy fuel oil combustion process were also performed, to obtain baseline level for further analysis and measured results evaluation and comparison to the results of emulsion combustion.

It is important to give a notice, that heavy oils are usually composed mostly of carbon (86 % wt), hydrogen (11 % wt), and sulphur (currently ranging between 0.18 and 4.36 % with an average about 2 % wt.). It also contains other impurities such as ash, metals and water.

The measurement results for the concentrations of CO in the exhaust flue gas are given in Table 2.8 and represented graphically in Fig. 2.17

Table 2.8 The measured concentration of CO emission in flue gas from heavy fuel oil combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	Limit value, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	266.0	highly sulphurous heavy fuel oil	CO	ppm	electrochemical	25	8.8	3.0	46.2	16.4	5.56	500
2.	269.0					7	8.6		12.8			
3.	270.0					10	7.4		16.6			
4.	268.0					8	7.8		13.6			
5.	267.2					9	8.1		15.8			
6.	265.4					6	7.3		9.9			
7.	264.1					5	7.6		8.5			
8.	265.4					5	6.5		7.8			

The heavy fuel oil (~ 2 % sulphur content) combustion emissions measurements were carried out in normal operational conditions. Measurements were conducted using electrochemical measurement method. As it is given in Table 2.8 and represented in Fig. 2.17, the exhaust flue gas temperature during combustion period varied in a range of 264.1 – 269.0°C. Meanwhile, the operational temperature in boiler is ~ 800 - 850°C with perceptible fluctuations. The measured of CO concentrations from heavy fuel oil combustion process are substantially smaller (measured average value 16.4 mg/Nm^3) than their established MAC value (500 mg/Nm^3). The low CO values could be attributed to the combustion at high temperature.

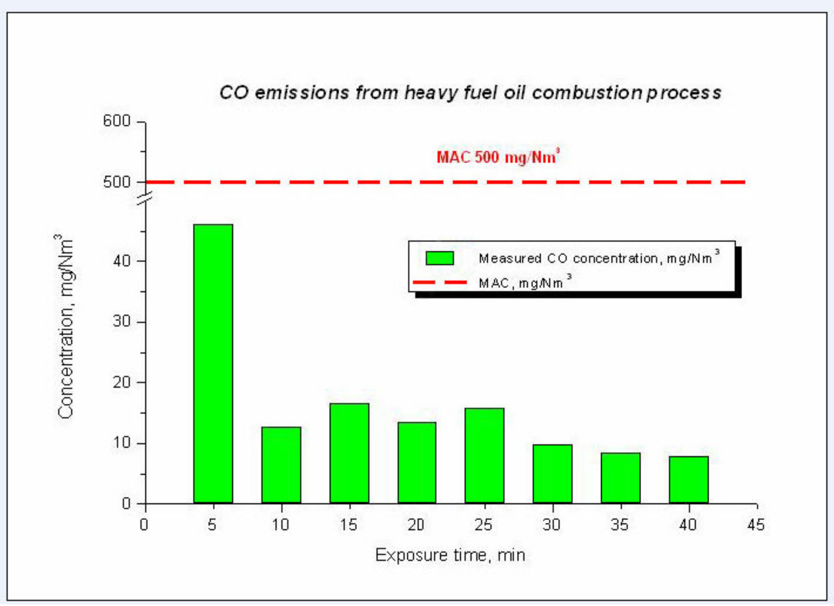


Fig. 2.17 CO emissions from heavy fuel oil combustion process

NO_x concentrations measurements in the exhaust flue gas are given in Table 2.9 and represented graphically in Fig. 2.18.

Table 2.9 The measured concentration of NO_x emission in flue gas from heavy fuel oil combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	Limit value, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	266.0	highly sulphurous heavy fuel oil	NO_x	ppm	electrochemical	202	8.8	3.0	610.8	582.2	5.56	650
2.	269.0					217	8.6		646.0			
3.	270.0					218	7.4		591.7			
4.	268.0					220	7.8		615.2			
5.	267.2					209	8.1		597.8			
6.	265.4					210	7.3		565.7			
7.	264.1					184	7.6		506.6			
8.	265.4					206	6.5		524.1			

The NO_x emissions from highly sulphurous heavy fuel oil combustion were measured using electrochemical measurement method. The exhaust flue gas temperature varied in the same range as for carbon monoxide emissions.

As it can be seen from data, given in the Table 2.9, the measured average NO_x concentration (582.2 mg/Nm^3) was similar to the MAC value, which is 650 mg/Nm^3 for NO_x. Either, in some measurement points concentration values were extremely close the MAC values. The peak value (646.0 mg/Nm^3) is observed along with a highest flue gas temperature (269°C), and practically approached the MAC value.

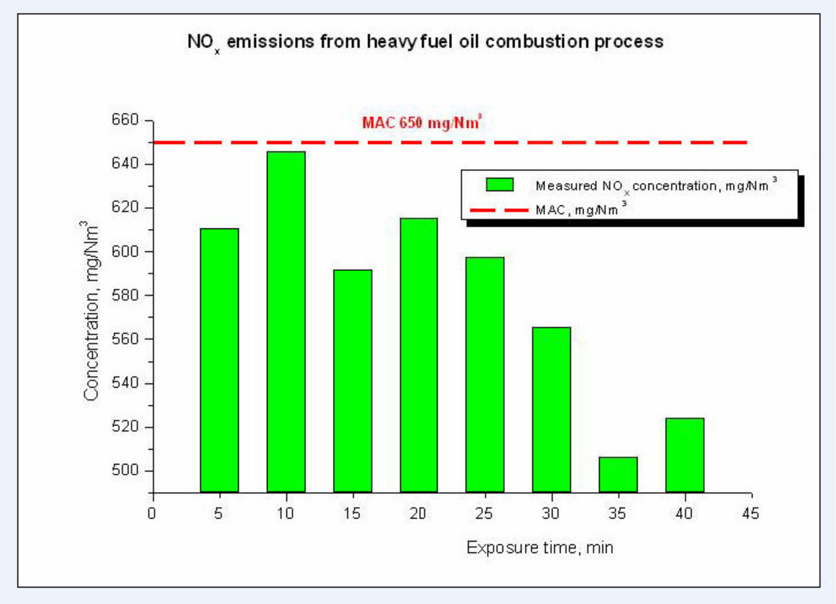


Fig. 2.18 NO_x emissions from heavy fuel oil combustion process

The SO_2 concentrations in the exhaust flue gas also were measured and recorded in Table 2.10 and represented graphically in Fig. 2.19.

Table 2.10 The measured concentration of SO_2 emission in flue gas from heavy fuel oil combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	MAC, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	266.0	highly sulphurous heavy fuel oil	SO_2	ppm	electrochemical	741	8.8	3.0	3202.5	3139.6	5.56	1700
2.	269.0					676	8.6		2875.9			
3.	270.0					709	7.4		2751.1			
4.	268.0					847	7.8		3386.6			
5.	267.2					818	8.1		3342.3			
6.	265.4					778	7.3		2894.8			
7.	264.1					805	7.6		3167.2			
8.	265.4					934	6.5		3396.4			

The obtainable SO_2 emission concentrations from highly sulphurous HFO combustion are almost entirely dependent on the sulphur content in the HFO. In this case, heavy fuel oil with a sulphur content of ~ 2 % by mass was operational. This fact is reflected by the obtained emission concentration which is indicated as extremely exceeding the MAC value. The average measured SO_2 value is 3139.6 mg/Nm^3, meanwhile SO_2 MAC is defined as 1700 mg/Nm^3 (according to EU Directive 1999/32EC and LAND 43-2001 „Norms for the exhaust of pollutants from large fuel burning equipment").

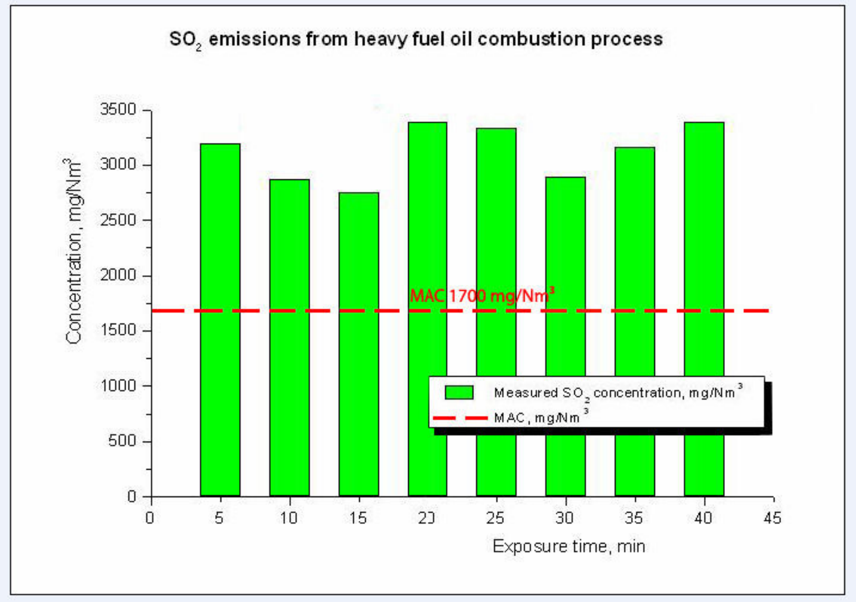


Fig. 2.19 SO_2 emissions from heavy fuel oil combustion process

The objective of this work is to lower SO_2 emission concentrations up to the allowable values and even more.

The measurement results for the concentrations of particulate matter in the exhaust flue gas are given in Table 2.11 and represented graphically in Fig. 2.20.

Table 2.11 The measured concentration of particulate matter emission in flue gas from heavy fuel oil combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	MAC, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	270.0	highly sulphurous heavy fuel oil	Particulate matter	mg/Nm^3	weight	87.7	8.4	3.0	125.3	120.4	5.56	200
2.	270.0					130.3	7.7		176.3			
3.	264.0					80.2	7.4		106.1			
4.	264.0					55.1	7.6		74.0			

The particulate matter emissions from heavy fuel oil combustion process are related to the oil sulphur content, because low sulphur oil, exhibits substantially lower viscosity and reduced asphaltene, ash, and sulphur contents, which results in better atomization and more complete combustion, reducing CO and particulate matter emissions.

The obtained PM emissions concentrations from highly sulphurous heavy fuel oil combustion were measured using weight method. As it is given in Table 2.11 and represented in Fig. 2.20, the exhaust flue gas temperature during combustion period varied in a range of 264.0 – 270.0°C, and remained sufficiently stable. The measured average particulate matter does not exceed the MAC value, thus the peak value (176.3 mg/Nm^3) alerts about possible PM values overdrafts.

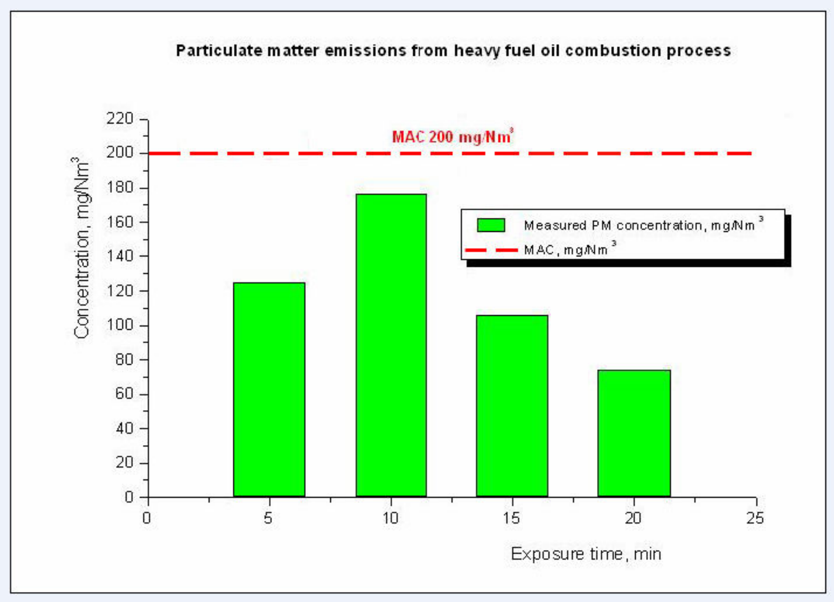


Fig. 2.20 Particulate matter emissions from heavy fuel oil combustion process

With a purpose to obtain MAC values for heavy fuel oil – glycerol emulsion, the calculations for heavy fuel oil modified by glycerol additive (1:1) concentrations were conducted, applying the known MAC values for biofuel (in our case wood as biofuel MAC values are taken into account) and heavy fuel oil. The calculations were perfomed when taking the arithmetic average of concentrations for heavy fuel oil and biofuel. Hereinafter, measurement results for heavy fuel oil – glycerol emulsion (1:1) combustion process are presented.

The experimental investigations for the heavy fuel oil-glycerol combustion and flue gas measurements in stack were conducted repeatedly. The heavy fuel oil-glycerol emulsion (1:1) with 10 % of H_2O, which is present in glycerol, was combusted in JSC "Rietavo veterinarinė sanitarija" thermal oxidizing boiler „UMISA -CR/11,9 (13) ". The obtained results are given hereinafter.

The measurement results for the concentrations of CO in the exhaust flue gas of heavy fuel modified by glycerol additive are given in Table 2.12 and represented graphically in Fig. 2.21.

Table 2.12 The measured concentration of CO emission in flue gas from heavy fuel oil-glycerol emulsion combustion process

No.	**Temperature, °C**	**Fuel type**	**Pollutant type**	**Units**	**Measurement method**	**Measured concentration**	**Measured O_2 concentration, %**	**Standard O_2 concentration, %**	**Converted concentration, mg/Nm^3**	**Converted average concentration, mg/Nm^3**	**Amount of exhaust emissions, Nm^3/s**	**MAC, mg/Nm^3**
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
2.	190.8	**modified heavy fuel oil** (heavy fuel oil-glycerol emulsion, mix ratio 1:1)	CO	ppm	electrochemical	824	16.5	3.0	4120	1758.1	4.17	**2250**
3.	209.0					54	15.6		225			
4.	210.1					93	15.6		387.7			
5.	210.5					55	15.4		221.1			
6.	212.1					50	15.3		197.4			
7.	209.9					477	15.5		1951.5			
9.	230.6					791	13.6		2405.2			
10.	235.0					622	13.3		1817.5			
11.	239.4					378	12.7		1024.7			
12.	234.3					930	17.0		5231.3			

The presence of CO in the exhaust flue gas from combustion system results principally from incomplete fuel combustion. Measurements were conducted using electrochemical measurement method. As it is given in Table 2.12 and represented in Fig. 2.21, the exhaust flue gas temperature during combustion period varied in a range of 190.8 – 239.4°C. The obtained CO concentrations from heavy fuel oil – glycerol emulsion combustion process fluctuated drastically during the measurements.

The observed CO concentrations varied in a wide range 197.4 – 5231.3 mg/Nm^3. This fact could be attributed to significant fluctuations in operational temperature in thermal boiler, as well as possible lack of supplied oxygen during certain moments in combustion process. Thus, the evaluated concentration average value 1758.1 mg/Nm^3 seems to be much lower than MAC value 2250 mg/Nm^3, though separate CO concentration measurements give high peaks, in the beginning of combustion (when the system is warming-up) and at the end due to some technical obstacles. It means that stable and sufficient temperature plays a siginificant role in complete emulsion combustion process, along with sufficient oxygen availability.

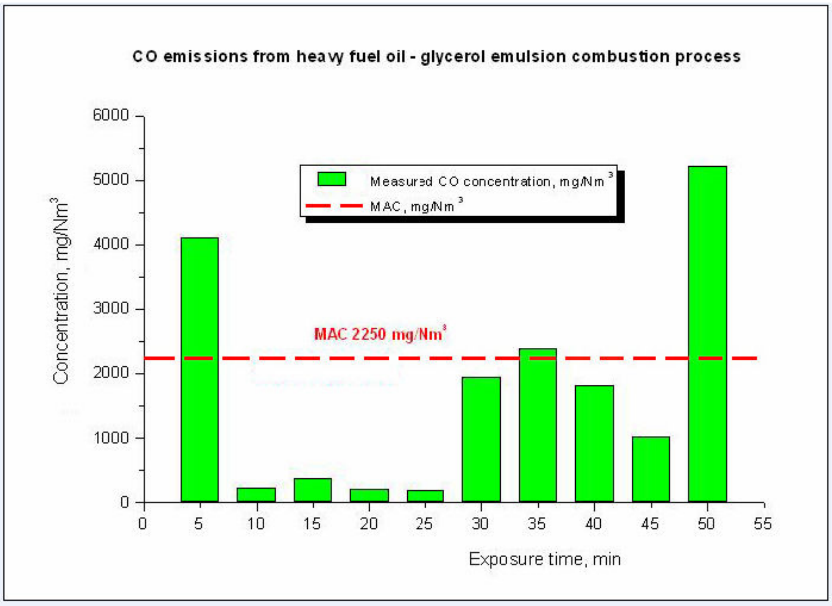


Fig. 2.21 CO emissions from heavy fuel oil – glycerol emulsion combustion process

NO_x concentrations measurements in the exhaust flue gas are given in Table 2.13 and represented graphically in Fig. 2.22.

Table 2.13 The measured concentration of NO_x emission in flue gas from heavy fuel oil-glycerol emulsion combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	MAC, mg/Nm^3
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1.	188.0	**modified heavy fuel oil** (heavy fuel oil-glycerol emulsion, mix ratio 1:1)	NOx	ppm	electrochemical	57	16.3	3.0	447.7	618.8	4.17	700
2.	190.8					57	16.5		467.6			
3.	209.0					83	15.6		567.3			
4.	210.1					84	15.6		574.0			
5.	210.5					85	15.4		560.3			
6.	212.1					90	15.3		582.6			
7.	209.9					67	15.5		449.7			
8.	216.3					115	15.2		731.8			
11.	239.4					203	12.7		902.6			
12.	234.3					98	17.0		904.1			

One of the most essential moments in this research is the observed concentrations of NO_x emission in flue gas. Data in the literature emphasizes the possible increment in NO_x concentrations during biodiesel combustion. The aim of this analysis is to provide heavy fuel oil – glycerol emulsion combustion process and to measure obtained NO_x concentrations, evaluate the observed results and to compare with the propositions given in literature.

Oxides of nitrogen (NO_x) formed in combustion processes are due to either to thermal fixation of atmospheric nitrogen in the combustion air ("thermal NO_x"), or to the conversion of chemically bond nitrogen in the fuel (‘fuel NO_x”). The term NO_x refers to the composite of nitric oxide (NO) and nitrogen dioxide (NO_2). Experimental measurements of thermal NO_x formation have shown that NO_x concentration is exponentially dependent on temperature and the residence time. Thus the formation of thermal NO_x is affected by four factors: (1) peak temperature, (2) fuel nitrogen concentration, (3) oxygen concentration, and (4) time of exposure at peak temperature.

The observed NO_x concentrations varied from 447.7 mg/Nm^3 till 904.1 mg/Nm^3. Thus some measured concentrations exceeded MAC value, but average concentration observed lower than the estimated MAC. The average measured NO_x value was 618.8 mg/Nm^3, when calculated MAC for NO_x in emulsion flue gas is 700 mg/Nm^3. However, the concentration increase for NO_x is observed due to technical obstacles and too low temperature in boiler at the end of experiment.

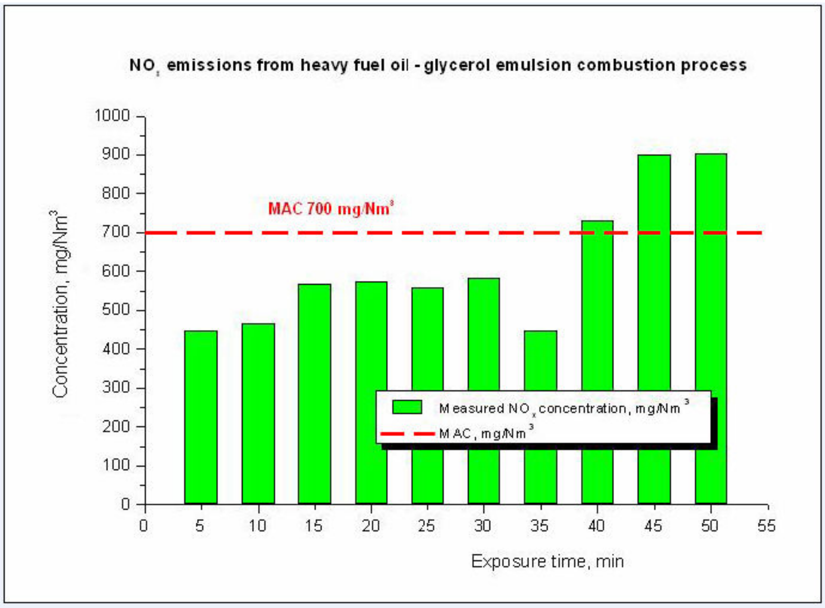


Fig. 2.22 NO_x emissions from heavy fuel oil – glycerol emulsion combustion process

In fossil fuel combustion fuel nitrogen content and combustion zone temperatures are main factors in the production of NO_x. The observed increase in NO_x concentrations may be due to the high temperature generated in the fairly complete combustion process on account of adequate presence of oxygen in the fuel.

The SO_2 concentrations in the exhaust flue gas also were measured and recorded in Table 2.14 and represented graphically in Fig. 2.23.

Table 2.14 The measured concentration of SO_2 emission in flue gas from heavy fuel oil-glycerol emulsion combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	MAC, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	188.0	**modified heavy fuel oil** (heavy fuel oil-glycerol emulsion, mix ratio 1:1)	SO_2	ppm	electrochemical	61	16.3	3.0	684.4	727.1	4.17	1700
2.	190.8					63	16.5		738.4			
3.	209.0					99	15.6		967.0			
4.	210.1					102	15.6		996.3			
5.	210.5					104	15.4		979.4			
6.	212.1					106	15.3		980.8			
7.	209.9					27	15.5		258.9			
8.	216.3					56	15.2		509.3			
9.	230.6					80	13.6		570.2			
10.	235.0					97	13.3		664.4			
11.	239.4					107	12.7		679.9			
12.	234.3					96	17.0		1265.9			

Sulphur oxides (SO_x) emissions are generated during oil combustion from the oxidation of sulphur contained in the fuel. The emissions of SO_x from conventional combustion systems are predominantly in the form of SO_2. Uncontrolled SO_x emissions are almost entirely dependent on the sulphur content of the fuel and are not affected by boiler size, burner design, or grade of fuel being fired. On average, more than 95 % of the fuel sulphur is converted to SO_2, about 1 to 5 % is further oxidized to sulphur trioxide (SO_3), and 1 to 3 % is emitted as sulphate particulate. SO_3 readily reacts with water vapor (both in the atmosphere and in flue gases) to form a sulphuric acid mist.

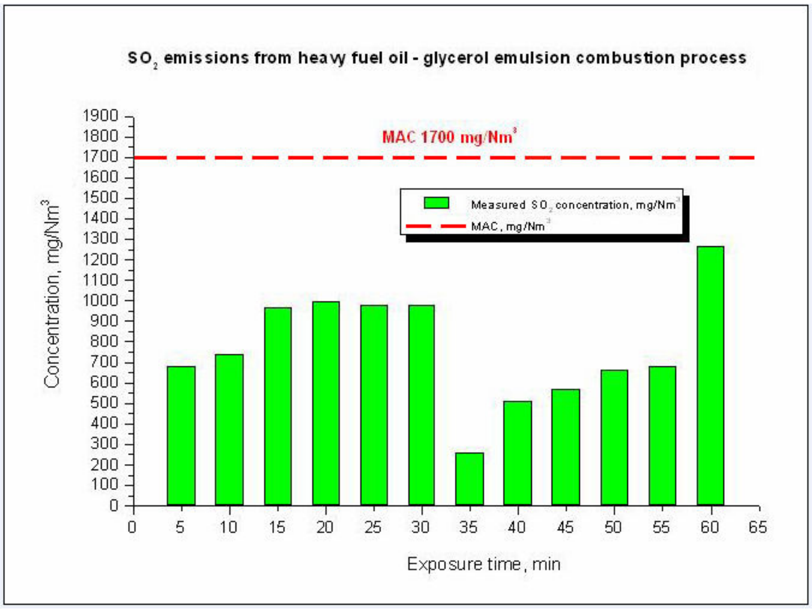


Fig. 2.23 SO_2 emissions from heavy fuel oil – glycerol emulsion combustion process

The observed SO_2 emission concentrations in the exhaust flue gas from emulsion combustion are the most importatant in this investigation, thus the main objective of this reserach is reduction in SO_2 emissions to fulfill Lithuanian and EU normative regulations, along with a cost-effective glycerol utilization. A substantial positive effect of the fuel sulphur dioxide emission concentrations is noted. The observed results showed that heavy fuel oil – glycerol emulsions gives a significant decrease in SO_2 - measured average concentration was only 727.1 mg/Nm^3, while for pure heavy fuel oil it is 3-4 times higher. This would allow easily meet the requirements for SO_2 MAC 1700 mg/Nm^3. So, it is true to say, that the exhaust emissions of sulphur oxides and sulphates from emulsion are essentially eliminated compared to heavy fuel oil SO_2 concentrations.

The measurement results for the concentrations of particulate matter in the exhaust flue gas of heavy fuel modified by glycerol additive are given in Table 2.15 and represented graphically in Fig. 2.24.

Table 2.15 The measured concentration of particulate matter emission in flue gas from heavy fuel oil-glycerol emulsion combustion process

No.	Temperature, °C	Fuel type	Pollutant type	Units	Measurement method	Measured concentration	Measured O_2 concentration, %	Standard O_2 concentration, %	Converted concentration, mg/Nm^3	Converted average concentration, mg/Nm^3	Amount of exhaust emissions, Nm^3/s	Limit value, mg/Nm^3
1	2	3	4	5	6	7	8	9	10	11	12	13
1.	210.1	**modified heavy fuel oil** (heavy fuel oil-glycerol emulsion, mix ratio 1:1)	Particulate matter	mg/Nm^3	weight	61	254.3	3.0	847.7	740.2	4.17	800
2.	212.0					63	231.8		732.0			
3.	230.0					99	274.2		641.0			

In general particulate matter emissions depend on the completeness of combustion as well as on the heavy fuel oil ash content. In this case, the heavy fuel oil with ash content max 0.14 wt % according to the GOST 1461 was operational.

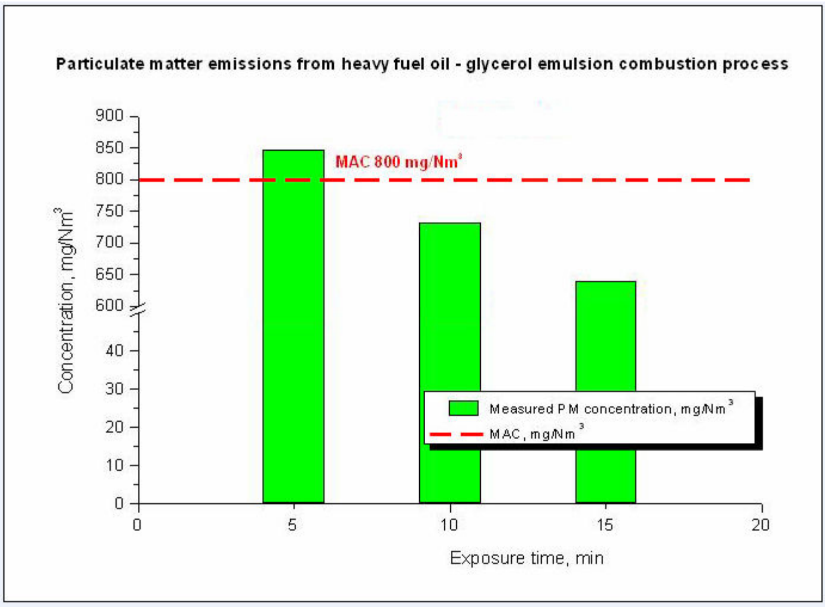


Fig. 2.24 Particulate matter emissions from heavy fuel oil – glycerol combustion process

Naturally, the particulate matter emissions from heavy fuel oil – glycerol emulsion combustion are related to the heavy fuel oil sulphur content. PM mass concentrations increases with an increment in fuel sulphur content. In our case, heavy fuel oil sulphur content corresponds to a high sulphurity, but due to the glycerol presence in the emulsion, sulphurity problem seems to be solved or at least mitigated to the acceptable rates. The reduction of fuel sulphur content could reduce particulate emissions from emulsion incineration if the equipment is properly maintained and operated.

The ash content of the samples was analyzed by determining the combustion residue at 850°C. Results are expressed in terms of filterable PM mass in mg/Nm^3 dry flue gas at standard temperature and pressure. As it is given in Table 2.15 and represented in Fig. 2.24, the measured average particulate matter 740.2 mg/Nm^3 does not exceed the MAC value, thus the peak value (847.7 mg/Nm^3) alerts about possible incomplete combustion during some combustion exposure intervals. Eventually, particulate matter MAC values are not exceeded.

Summary and comparison of results from heavy fuel oil and hevay fuel oil-glycerol emulsion (1:1) combustion process

The experimental investigations of heavy fuel oil – glycerol emulsion combustion were carried out at the JSC “Rietavo veterinarinė sanitarija” in thermal oxidizing boiler in September - November 2005 repeatedly. Few combustion proceses were carried out, because of the insufficient amount of the emulsion only 550°C temperature was reached during the first test combustion investigation in September 2005, meanwhile the operational temperature of boiler is 850°C and the recommended temperature for glycerol combustion ~ 1000°C. Consequently, the repeated experiment was carried out in November 2005.

The summary and comparison of the measured emission concentrations in the exhaust flue gas from heavy fuel oil and heavy fuel oil – glycerol emulsion (1:1) combustion process are given in Table 2.16 and represented graphically in Fig. 2.25 and Fig. 2.26 hereinafter.

Table 2.16 Summary of pollutants concentrations measurement results and comparison with MAC values

No.	Pollutant	MAC for HFO, mg/Nm^3	MAC for biofuels*, mg/Nm^3	HFO-G emulsion (1:1) MAC, mg/Nm^3	Measured HFO concentration mg/Nm^3,	Measured HFO-G emulsion (1:1) concentration, mg/Nm^3
1	Carbon monoxide (CO)	500	4000	2250	16.4	1758.1**
2	Nitrogen oxides (NO_x)	650	750	700	582.2	618.8
3	Sulphur dioxide (SO_2)	1700	1700	1700	3139.6	727.1
4	Particulate matter (high-density biofuel wood)	-	800	800	120.4	740.2

* Goverment resolution No. 486 (28 September, 2001 “Regarding exhaust pollutant emission and large fuel burning equipment norms and exhaust pollutants from fuel burning equipment norms LAND 43-2001 establishement” (“Valstybės žinios”, 2001, No. 88-3100; supplement 2001, No. 101-3826). Here MAC values are considered for wood as solid biofuel.

** This is more than two times less than the norm for burning solid biofuel. So, the emissions into the atmosphere should be limited according to PM levels.

The heavy fuel oil and prepared heavy fuel oil - glycerol emulsion (1:1) combustion was carried out in the thermal oxidizing boiler which operating temperature is ~ 850°C, with few fluctuations due to technical obstacles. As the investigation results indicated, temperature is of the high importance in the combustion process completeness.

As we can see from data given in Fig. 2.25, the highly sulphurous heavy fuel oil combustion gives the extremely high concentrations of SO_2. The measured CO, NO_x and particulate matter emission concentration values in the exhaust flue gas during this investigation does not exceed MAC values, thus the obtained some concentration peak values for NO_x (646.0 mg/Nm^3) and particulate matter (176.3 mg/Nm^3) alerts about possible admissible concentration values overdrafts. The relatively low CO values (average concentration 16.4 mg/Nm^3) could be attributed to the combustion at high temperature. The observed average SO_2 concentration value is 3139.6 mg/Nm^3, meanwhile SO_2 MAC value is 1700 mg/Nm^3. Thus, the obtained emission concentration significantly exceeds admissible value, due to high sulphur content by mass in heavy fuel oil operational in this investigation.

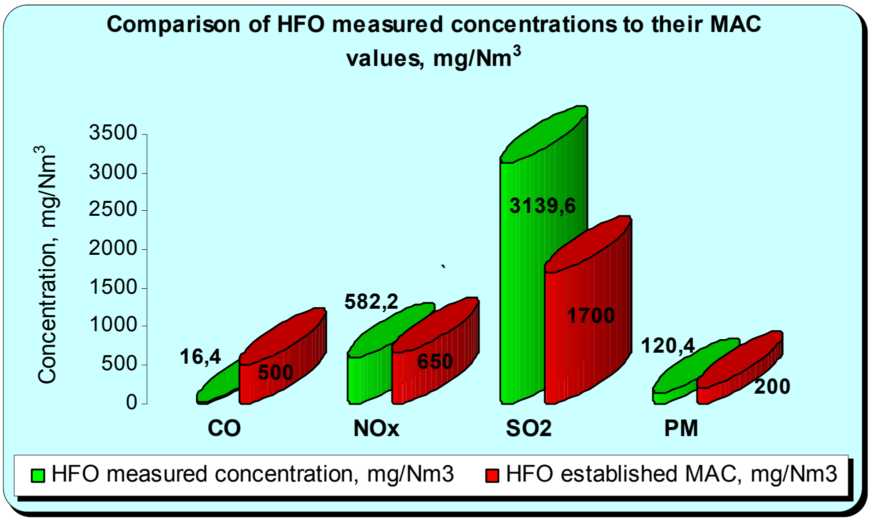


Fig. 2.25 Comparison of HFO measured concentrations to their MAC values, mg/Nm^3

In general, it should be particularly emphasized that the observed emission concentrations for heavy fuel oil – glycerol emulsion combustion process indicate a significant decrease in SO_2 emission amount – the measured average concentration was only 727.1 mg/Nm^3, while for pure heavy fuel oil it is 3-4 times higher (Fig. 2.26). This would allow readily meet the requirements for SO_2 MAC 1700 mg/Nm^3. So, it is true to say, that the exhaust emissions of sulphur oxides and sulphates from emulsion are essentially eliminated compared to heavy fuel oil SO_2 concentrations.

Still, it is observed the increment of nitrogen oxides emission concentration during heavy fuel oil – glycerol emulsion combustion process. The average measured NO_x concentration value is 618.8 mg/Nm^3, whereas the evaluated MAC value for NO_x in emulsion combustion flue gas is 700 mg/Nm^3. Thus, the MAC value is not exceeded, in some measurement points concentrations overdrafts are indicated. However, the concentration increase for NO_x up to10 % is observed due to technical obstacles and too low and shifting temperature in boiler at the end of the experiment. The measured average concentrations for CO and particulate matter do not exceed their estimated maximum admissible values. The measured average particulate matter concentration 740.2 mg/Nm^3 does not exceed the MAC value, thus the peak value (847.7 mg/Nm^3) alerts about possible incomplete combustion during some combustion exposure intervals. The evaluated CO concentration average value 1758.1 mg/Nm^3 seems to be much lower than MAC value 2250 mg/Nm^3, though separate CO concentration measurements give higher peaks due to some technical obstacles.

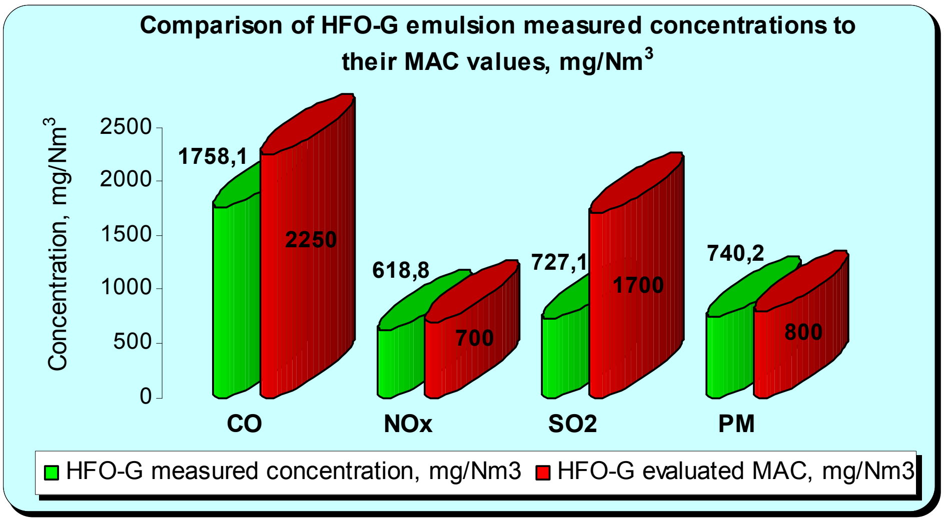


Fig. 2.26 Comparison of HFO-G emulsion measured concentrations to their MAC values, mg/Nm^3

Finally, based on the accomplished investigation results, the heavy fuel oil modified by glycerol additive technological regulation was prepared (Annex 5). This regulation provides technical data for the heavy fuel oil – glycerol emulsion preparation and combustion conditions. The technical conditions could be adjusted considering boiler construction, operational burner types and boiler capacity.

2.4. GLYCEROL AS SULPHUR MODIFIER (PLASTICIZER)

Some experiments were carried out to examine the possibility to use glycerol for sulphur plastification along with the main heavy fuel oil emulsion combustion experimental investigations. The need to plasticize sulphur for use to replace cement was recognized during the 1930s. Many types of organics have been employed in an effort to accomplish production of durable cements [67].

Sulphur has been employed for various types of chemical uses. The significant potential uses that utilize the unique physical properties of sulphur, sometimes requires the addition of plasticizer. Sulphur paint can be used as a material that offers exceptional chemical and water resistant properties. The formulation used to paint the walls should consist of 97 % of sulphur, 1 % plasticizer, 1 % chopped strand glass fibers and the remainder decorative materials. These ingredients are heated in an open vessel to a temperature just above the melting point of sulphur and spread in a thin layer on a surface of concrete blocks.

Some experiments with a purpose to investigate the use of glycerol as sulphur plasticizer possibilities were carried out. For the experiments sulphur from JSC "Lifosa" and glycerol from JSC "Rapsoila" were operational.

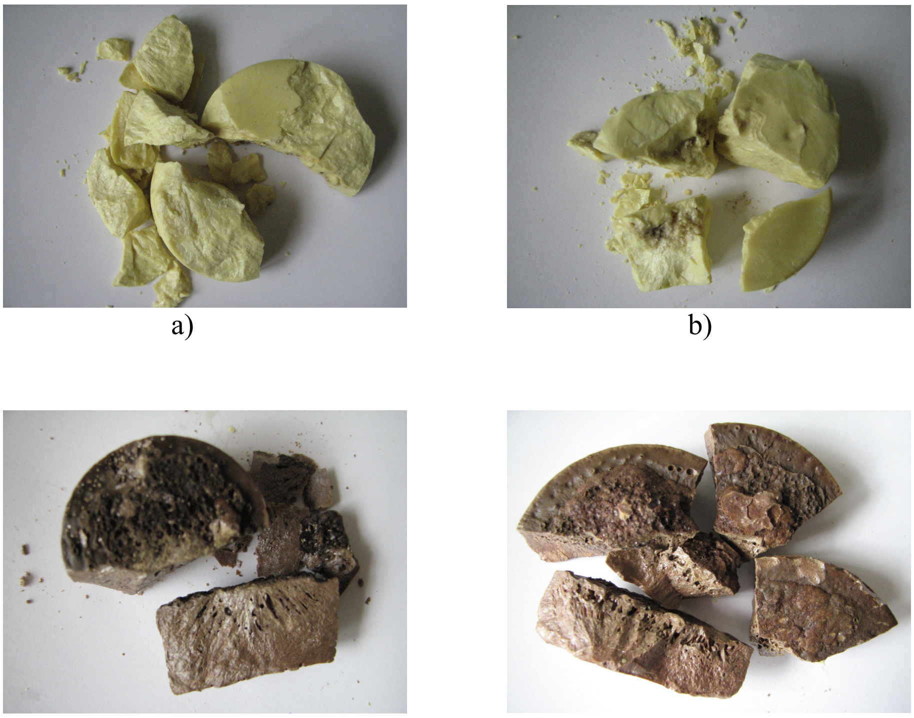
During the experiment, 4 sample mixtures with different glycerol additive to sulphur concentrations were prepared and combusted in 160°C and 180°C. The experiment data are presented in the 2.17 table:

Table 2.17 Sulphur modification with glycerol additive

Sample	I	II	III	IV
Plate weight, g	45,97	106,80	49,13	79,47
Sulphur mass, g	50,00	100,00	50,00	100,00
Glycerol mass, g	4,80	20,68	4,96	17,95
Glycerol mass, %	9,60	20,68	9,90	17,95
Combustion temperature, °C	160	160	180	180
Combustion time, h	5	5	5	5
Cooling time, h	24	24	24	24
Desiccation time, h	48	48	48	48

At the beginnning of the experiment, 4 samples of sulphur and glycerol mixture were prepared. The prepared samples were combusted 5 hours in the drying oven, 2 samples in 160°C and 2 samples in 180°C temperature. The mixture should be periodically stirred in order to get it homogenous as much as possible. Then cooled in the room temperature for 24 hours, glycerol residue washed out and samples desiccated for 48 hours.

The following Fig. 2.27 (a, b, c, d) represents samples I, II, III and IV after dessication:



a) b)

c) d)

Fig. 2.27 Sulphur modification with glycerol as a plasticizer

After the dessication samples were weighed and then glycerol part absorbed by sulphur was measured. The obtained results is presented in Table 2.18.

Table 2.18 The glycerol part (%) absorbed by sulphur

Sample	I	II	III	IV
Sample initial weight, g	95,97	206,80	99,13	179,47
Sample final weight, g	97,82	210,67	101,35	184,6
Glycerol share absorbed by sulphur, %	38,5	18,7	44,8	28,6

As we can see from the experiment results presented in Table 2.18, the highest glycerol to sulphur absorptivity is obtained in the IIIrd sample, where glycerol share in sulphur is 9.9% and combustion temeperature 180°C. Sulphur changes its structure and shifts from crystalline to the polymeric (plastic) in temperature >160°C. The linear chain is formed, so the glycerol melts and enters the sulphur more easily.

2.5. CONCLUSIONS

1. The experimental investigations were carried out in September-December 2005 and 2006 at JSC “Rapsoila”, JSC “Rietavo veterinarinė sanitarija“ and VGTU Institute of Thermal Insulation.
2. During laboratory and pilot investigations a technology for highly sulphurous heavy fuel oil - glycerol emulsion preparation was developed. The heavy fuel oil modified by an additive of technical glycerol is a complex material, composed of heavy fuel oil and glycerol mixture by ratio 1:1 and emulsificated in $t > 70°C$ up to the complete homogeneity
3. The microscopic investigation showed that prepared emulsions are homogenous if freshly made, after some time period the aggregation process breaks down the homogeneity. Thus, after mechanical activation the emulsion homogeneity is reinstated.
4. The emulsion X-ray diffraction pattern analysis of crystalline structure and computer-based quantitative impurity analysis indicated compound of the $Na_5P_3O_{10}$ composition present in emulsion ash. The observed traces of Na and K indicate about the catalyst, used in the transesterification process, during the biodiesel production. In this case, the base added as a single reagent was NaOH or KOH. Also, we can draw a conclusion, that glycerol used for heavy fuel oil-glycerol emulsion preparation was of relatively high purity, thus the X – ray diffraction indicates non-significant peaks due to the small amounts of additives.
5. The crude heavy fuel oil and heavy fuel oil modified by glycerol combustion process and measurements were carried out at the JSC „Rietavo veterinarinė sanitarija“ and could be used for heat production.
6. During the measurements of pollutants, exhaust from the heavy fuel oil with a high sulphur content by mass combustion process, the extremely high concentrations of SO_2 are obtained. The observed average SO_2 concentration value is 3139.6 mg/Nm^3, meanwhile SO_2 MAC value is 1700 mg/Nm^3. Thus, the obtained emission concentration significantly exceeds admissible value, due to the high sulphurity in the heavy fuel oil.
7. The obtained CO, NO_x and particulate matter average emission concentration values in the exhaust flue gas during HFO combustion process do not exceed MAC values, thus some obtained concentration peak values for NO_x (646.0 mg/Nm^3) and particulate matter (176.3 mg/Nm^3) alerts about possible admissible concentration value overdrafts.
8. The observed relatively low CO values (average concentration 16.4 mg/Nm^3) for heavy fuel oil could be attributed to the combustion at high temperature.
9. It should be particularly emphasized that the observed emission concentrations for heavy fuel oil – glycerol emulsion combustion indicate a significant decrease in SO_2 emission amount. The

measured average concentration was only 727.1 mg/Nm^3, meanwhile for pure heavy fuel oil it is 3-4 times higher. This would allow readily meet the requirements for SO_2 MAC 1700 mg/Nm^3. So, the exhaust emissions of sulphur oxides from emulsion are essentially eliminated compared to heavy fuel oil SO_2 concentrations.

10. However, the increase of ~ 10 % for NO_x emission concentration was observed due to the technical obstacles and too low and shifting temperature in the boiler. However, the average measured NO_x value is 618.8 mg/Nm^3 and does not exceed the evaluated MAC value for NO_x which is 700 mg/Nm^3.
11. The measured average concentrations for CO (1758.1 mg/Nm^3) and particulate matter (740.2mg/Nm^3) do not exceed their estimated maximum admissible values.
12. Due to the insufficient temperature and some technical obstacles in some points of measurements the obtained concentration values exceeded the allowable ones, but the average concentration value does not exceed limit value and are lower than their MAC values. The attainment of sufficient temperature in the boiler plays a siginificant role for a complete emulsion combustion process, along with adequate oxygen availability. The operating boiler temperature is 850°C, and it is considered that complete emulsion combustion requires ~ 950-1000°C.
13. It was determined that glycerol could be used to plasticize sulphur for its use in sulphur concretes. The glycerol part up to 10 % and temperature >160°C is found to be operational. Thus, the broader investigations are required.
14. Finally, based on the accomplished investigation results, the heavy fuel oil modified by glycerol additive technological regulation is prepared, which provides technical data for heavy fuel oil – glycerol emulsion preparation and combustion conditions.

3. ATMOSPHERIC AIR POLLUTION DISPERSION MODELLING

3.1. INTRODUCTION

A mathematical model is an assembly of concepts or phenomena in the form of one or more mathematical equations, which approximate the behaviour of a natural system or phenomena to predict the impacts or concentration of parameters under different types of current or future parameters, using readily available or measured input data.

The objective of this simulation study is to investigate the effect of two variables - atmospheric stability (Pasquill stability classes A-F) and wind speed (1-5 m/s)- on the downwind transport of the pollutants, to observe which type of atmosphere, from stable to unstable, has more effect downwind from the smokestacks.

In this chapter the atmospheric air pollution from point source dispersion modelling in the region, applying Gaussian Plume Model and computer-based program LabVIEW 8.0 is performed. The experimentally obtained emission concentrations of heavy fuel oil and heavy fuel oil - glycerol emulsion combustion are operational.

3.2. METHODOLOGY OF AIR POLLUTION DISPERSION SIMULATION

Prediction of pollution levels resulting from a given emission is carried out with the help of air pollution dispersion models, which compute atmospheric transport and dispersion of pollutants being emitted into the atmosphere. At present, Gaussian plume model is the most widely used model for point source emission predictions. The fuel combustion atmospheric air pollution dispersion modeling is performed on the basis of Gaussian plume model in order to determine the possible contribution of the emissions to the background air pollution.

The Gaussian plume model is the most accepted computational approach to calculating the concentration of a pollutant at a certain point. This model describes the transport and mixing of the pollutants. It assumes dispersion in the horizontal and vertical direction will take the form of a normal Gaussian curve with the maximum concentration at the center of the plume [68].

Fig. 3.1 shows schematically the dispersion in the atmosphere of pollution released from a stack. Most attention to modelling this behaviour centres on describing in mathematical equations the spread of airborne material as a function of downwind distance. This is shown in an idealised way in Fig. 3.1, where the shape of the dispersing plume is assumed to have the form of a Gaussian function, examples of which are drawn on the diagram.

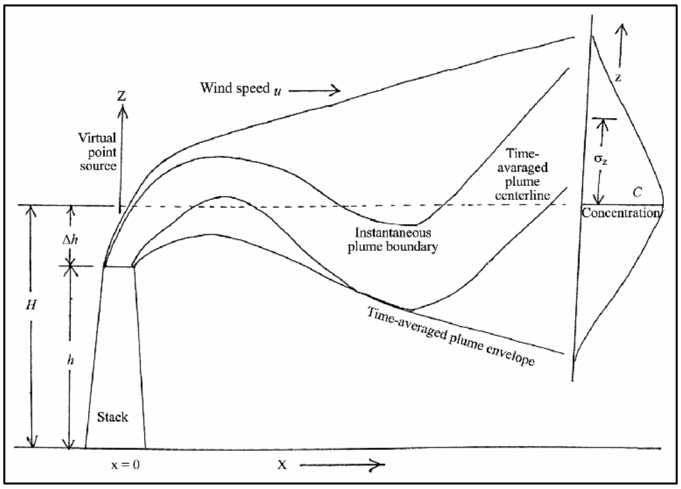


Fig. 3.1 The schematic geometry of Gaussian plume model

There are several versions of the Gaussian plume model. A classic equation 3.1 is the Pasquill-Gifford model [68, 69].

$$C(x,y,z) = \frac{Q}{2\pi u \sigma_y \sigma_z} \times \left[\exp - \left(\frac{y^2}{2\sigma_y^2} \right) \right] \left\{ \exp\left(\frac{-(z-H)^2}{2\sigma_z^2} \right) + \exp\left(\frac{-(z+H)^2}{2\sigma_z^2} \right) \right\} \qquad 3.1$$

Here:

C – concentration of the chemical air, [μg/m3];
Q – rate of chemical emissions, [μg/s];
u – wind speed in x direction, [m/s];
σ_y – standard deviation in y direction, [m];
σ_z – standard deviation in z direction, [m];
y – distance along a horizontal axis perpendicular to the wind, [m];
z – distance along a vertical axis, [m];
H – effective stack height, [m].

The horizontal displacement is due to wind speed. The higher the speed, the greater the displacement. The vertical rise is due to:

- buoyancy - when the exit gas mass is less than the surrounding air mass, the plume is more buoyant;
- exit temperature - when the exit temperature is greater than the ambient air temperature, the plume has positive buoyancy;

- exit velocity - an increase in exit velocity will increase the vertical inertia which leads to higher plume rise;
- wind speed - an increase in wind speed will decrease the plume rise by bending the plume over more rapidly.

Fuel is burnt and a plume of emissions is produced. A plume is the region of space containing the gases and particulates released from a smokestack as fuel is burnt. This may look like flue gas and could contain one or more pollutants. Because the plume is hot, it will rise, since hot air is less dense. The plume will rise to a certain point and this is called the "effective stack height". The effective stack height depends on three main factors:

- the exit velocity of the gas from the stack;
- the temperature of the plume;
- the temperature of the surrounding air.

The effective stack height is equal to the physical stack height plus the plume rise [68, 69].

$$\Delta H = \frac{1.6 F_b^{1/3} x^{2/3}}{u} \tag{3.2}$$

$$F_b = g \frac{d^2 V}{4} \left(\frac{T_s - T_a}{T_s} \right) \tag{3.3}$$

Here:

ΔH – plume rise as defined by Briggs equation, [m]

x – downwind distance, [m];

u – wind speed in x direction, [m/s];

F_b – buoyancy flux, [m^4/s^3];

g – acceleration due to gravity, [m/s^2];

d – stack diameter, [m];

V – exit velocity, [m/s];

T_s – absolute gas temperature, [deg];

T_a – absolute air temperature, [deg].

After the plume reaches the effective stack height, the plume starts to disperse in three different directions:

- the plume can move downwind. The amount that the plume moves is directly proportional to the wind speed and in the direction of the prevailing wind.
- the plume can move in a cross-wind direction. This is determined by the Gaussian plume equations.
- the plume can move in a vertical direction, either up or down. This is also determined by the Gaussian plume equations.

The Gaussian plume model is the most commonly used model to make the calculations needed to predict the movement of a pollutant in complex situations. In order to do this, several assumptions need to be made:

- the smokestack emission is continuous and constant to allow for steady state analysis;
- the terrain is relatively flat;
- there are no reactions degrading the pollutants. Also, when the pollutants hit the ground, they are reflected and not absorbed;
- the wind speed is constant in time and in elevation;
- the concentration of the pollutants has a normal distribution;
- the concentration at the edge of the plume is one tenth of the concentration of the centerline.

As a result the Gaussian plume model will only work well over short distances of up to 50 km from the source of the pollutant to the receptor. The receptor could be a measuring instrument, but it might well be a neighborhood in the path of the pollutant flow. The model will also not work well in areas where the terrain is very complex or in a coastal area where sea and land-breezes can cause dramatic changes in meteorological conditions.

Industrial effluents are discharged through smokestacks. The exhaust plume from the stack mixes with ambient air. This mixing dilutes the effluent. Wind speed affects the rate of mixing (Fig. 3.2). Increase in speed will increase the dilution. Strong wind drags pollution torch, enhances dynamic convection so pollution concentration decreases. This will result in a lower downwind concentration, the area contaminated will increase. Also, the more unstable the atmosphere, the greater the dilution. Turbulent diffusion causes the pollutants to become more dispersed. The plume experiences a horizontal and vertical movement [70].

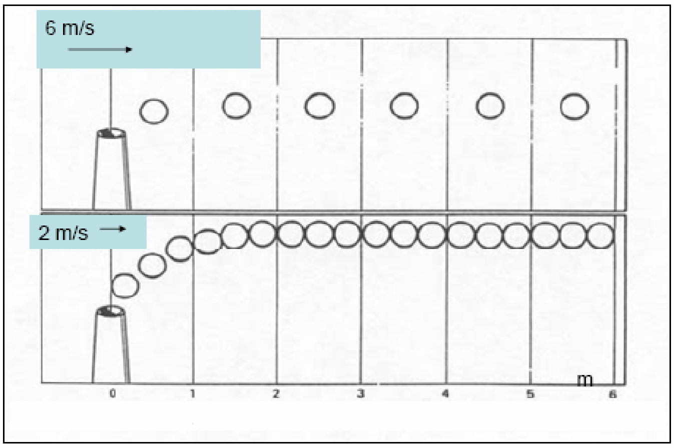


Fig. 3.2 Wind effect on pollution dispersion

The factors that affect transport, dilution and dispersion of air pollutants are grouped into:

- source or emission characteristics;
- the nature of pollutant material;
- the effects of terrain and anthropogenic structures;
- meteorological characteristics;
- wind and air humidity;
- turbulence and stratification;

Source characteristics

Most industrial pollution is discharged vertically from a stack or duct into the open air. As the contaminated gas stream is emitted, the plume (body of polluted air) expands and plume means the body of polluted air. Wind that is horizontal air movement will bend the plume in the downwind direction. At some distance from the source, the plume will level off. While the plume is rising, bending, and starting to move with the wind in the downwind direction, the flue gas is being mixed and diluted by the ambient air. As the gas is being diluted by increasing volumes of air, the contaminant will eventually reach the ground.

The initial rise of the plume is due to the upward inertia of the gas stream exiting the stack, and by its buoyancy. The vertical inertia is related to the exit velocity and mass of the gas. The buoyancy is related to the density relative to the surrounding air, primarily determined by temperature. Increasing exit velocity and increasing exit temperature will increase the plume rise. Increasing emission rates will therefore lead to a proportional increase in ambient concentrations.

Downwind distance

The greater the distance from the discharge point, the greater the volume of air available for dilution. However, since the plume starts above the ground and needs some time to reach the ground (by bending and spreading), there is no concentration observable in the immediate vicinity of the stack, then we can observe an increase for some distance as the plume approaches the ground. After this, the ground-level concentration will decrease with increasing distance from the emission source.

Wind speed and direction

Wind direction will determine the direction in which the plume will move across local terrain. Wind speed affects the plume rise (fast wind will bend the plume faster), and will increase the rate of dilution. Thus, the effects of wind speed work in two opposite directions:

- increasing wind speed will decrease plume rise, thus increase ground level concentrations;
- increasing wind speed will increase mixing, thus decreasing ground level concentrations.

Depending on the specific conditions, one or the other of these phenomena will prevail. These effects also determine the distance from the source where the maximum concentration will occur.

Atmospheric stability

“Stability” in this sense refers to the propensity of air to rise or fall. In other words, the tendency of the atmosphere to resist or enhance vertical motion and thus turbulence. Stability is related to both the change of temperature with height (the lapse rate) and wind speed. A neutral atmosphere neither enhances nor inhibits mechanical turbulence. An unstable atmosphere enhances turbulence, whereas a stable atmosphere inhibits mechanical turbulence. The turbulence of the atmosphere is by far the most important parameter affecting dilution of a pollutant. The more unstable atmosphere, the greater the dilution. The amount of turbulence in the ambient air has a major effect upon the rise and dispersion of air pollutant plumes. The amount of turbulence can be categorized into defined increments or "stability classes" (Table 3.1).

Table 3.1 Pasquill stability classes

	Day Incoming Solar Radiation			Night Cloud Cover	
Wind Velocity (u) (at z = 10 m, in m· s^{-1})	Strong	Moderate	Weak	Thinly Overcast	Mostly Cloudy
<2	A	A-B	B	E	F
2-3	A-B	B	C	D	E
3-5	B	B-C	C	D	D
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

The most commonly used categories are the Pasquill stability classes A, B, C, D, E and F. Class A denotes the most unstable or most turbulent conditions and class F denotes the most stable or least turbulent conditions, meanwhile D represents neutral conditions.

3.3. ANALYSIS OF POLLUTION DISPERSION SIMULATION RESULTS

In this section the heavy fuel oil and heavy fuel oil – glycerol emulsion combustion process and the measured SO_2 emission concentrations are operational. Hereinafter, the heavy fuel oil and heavy fuel oil – glycerol emulsion combustion in the industrial boiler-house furnace is under simulation consideration , with a special emphasis on pollutant emissions dispersion tendencies and dependency on several variables, mainly on:

- changes to emission concentration (different SO_2 emission concentrations for heavy fuel oil and heavy fuel oil – glycerol emulsion are applied);
- alteration in Pasquill stability classes;
- changes to wind velocity;

The tasks of this section are the following:

- operating with a computer-based program LabVIEW (Laboratory virtual instrumentation engineering workbench) to develope pollution dispersion from point source model (based on Gaussian Plume Model);
- using simulation tools to predict trajectory of effluent disharge;
- to investigate the influence of different emission concentrations on the dispersion trajectory;
- to simulate pollution dispersion dependency on Pasquil ctability classes and alterations in wind velocities;

- to present pollution dispersion simulation results - top view, side view and crossections for pollution plumes, as it is presented schematically in the Fig. 3.3.

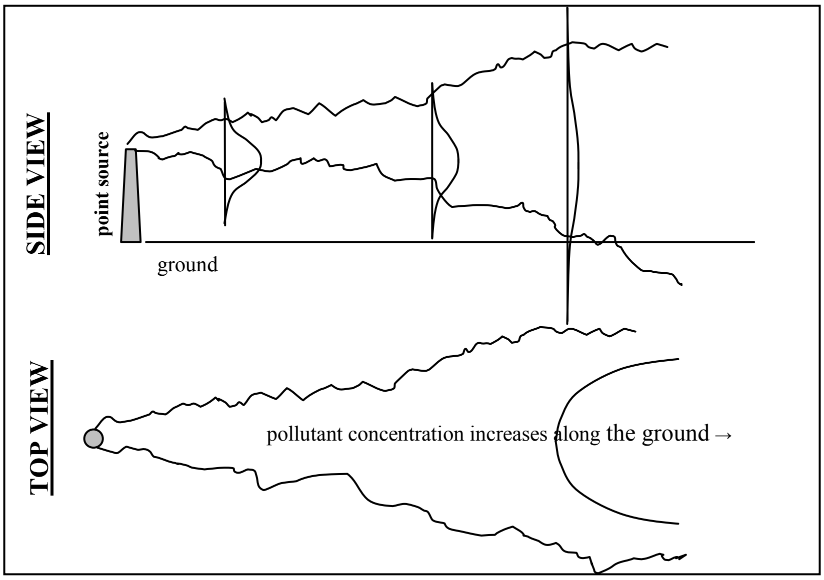
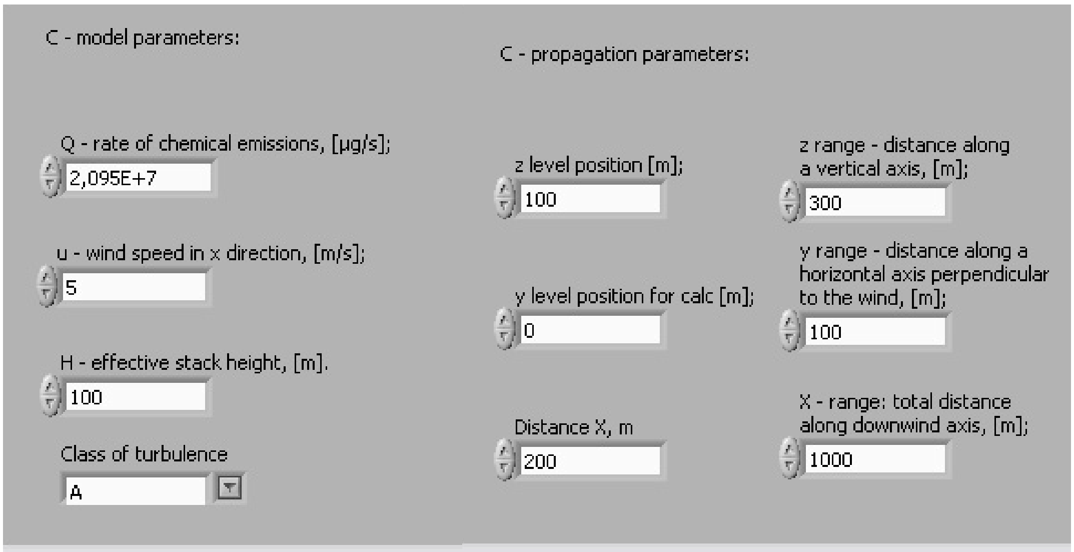


Fig. 3.3 Schematic Gaussian Plume model: side and top view

A general concept for modeling pollution dispersion with Gaussian plumes – is that unless wind vectors are changing direction sporadically, concentration of a pollutant will spread regularly from a point source, forming a Gaussian distribution of pollutant.

Primarily, the pollution dispersion modeling for SO_2 emission concentration from pure HFO combustion process is performed.

The following dispersion model and pollution propagation parameters were operational (Fig. 3.4):



C - model parameters:

Q - rate of chemical emissions, [µg/s]; 2,095E+7

u - wind speed in x direction, [m/s]; 5

H - effective stack height, [m]. 100

Class of turbulence A

C - propagation parameters:

z level position [m]; 100

y level position for calc [m]; 0

Distance X, m 200

z range - distance along a vertical axis, [m]; 300

y range - distance along a horizontal axis perpendicular to the wind, [m]; 100

X - range: total distance along downwind axis, [m]; 1000

Fig. 3.4 Operational pollution model and dispersion parameters

The pollution dispersion simulation is performed for the SO_2 emission from pure heavy fuel oil combustion process. Primarily, the pollution from point source (smokestack) dispersion reliance and alteration within Pasquill stability classes is simulated. The so called Pasquill stability classes are denoted as follows:

A – very unstable;
B – moderately unstable;
C – slightly unstable;
D – neutral;
E – slightly stable;
F - moderately stable

The pollution dispersion simulation for the measured SO_2 emission concentration (3139.6 mg/Nm^3) from the heavy fuel oil combustion process experimental investigations is carried out. During fuel combustion process a plume is formed, which is the region of space containing gases and particulates released from a smokestack as fuel is burnt. Hereinafter, the pollution dispersion simulation results are given in the Fig. 3.5, 3.6 and Fig. 3.7, which represents top, side and crossection views respectively of pollution plume.

The aim of model is to show concentration of the pollution dispersion at various distances downwind from the stack, applying different factors. In this case these factors are Pasquill stability classes and wind speed. The flue gas released from the smokestack, blown by the wind, although it certainly moves mainly in the wind direction, also exhibits seemingly random motions at right angles to it. Such randomness is called “turbulence” and is reflected by the Pasquil stability classes.

Primarily, the simulation was performed for constant wind speed (u = 5 m/s) and for different Pasquil stability classes. It is assumed that the effective smokestack height is 100 m, pollution dispersion and intensity distribution is projected in 1000 m distance along downwind direction.

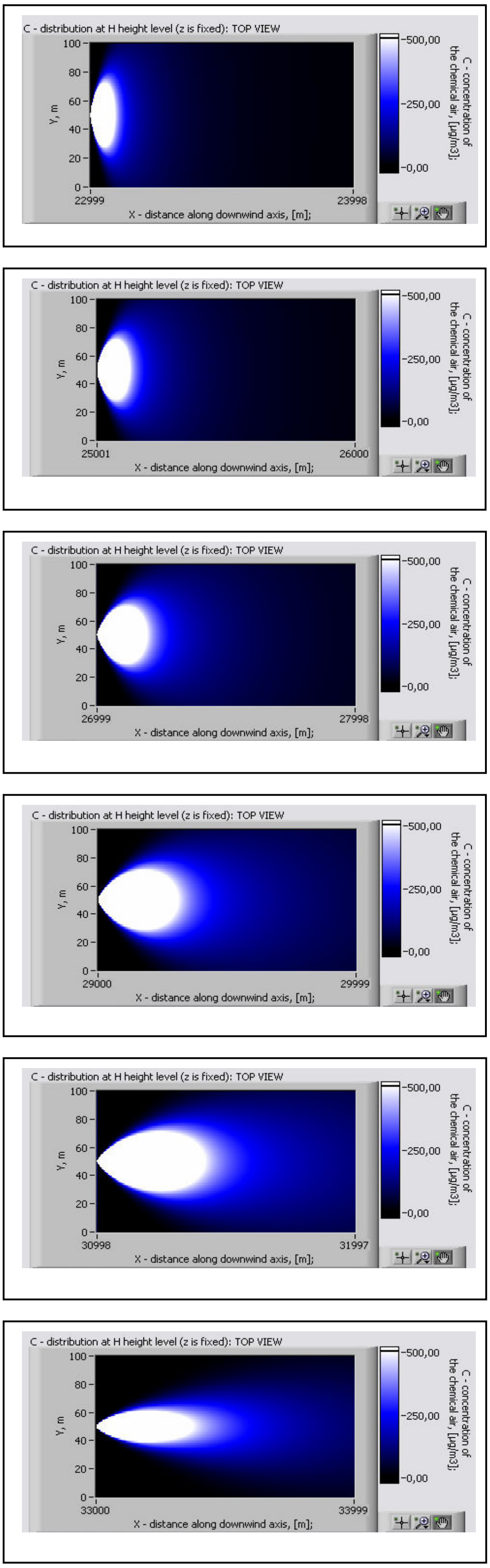
The Pasquill stability classes denote turbulence of the atmosphere, which is by far the most important parameter affecting dilution of a pollutant. The more unstable atmosphere, the greater the dilution.

To get the more clear pollution dispersion scenery, the pollution plume in the top and side view, also the plume crossection is given (Fig. 3.5, Fig. 3.6, and Fig. 3.7).

The obtained simulation results express the distribution of the dispersed concentration averages with regard to the plume centerline. The intensity grid for the plume crossection visualizations is 1000 points.

The colors in the simulation pictures represent concentration distribution in the area and its intensity in the certain points of observation. White color represents the most intensive concentration areas, the dark blue – the lowest concentration zone. When the Pasquill stability class is “A” as very unstable and due to a fact that the unstable atmosphere enhances turbulence, the plume moves drastically in z axis vertical direction. The most intensive concentration distribution is obtained not far from the pollution source - ~ 100 m. Conversely, under moderately stable atmospheric condition (class “F”) the plume moves along its downwind distance ~ 500 m, untill it looses its highest concentration intensity, and dissipates in the atmosphere. Due to the small turbulence, pollution plume weakens and moves downwards.

The visualizations are performed to clarify the behavior of the plume as a result of atmospheric stability. Also, it is easier visually to examine not only the downwind distance that the plume travels but also the concentration of the downwind pollution. The atmospheric condition, described as stability class “E” or slightly stable, causes the pollution plume to travel fastest and longest distance along downwind direction. The highest pollution concentration in the plume is observed near the pollution source and under very unstable (class “A”) atmospheric conditions. In a case of very unstable atmospheric conditions the pollution disperses mostly in vertical direction, meanwhile, the more stable atmospheric conditions, the larger polluted area along x axis in downwind direction is observed.



(a) **Class "A"** (very unstable)

(b) **Class "B"** (moderately unstable)

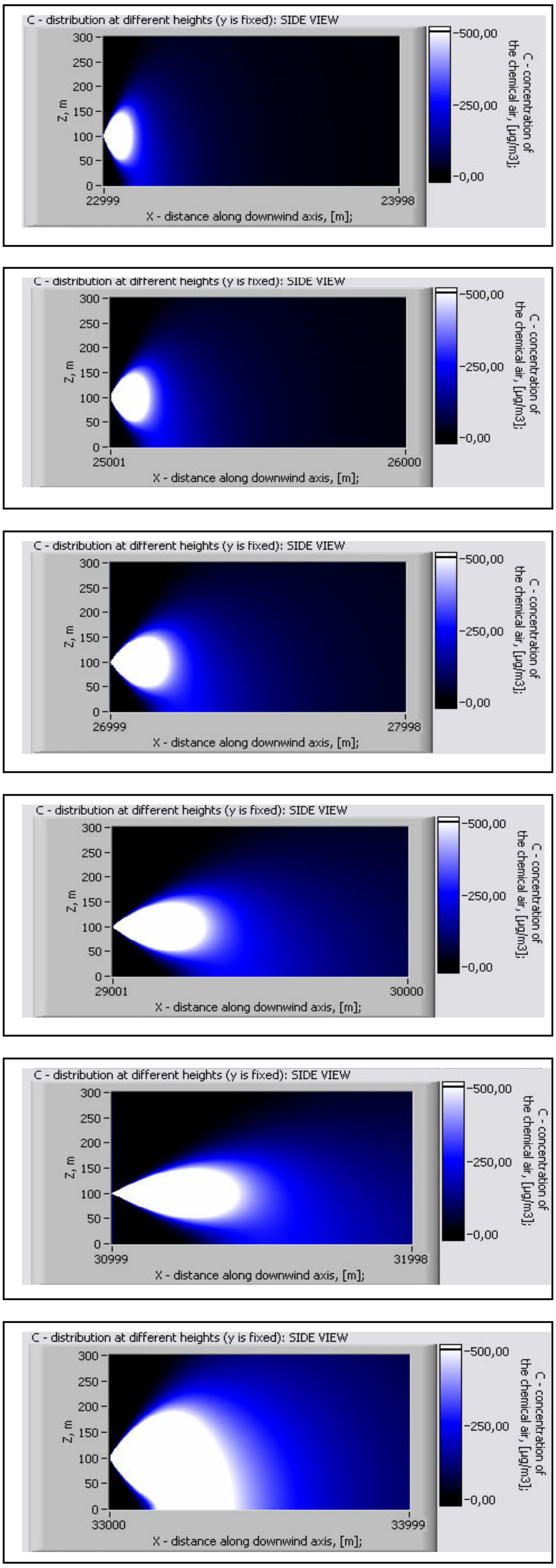
(c) **Class "C"** (slightly unstable)

(d) **Class "D"** (neutral)

(e) **Class "E"** (slightly stable)

(f) **Class "F"** (moderately stable)

Fig. 3.5 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (Top view)



(a) **Class "A"** (very unstable)

(b) **Class "B"** (moderately unstable)

(c) **Class "C"** (slightly unstable)

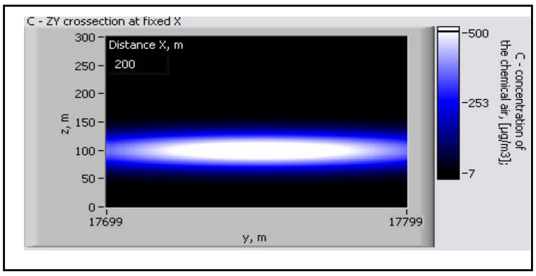
(d) **Class "D"** (neutral)

(e) **Class "E"** (slightly stable)

(f) **Class "F"** (moderately stable)

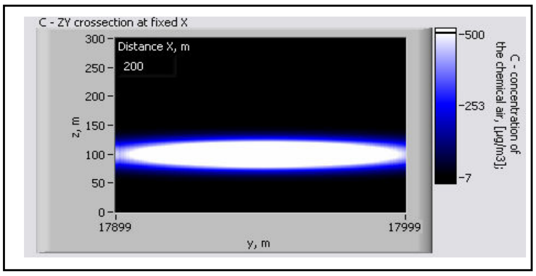
Fig. 3.6 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (Side view)

(a)



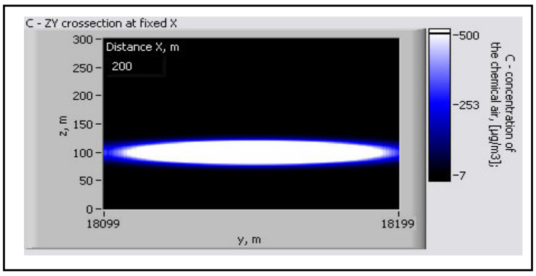
Class "A"
(very unstable)

(b)



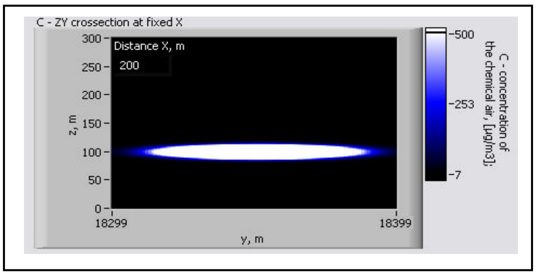
Class "B"
(moderately unstable)

(c)



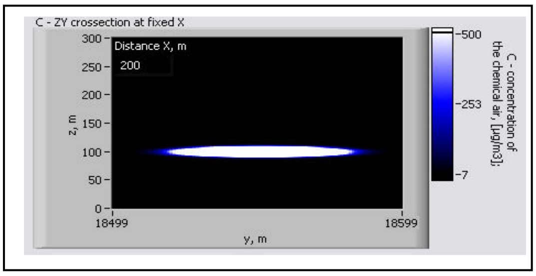
Class "C"
(slightly unstable)

(d)



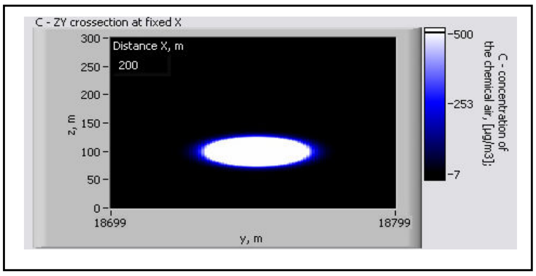
Class "D"
(neutral)

(e)



Class "E"
(slightly stable)

(f)

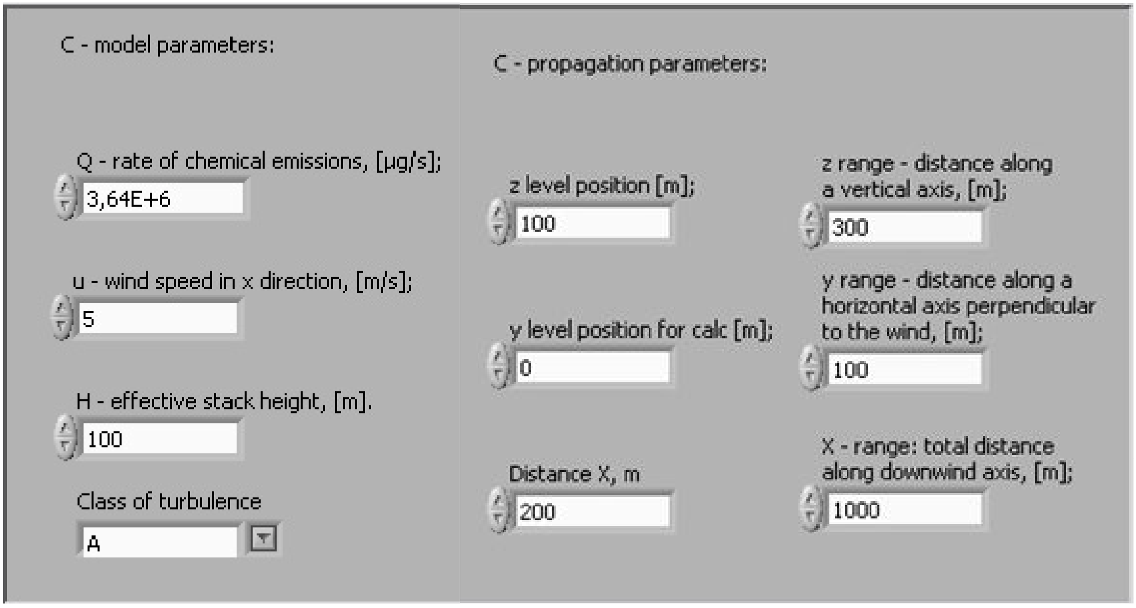


Class "F"
(moderately stable)

Fig. 3.7 Heavy fuel oil combustion pollution dispersion related to alternation in Pasquill stability class (plume crossection)

Thus one of the main issues of this master work is to lower SO_2 emission concentrations to the allowable values, replacing part of heavy fuel oil by the glycerol additive, so the SO_2 emission concentration from the prepared heavy fuel oil –glycerol emulsion combustion process is also simulated. The obtained simulation results are then compared to the dispersion model for pure heavy fuel oil SO_2 emission concentration discussed previously. The following emission dispersion modeling is performed for the measured emulsion SO_2 concentration 727.1 mg/Nm^3.

The following dispersion model and pollution propagation parameters are operational (Fig. 3.8):



C - model parameters:

Q - rate of chemical emissions, [μg/s]; 3,64E+6

u - wind speed in x direction, [m/s]; 5

H - effective stack height, [m]. 100

Class of turbulence A

C - propagation parameters:

z level position [m]; 100

z range - distance along a vertical axis, [m]; 300

y level position for calc [m]; 0

y range - distance along a horizontal axis perpendicular to the wind, [m]; 100

Distance X, m 200

X - range: total distance along downwind axis, [m]; 1000

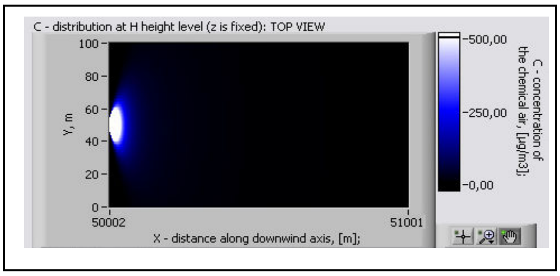
Fig. 3.8 Operational pollution model and dispersion parameters

The same model and dispersion parameters as for pure heavy fuel oil emission modeling are operational, except the concentration, which is considerably different for pure heavy fuel and for heavy fuel oil - glycerol emulsion. So, the objective is to investigate the effect of emission concentration for the pollution dispersion intensity and distribution.

Hereinafter, the heavy fuel oil – glycerol emulsion SO_2 emission concentration simulation results are given in Fig. 3.9, Fig. 3.10 and Fig. 3.11. To get the more clear pollution dispersion scenery, the pollution plume is from top and side view, also the plume crossection are presented.

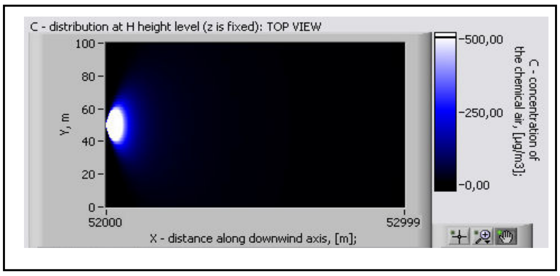
As it can be seen from the simulation results, lower concentration leads to a significantly smaller polluted area, and lower dispersion intensity consequently.

(a)



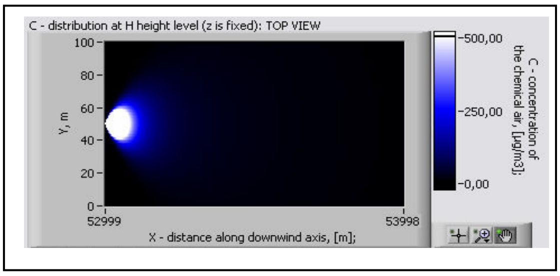
Class "A"
(very unstable)

(b)



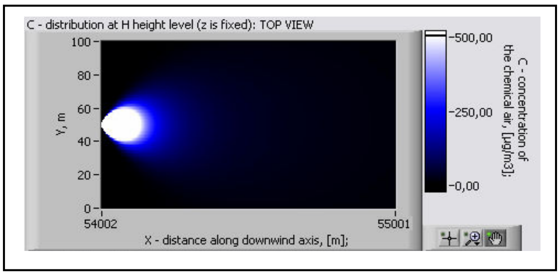
Class "B"
(moderately unstable)

(c)



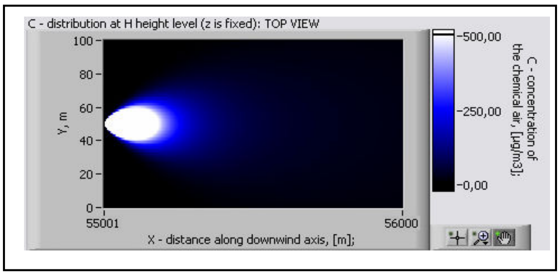
Class "C"
(slightly unstable)

(d)



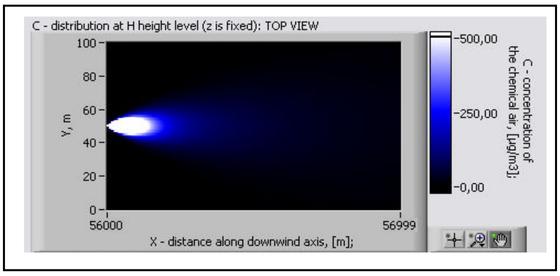
Class "D"
(neutral)

(e)



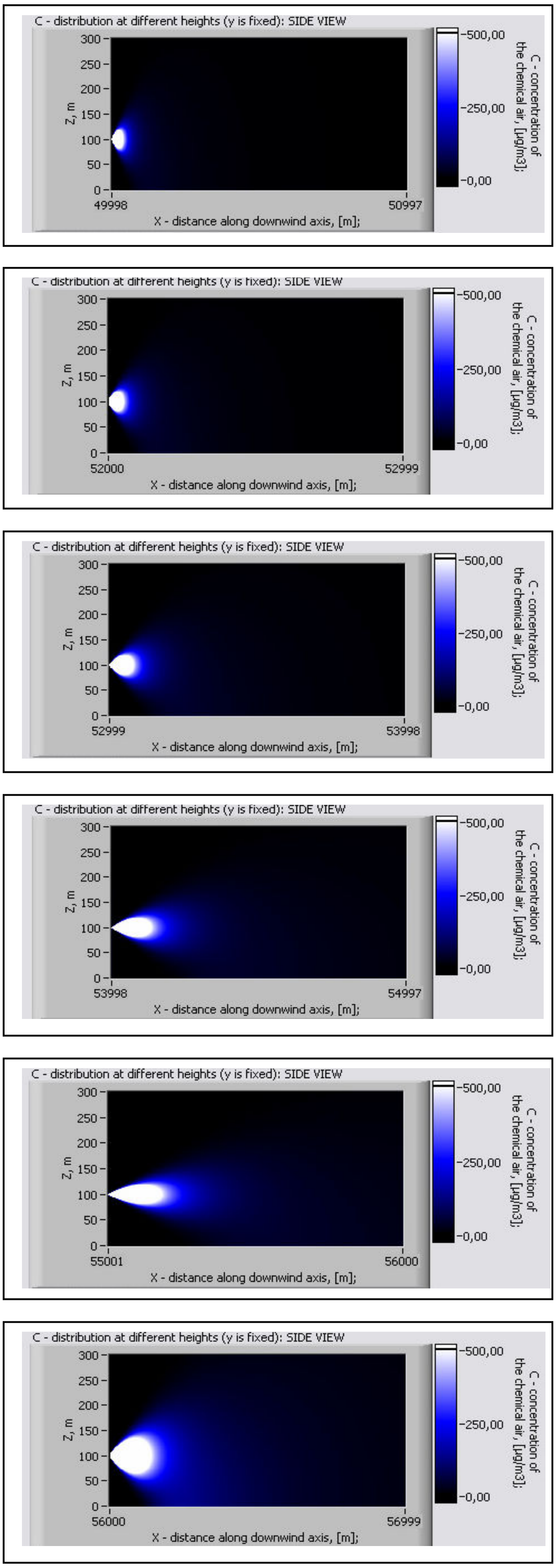
Class "E"
(slightly stable)

(f)



Class "F"
(moderately stable)

Fig. 3.9 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (Top view)



(a) **Class “A”** (very unstable)

(b) **Class “B”** (moderately unstable)

(c) **Class “C”** (slightly unstable)

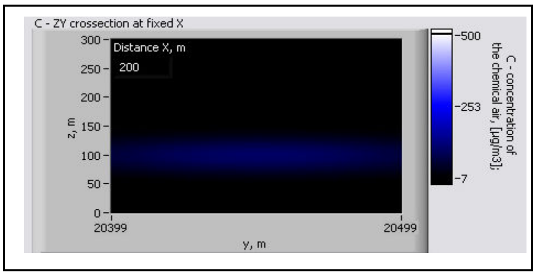
(d) **Class “D”** (neutral)

(e) **Class “E”** (slightly stable)

(f) **Class “F”** (moderately stable)

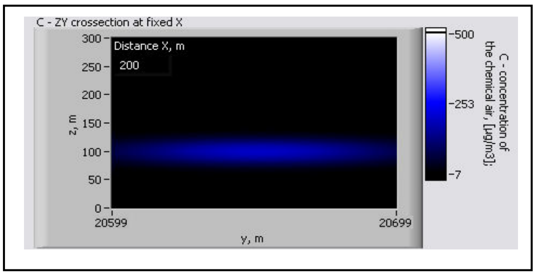
Fig. 3.10 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (Side view)

(a)



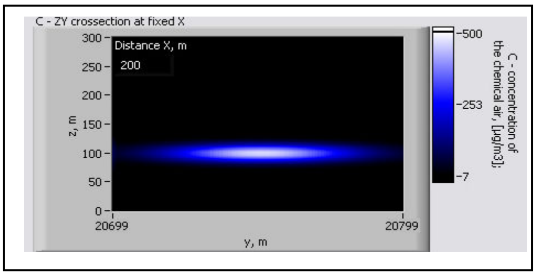
Class “A”
(very unstable)

(b)



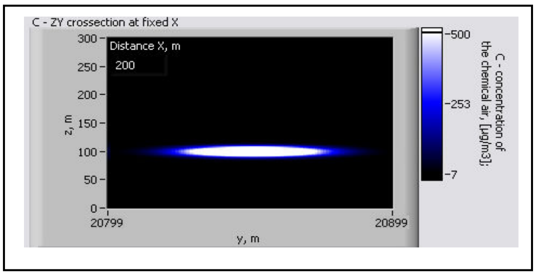
Class “B”
(moderately unstable)

(c)



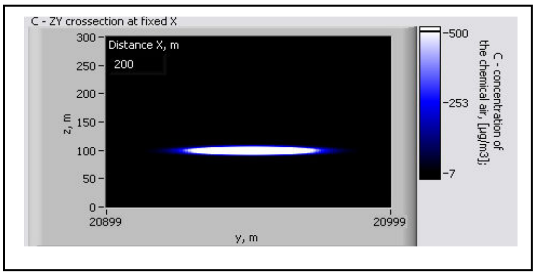
Class “C”
(slightly unstable)

(d)



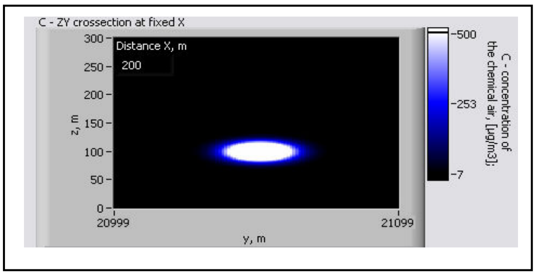
Class “D”
(neutral)

(e)



Class “E”
(slightly stable)

(f)



Class “F”
(moderately stable)

Fig. 3.11 Heavy fuel oil - glycerol emulsion combustion pollution dispersion related to alternation in Pasquill stability class (plume crossection)

The heavy fuel oil - glycerol emulsion pollution dispersion plume is acting similar as in the case of heavy fuel oil, thus it should be mentioned that a smaller pollution concentration disperse and pollutes atmosphere to a relatively lesser degree. In this case, the most intensive concentration distribution is observed also near the pollution source, approximately 40 m, meanwhile the most intensive concentration for heavy fuel oil is obtained in a distance of ~ 100 m from the stack. Also the different plume behaviour for HFO and HFO-G emulsion under moderately stable atmospheric conditions is observed. In a case of heavy fuel oil, the plume looses its concentration intensity and dissipates downwards, meanwhile in case of emulsion, the plume disperses gradually declining along downwind direction.

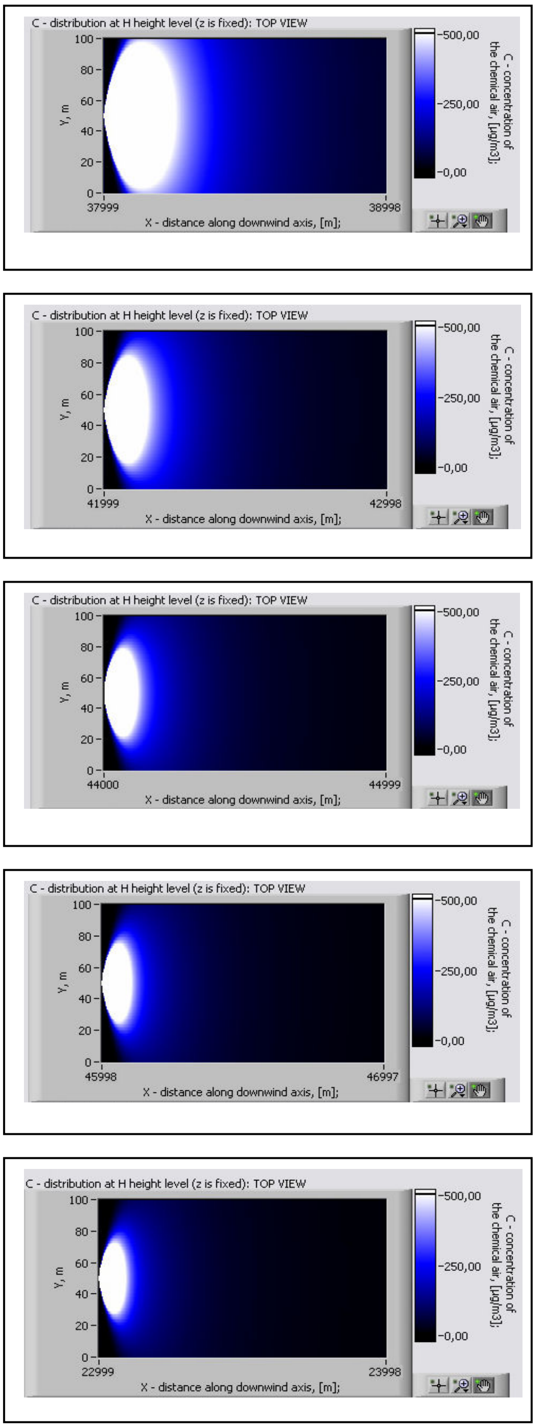
When the exhaust plume from the stack mixes with ambient air it dilutes the effluent. Wind speed is important factor affecting the rate of mixing. Thus, the simulation for heavy fuel oil and heavy fuel oil - glycerol emulsion SO_2 emission concentration dispersion dependency on wind speed is performed.

The dependency of pollution dispersion plume on wind speed is simulated in a range of u = 1-5 m/s for Pasquill stability class “A”. This class is chosen with a purpose to observe the plume behaviour under the most unstable atmospheric condition.

Pollution emission concentrations, the same as for plume dispersion simulation within alternation in stability classes are operational: SO_2 for heavy fuel oil – 3139.6 mg/Nm^3, and for emulsion SO_2 concentration – 727.1 mg/Nm^3.

The plume particle traces colored by the concentration intensity level show the dilution and trajectory of the pollution. White color indicates the most intensive concentration areas, the dark blue – points of lower concentration intensity.

Hereinafter, the HFO (Fig. 3.12, Fig. 3.13 and 3.14) and HFO-G (Fig. 3.15, 3.16 and 3.17) emulsion emission concentration dispersion fluctuations due to alternation in wind speed is presented.



(a) u = 1 m/s

(b) u = 2 m/s

(c) u = 3 m/s

(d) u = 4 m/s

(e) u = 5 m/s

Fig. 3.12 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (Top view)

Under the calm conditions, when the wind speed is very small or approaches to zero, the Gaussian equation with wind speed in the denominator gives an infinite concentration. This fact is approved by picture (a), where wind speed is 1m/s, and the pollution is spread widely.

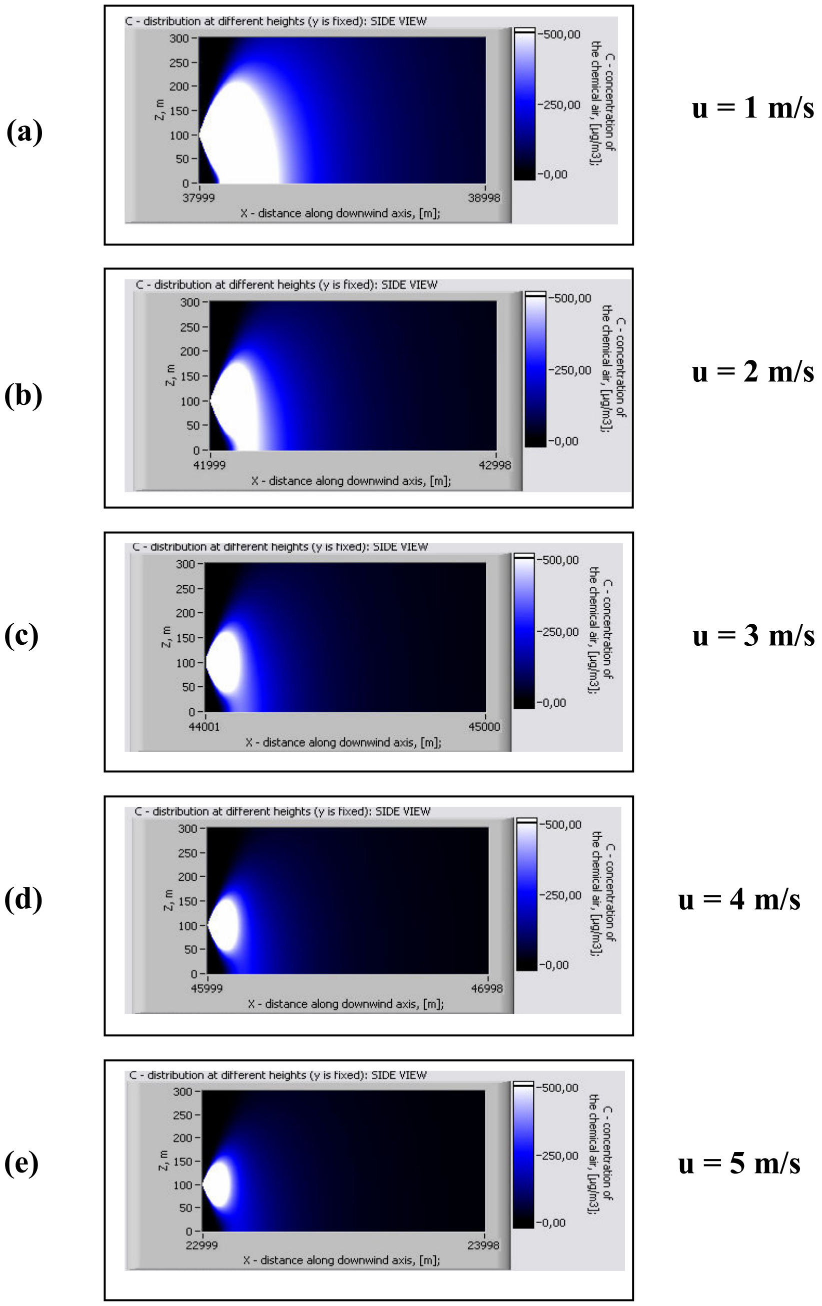
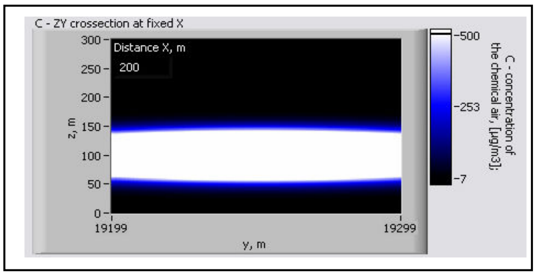


Fig. 3.13 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (Side view)

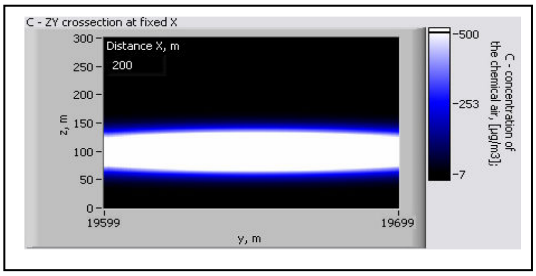
Increase in speed enhances the dilution. Strong wind drags pollution torch, enhances dynamic convection so pollution concentration decreases, as it can be seen in picture (e), where wind speed is 5 m/s. This will result in a lower downwind concentration, the area contaminated will increase.

(a)



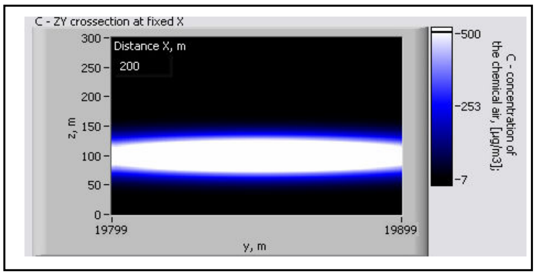
u = 1 m/s

(b)



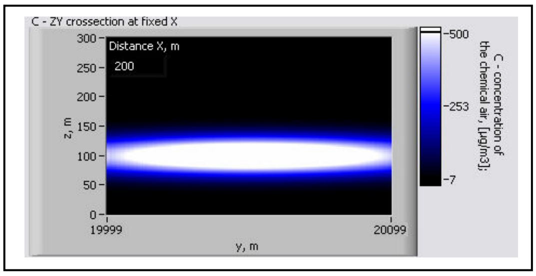
u = 2 m/s

(c)



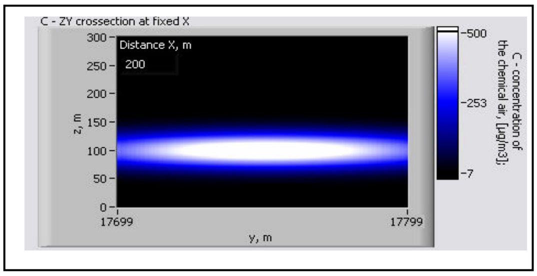
u = 3 m/s

(d)



u = 4 m/s

(e)



u = 5 m/s

Fig. 3.14 Heavy fuel oil combustion pollution dispersion related to alternation in wind speed (plume crossection)

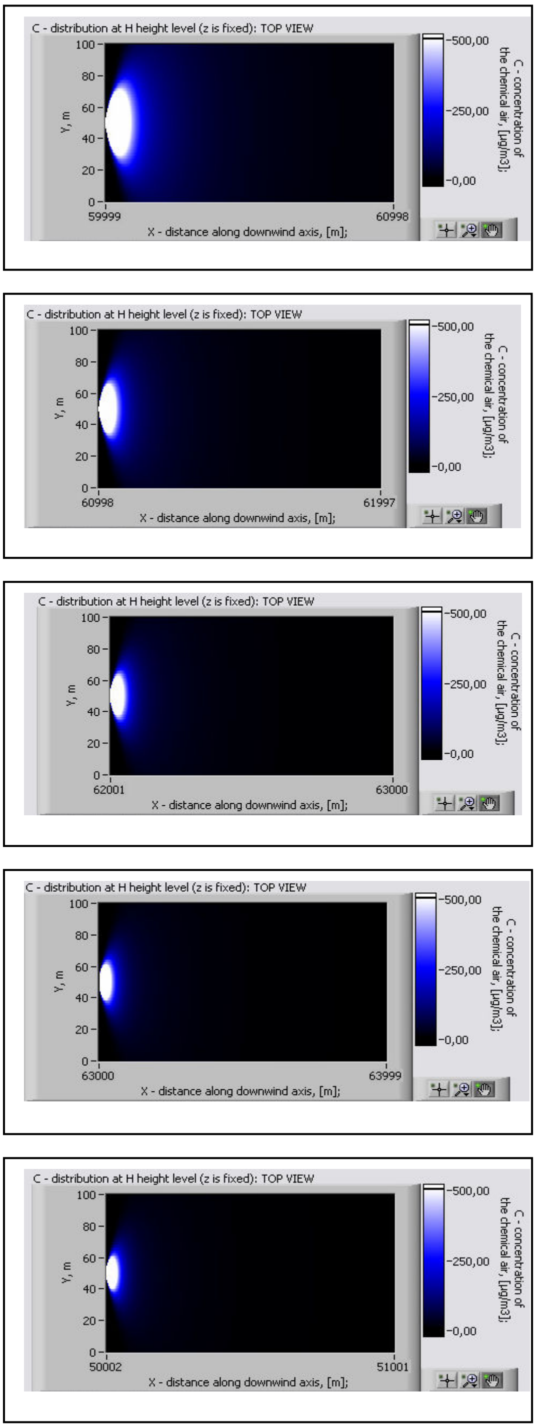


Fig. 3.15 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (Top view)

The more unstable the atmosphere, the greater dilution is. Turbulent diffusion causes the pollutants to become more dispersed. Here, Fig. 3.15 reflects the plume behaviour in Pasquil stability class “A”, which is denoted as very unstable.

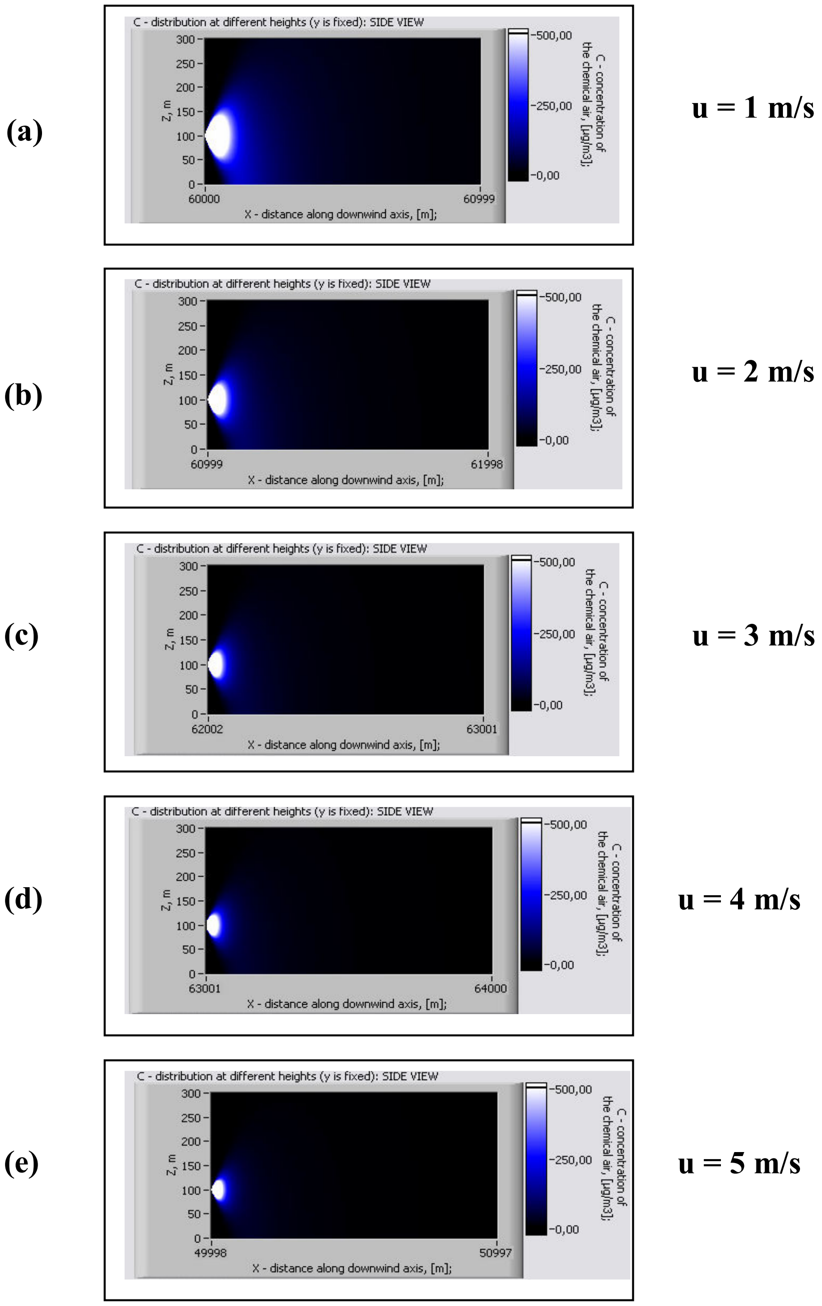


Fig. 3.16 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (Side view)

As it can be seen in Fig. 3.16 an increase in wind speed will decrease the plume rise by bending the plume over more rapidly. Also, the higher the speed, the greater pollution displacement is observed.

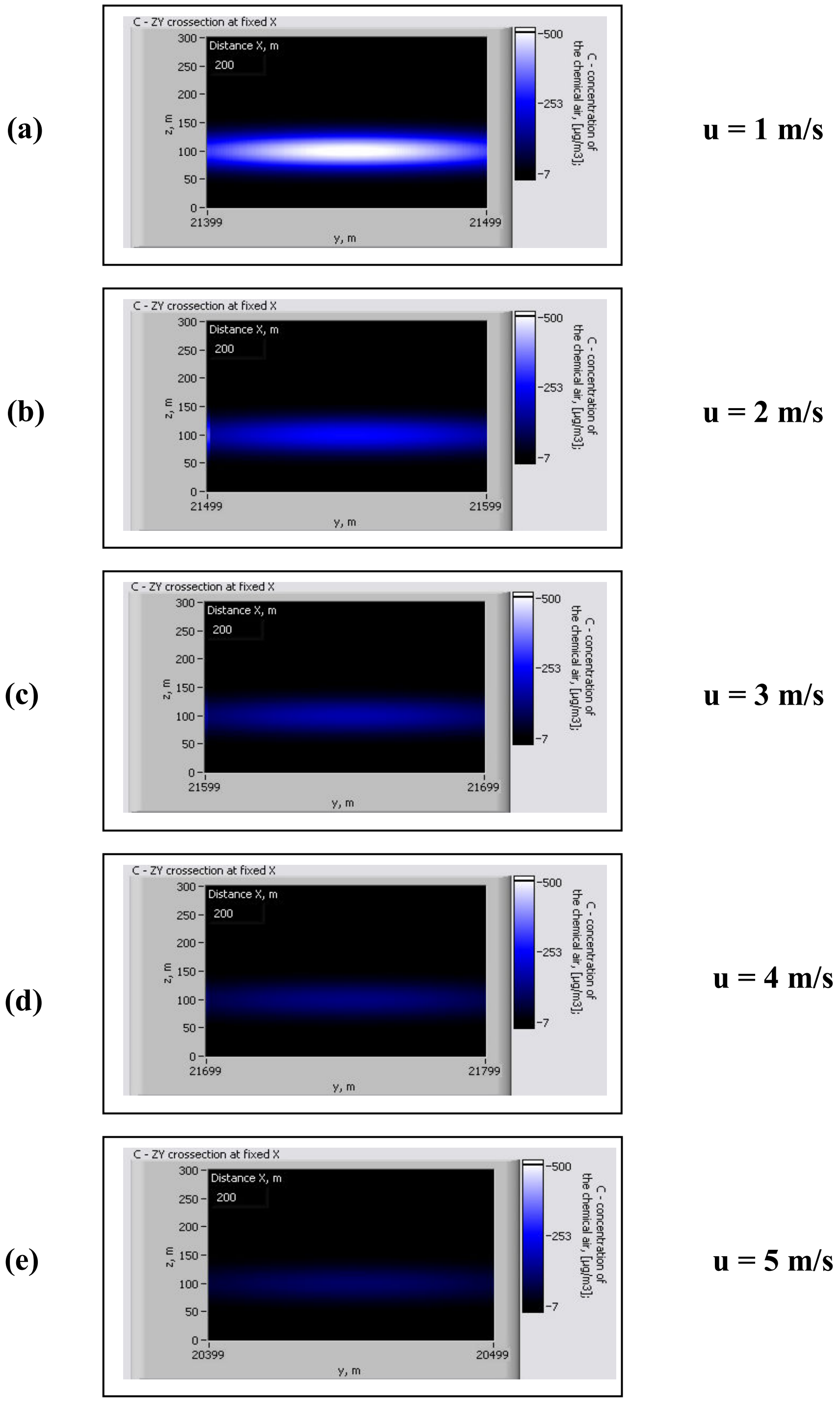


Fig. 3.17 Heavy fuel oil – glycerol emulsion combustion pollution dispersion related to alternation in wind speed (plume crossection)

The HFO-G emulsion concentration is significantly lower than for pure HFO. This is clear reflected by the plume crossections for these fuels. As it can be seen from Fig. 3.15 picture (e), high wind speed stipulates the lower concentration intensity. This is visualized by dark blue color. There is no zones of high concentration intensity (white color), except for small wind speed (u = 1 m/s).

3.4. CONCLUSIONS

1. During the fuel combustion process a pollution plume is formed. A plume is the region of a space containing the gases and particulates released from a smokestack as fuel is burnt.
2. The pollution dispersion modeling is performed based on the Gaussian equation and computer-based program LabVIEW.
3. The objective of this simulation study is to investigate the effect of two variables - atmospheric stability (Pasquill stability classes A-F) and wind speed (1-5 m/s) - on the downwind transport of the pollutants, to observe which type of atmosphere, from stable to unstable, has more effect downwind from the smokestacks.
4. To get more clear pollution dispersion scenery, the pollution plume is presented from top and side view, also the plume crossection is given.
5. The obtained simulation results express the distribution of the dispersed concentration averages with regard to the plume centerline.
6. The atmospheric condition, described as stability class “E” or slightly stable, causes the pollution plume to travel fastest and longest distance along downwind direction.
7. The highest pollution concentration in the plume is observed near the pollution source and under very unstable (class “A”) atmospheric conditions. In a case of very unstable atmospheric conditions the pollution disperses mostly in vertical direction, meanwhile, the more stable atmospheric conditions, the larger polluted area along x axis in downwind direction is observed.
8. Simulation results denote, that the lower concentration leads to a significantly smaller polluted area, and lower dispersion intensity consequently.
9. The pollution plume dispersion dependency on wind speed is tested in a range of u = 1-5 m/s for Pasquill stability class “A”. It is observed, that strong wind drags pollution torch, enhances dynamic convection so pollution concentration decreases. This results in a lower downwind concentration, the area contaminated inreases.

4. GENERAL CONCLUSIONS AND RECOMMENDATIONS

General conclusions

1. Analysis of biodiesel situation shows, that with the substantial increases in biodiesel output, there is inevitably proportionate increase in glycerol volumes. This could saturate market and significantly reduce profitability for the biodiesel use.
2. The expansion of biodiesel production worldwide is driving down the value of glycerol and reducing by-product revenue of biodiesel and oleochemical producers. The biodiesel production costs are higher than those of mineral diesel, therefore only efficient use of by-products could enable biodiesel compete with coventional diesel in respect of production costs. To ensure the future of this biofuel technology, the new outlets must be found for this by-porduct.
3. Lithuania, according to the EU Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport requirements also promotes biodiesel production and consumption. According to the commitments to EU, at least ~ 40.000 tons of biodiesel should be supplied to the market in 2010, and this would lead to 4.000 tons of glycerol. Recently, major part of produced glycerol is stored in the repositories.
4. The heavy fuel oil still is one of the most popular types in the major heat supply and industrial boiler-houses in Lithuania. Currently, according to the norm LAND 43-2001 “Norms for the exhaust of pollutants from large fuel burning equipment“, SO_2 emission level can not exceed value of 1 700 mg/Nm^3. In such a case, heavy fuel oil with sulphur content ~ 2.2 % could be combusted in large fuel combustion equipment only if combined with at least 50-55 % of biofuel. The biodiesel, produced from rape seed, does not emit sulphur compounds during the combustion process.
5. During laboratory and pilot investigations a stable heavy fuel oil – glycerol emulsion was obtained and its formation conditions were established. Laboratory and pilot plant experiments allowed to optimize the emulsion composition containing < 10 % water and to estimate the optimal heavy fuel oil and glycerol mixing ratio 1:1.
6. One of the important topics in emulsion formation – maintenance of its stability and homogeneity. The microscopic investigation indicated that the prepared emulsion is homogenous if freshly made, thus after some irregular time period the aggregation process breaks down the homogeneity. It was estimated, that after the mechanical activation the emulsion homogeneity is reinstated.

7. The emulsion X-ray diffraction pattern analysis of crystalline structure of emulsion and computer-based quantitative impurity analysis indicated compound of the $Na_5P_3O_{10}$ composition present in emulsion ash.
8. During the highly sulphurous heavy fuel oil combustion process the observed SO_2 emission concentration values significantly exceed admissible value, due to high sulphur content by mass in heavy fuel oil operational in this investigation. The observed average SO_2 concentration value is 3139.6 mg/Nm^3, meanwhile SO_2 MAC value is 1700 mg/Nm^3. Meanwhile, heavy fuel oil – glycerol emulsion combustion indicate a significant decrease in SO_2 emission concentration. The measured average concentration was only 727.1 mg/Nm^3, meanwhile for pure heavy fuel oil it is 3-4 times higher.
9. However, the substantial SO_2 emission problem is solved along with a slight increase (~ 10 %) in NO_x emission concentration. Though the measured average value 618.8 mg/Nm^3 for heavy fuel – oil emulsion combustion process does not exceed MAC value 700 mg/Nm^3, some high concentration peaks are obtained during the measurements (902.6 – 904.1 mg/Nm^3).
10. During HFO-G emulsion combustion process measured average concentration for CO (1758.1 mg/Nm^3) and particulate matter (740.2mg/Nm^3) do not exceed their estimated maximum admissible values. The observed CO concentration value is more than two times less than the norm for burning solid biofuel (2250 mg/Nm^3), so the emissions into the atmosphere should be limited according to PM levels.
11. Due to the insufficient temperature and some technical obstacles in some points of measurements, the obtained concentration values exceeded the allowable ones, but the average concentration values were lower than their MAC values. The attainment of sufficient temperature in the boiler plays a siginificant role for a complete emulsion combustion process. The investigations indicated that ~ 850°C (operational temperature of thermal oxidizing boiler) is not sufficient for complete combustion process and should be increased if possible.
12. The investigations approved the possibility for heavy fuel oil – glycerol usage as a fuel in industrial boiler-houses for heat production
13. It was determined that glycerol could be used to plasticize sulphur for its use in sulphur concretes. Thus, the broader further investigations are required.
14. The technological regulation which provides technical data for heavy fuel oil – glycerol emulsion preparation and combustion conditions was prepared on the bases of the investigations carried out at JSC “Rietavo veterinarinė sanitarija” and VGTU Institute of Thermal Insulation.
15. A pollution dispersion simulation model for a point source emission was developed to estimate pollutant concentration distribution in the downwind direction. The model is based on the

Gaussian equation. The option of using different Pasquill stability classes and alternation in wind velocities is included in the model. Simulation results denote, that the lower concentration leads to a significantly smaller polluted area, and a lower dispersion intensity consequently.

Recommendations

1. To use heavy fuel oil – glycerol emulsion as a fuel in the heat supply and industrial boiler-houses for heat production.
2. It is recommended to use optimal heavy fuell oil and glycerol mixing ratio 1:1 for the emulsion preparation and emulsification temperature t > 70°C up to the complete homogeneity. The mechanical activation reinstates emulsion homogeneity if it's necessary.
3. It is recommended to increase temperature in boiler during combustion process, at least up to 950°C. The experiments in such temperature were not carried out in this work, but due to the fact that combustion process in 850°C gives an incomplete combustion products and increment in emission concentrations in exhaust flue gas, and according to the data, found in the literature, it is recommended to provide combustion process in higher temperatures if possible.
4. To take into account the prepared technological regulation which provides technical data for heavy fuel oil – glycerol emulsion preparation and combustion conditions. The technical conditions could be adjusted to a particular company considering boiler construction, operational burner types and boiler capacity.

REFERENCES

1. Biodiesel: Overview of global production and policy, 2006. Department of Agriculture and Food Government of Western Australia [searched 2007-05-15]. Internet approach: http://www.agric.wa.gov.au/pls/portal30/docs/FOLDER/IKMP/SUST/BIOFUEL/200511_BDWorldOverview.pdf.
2. Biodiesel 2020: A global market survey, 2006. Emerging Markets Online (EMO) [searched 2007-04-10]. Internet approach: http://www.emerging-markets.com/biodiesel/press.htm.
3. "Biodiesel car review", *Renew Magazine*, Alternative Technology Association, Issue 79, 2002.
4. Biodiesel, 2006. EUBIA (European Biomass Industry Association) [searched 2007-04-14]. Internet approach: http://p9719.typo3server.info/214.0.html.
5. EU: Biodiesel Industry Expanding Use of Oilseeds, 2003. Production Estimates and Crop Assessment Division Foreign Agricultural Service [searched 2007-04-10]. Internet approach: www.biodiesel.org/resources/reportsdatabase/ reports/gen/20030920_gen330.pdf
6. The EU Strategy on Biofuels: from field to fuel, 2006. The United Kingdom Parliament [searched 2007-04-10]. Internet approach: http://www.publications.parliament.uk/pa/ld200506/ldselect/ldeucom/267/26704.htm.
7. Overview, 2007. Biopetrol Industries AG [searched 2007-05-10]. Internet approach: http://www.biopetrol-ind.com/prod_uebersicht_e.htm.
8. Directive 2003/30/EC of the European Parliament and the Council of 8 May 2003 on the promotion of the use of Biofuels or other renewable fuels for transport.
9. Lietuvos Respublikos Biokuro, biodegalų ir bioalyvų įstatymas Nr. VIII-1875 (Valstybės Žinios, 2000, Nr.64 – 1940). Priimtas 2004 m. vasario 5 d. Lietuvos Respublikos Biokuro įstatymo pakeitimo įstatymu Nr. IX-1999 (Valstybės Žinios, 2004, Nr. 28-870).
10. Lietuvoje plečiama biodegalų gamyba, 2006. Lietuvos agrarinės ekonomikos institutas [searched 2007-05-15]. Internet approach: http://eko.laei.lt/index.php?option=com_content&task=view&id=293&Itemid=36.
11. Biokuro gamybos ir naudojimo skatinimo 2004 – 2010 metais programa. Patvirtinta Lietuvos Respublikos Vyriausybės 2004 m. rugpjūčio 26 d. nutarimu Nr. 1056 (Valstybės Žinios, 2004, Nr.133 – 4786)
12. Kalnaitienė, J. Back to basics with Biofuel. *Lithuania in the world*. Vol. 14, No 4, 2006.
13. Diesel. Wikipedia, the free encyclopedia [searched 2006-11-10]. Internet approach: http://en.wikipedia.org/wiki/Diesel.

14. Energy of future: renewable sources of energy. White Paper for a Community Strategy and Action plan. Communication from the Commission (COM/97)0599-0047/98).
15. Products, 2003. LUKOIL Oil Company [searched 2007-04-14]. Internet approach: http://www.lukoil.lt/en/products.
16. Biodiesel and your vehicle, Journey to Forever [searched 2006-11-10]. Internet approach: http://journeytoforever.org/biodiesel_vehicle.html
17. Benefits of Biodiesel, 2004. National Biodiesel Board [searched 2006-11-11]. Internet approach: http://www.biodiesel.org/pdf_files/fuelfactsheets/Benefits%20of%20Biodiesel.Pdf.
18. "Biodiesel as Automobile", 2007. Central Pollution National Board [searched 2007-04-15]. Internet approach: http://www.cpcb.nic.in/diesel/ch30902.htm.
19. Mikkelsen, J. Biodiesel engine testing MECH-457 Final report, 2005 [searched 2006-12-11]. Internet approach: http://www.sustain.ubc.ca/pdfs/seeds_05/winter/Biodiesel%20Engine%20Testing_Mech%20457%20Final%20Report.pdf.
20. Problems with and Disadvantages of Biodiesel, 2007. BDPedia - Biodiesel WWW Encyclopedia [searched 2007-05-19]. Internet approach: http://www.bdpedia.com/biodiesel/alt/alt.html.
21. McCormick, R.L.; Alleman, T.L. Impact of Biodiesel Fuel on Pollutant Emissions from Diesel Engines. National Renewable Energy Laboratory [searched 2007-05-15]. Internet approach: http://www.uidaho.edu/bioenergy/BiodieselEd/publication/05.pdf.
22. "How biodiesel works", 2007. HowStuffWorks [searched 2007-01-20]. Internet approach: http://auto.howstuffworks.com/biodiesel.htm.
23. A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions. Environmental Protection Agency. US EPA Draft Technical Report 420-P-02-001; National Service Center for Environmental Publications: Cincinnati, OH, October 2002.
24. Biodiesel FAQs., 2007. National Biodiesel Board [searched 2007-04-15]. Internet approach: http://www.biodiesel.org/resources/faqs/.
25. Zappi, M.; Hernandez, R.; Sparks, D.; Horne, J.; Brough, M. A review of the engineering Aspects of the Biodiesel Industry", MSU E-TECH Laboratory Report, ET-03-003, Mississippi University Consortium for the Utilization of Biomass MSU Environmental Technology Research and Application Laboratory, 2003.
26. Ma, F.; Hanna, M.A. Biodiesel production: a review. *Bioresource Technology* V70, 1999. p. 15.

27. Van Gerpen, J.H. “Biodiesel production and fuel quality”, 2005. University of Idaho [searched 2006-11-16]. Internet approach: http://www.uidaho.edu/bioenergy/biodieselED/publication/01.pdf
28. Informacinis leidinys “Biodegalų gamyba ir naudojimas Lietuvoje“, 2004. Lietuvos energetikos institutas.
29. Janulis, P.; Makarevičienė, V. Biodegalų ir bioalyvų naudojimas Lietuvoje. Vilnius: LŽŪU leidybos centras, 2004. 13 p.
30. Liubarskis, V.; Burneika, G. „Biodegalų gamyba ir naudojimas“. LŽŪU Žemės ūkio inžinerijos institutas. Raudondvaris, 2003. 28 p.
31. Biodiesel production and economics, 2006. Department of Agricultute and Food Government of Western Australia [searched 2007-05-15]. Internet approach: http://www.agric.wa.gov.au/servlet/page?_pageid=449&_dad=portal30&_schema=PORTAL30&p_start_url=/pls/portal30/docs/folder/ikmp/sust/biofuel/biofuels_biodiesel_2007.htm
32. Shaine Tyson, K.; Bozell, J.; Wallace, R.; Petersen, E.; Moens, L. „Biomass Oil Analysis: Research Needs and Recommendations“. National Renewable Energy Laboratory Technical report, 2004.
33. Duncan, J. Costs of Biodiesel Production, 2003. Report prepared for Energy Efficiency and Conservation Authority [searched 2006-12-12]. Internet approach: http://www.esru.strath.ac.uk/EandE/Web_sites/02-03/biofuels/what_biodiesel.htm
34. Meghan, K.R. Biofuels: Production processes, 2007. Issues in agricultural biotechnology [searched 2007-05-05]. Internet approach: http://home.cc.umanitoba.ca/~umrose/PLNT4600/mini3/mini3.1.html.
35. Bulan, C.A. Biodiesel as an alternative fuel leading to cleaner environment, 2004. Chemicals and Mineral Division-Industrial Technology Development Institute Department of Science and Technology, DOST Compound, Bicutan, Taguig, Metro Manila, Philippines [searched 2007-05-15]. Internet approach: http://www.cleanairnet.org/baq2003/1496/articles-58089_resource_1.doc
36. He, B. „Biodiesel By-Products Research Produces Promising Results“, 2003. University of Idaho [searched 2006-12-16]. Internet approach: http://www.newswise.com/articles/view/501981/.
37. Uses for canola meal, 2007. Department of Agriculture and Food Government of Western Australia [searched 2007-05-15]. Internet approach: http://www.agric.wa.gov.au/servlet/page?_pageid=449&_dad=portal30&_schema=PORTAL30&p_start_url=/pls/portal30/docs/folder/ikmp/sust/biofuel/biofuels_biodiesel_2007.htm.

38. Janulis, P.; Makarevičienė, V. Biodyzeliniai degalai: gamyba, kokybė, perspektyvos. Mokslas *ir gyvenimas* 2001/6. 15 p.
39. Schröder, A.; Südekum, K.H. Glycerol as a by-product of biodiesel production in Diets for ruminants. Institute of Animal Nutrition, Physiology and Metabolism, University of Kiel, 24098 Kiel, Germany [searched 2007-05-20]. Internet approach: http://www.regional.org.au/au/gcirc/1/241.htm.
40. Glycerol. Wikipedia, the free encyclopedia [searched 2006-11-10]. Internet approach: http://en.wikipedia.org/wiki/Glycerin.
41. Maneely, T. Glycerol production and utilization. Biodiesel one – day course. From field to fuel, 2006. University of Idaho [searched 2007-05-12]. Internet approach: http://www.uidaho.edu/bioenergy/Feild2fuel_cda06/Tim_Glycerol%20biodiesel%20course%20061506_2.pdf.
42. Fulton, L. Biofuel costs and market impacts in the transport sector, 2005. Principal Administrator *Energy Technology Policy Division.* ENERGY PRICES & TAXES, 1st Quarter 2005 [searched 2007-05-14]. Internet approach: http://data.iea.org/ieastore/assets/products/eptnotes/feature/FTR05Q1A.pdf.
43. Biodiesel production and economics, 2006. Department of Agricultute and Food Government of Western Australia [searched 2007-05-15]. Internet approach: http://www.agric.wa.gov.au/servlet/page?_pageid=449&_dad=portal30&_schema=PORTAL30&p_start_url=/pls/portal30/docs/folder/ikmp/sust/biofuel/biofuels_biodiesel_2007.htm.
44. Uses for Methyl esters, Glycerol. National Biodiesel Board [searched 2007-05-12]. Internet approach: http://www.nationalbiodieselboard.org/resources/reportsdatabase/reports/gen/19960901_gen-051.pdf.
45. Claude, S. "Research of New Outlets for Glycerol – Recent Developments in France", Lipid, 1999. p. 101-104.
46. Bjørnar, K.S.; Grinna, C.B. Hydrogen Status og muligneter Bellona rapport Nr. 6 , 2002. The Bellona Foundation [searched 2007-05-20]. Internet approach: http://www.bellona.org/filearchive/fil_Hydrogen_6-2002.pdf
47. Pachauri, N.; He, B. Value-added Utilization of Crude Glycerol from Biodiesel Production: A Survey of Current Research Activities, 2006. An ASABE Meeting Presentation Paper Number: 066223 [searched 2007-04-28]. Internet approach: http://www.webpages.uidaho.edu/~bhe/pdfs/asabe066223.pdf.

48. Thiruchitrambalam, V. “Hydrogen or Syn Gas Production from Glycerol Using Pyrolysis and Steam Gasification Processes”, 2004. University of Saskatchewan Saskatoon, Saskatcewan.
49. Rapagna, S.; Jand, N. Foscolo U.P. “Catalytic gasification biomass to produce hydrogen rich gas”. *International Journal Hydrogen Energy 23, 1998.* p. 551-557.
50. Chaudari, S.T.; Bakhshi, N.N. “Steam gasification of chars and bio-oils”. Report to Bioenergy development program renewable energy branch, Energy, Mines and resources Canada, Ottawa, Canada, 2002. p. 396-436.
51. Antal, M.J.; Mok, W.S.L.; Roy, J.C.; Raissi, A.T. “Pyrolytic sources of hydrocarbons from biomass”. *Journal of analytical and applied pyrolysis 8*, 1985. p. 291-303.
52. Franco, C.; Pinto, F.; Gulyurtlu, I.; Cabrita, I. “The study of reactions influencing Biomass steam gasification process”. *Fuel 82*, 2003. p. 835-842.
53. Czernik, S.; French, R.; Feik, C.; Chornet, E. “Production of hydrogen from biomass-derived liquids”, 2002. Proceedings of the 2000 DOE Hydrogen program review.
54. Davda, R.R.; Shabaker, J.W.; Huber, G.W.; Cortright, R.D.; Dumesic, J.A. “Aqueous-phase reforming of ethylene glycol on silica-supported metal catalysts”. *Applied catalysis B: environemental 43*, 2003. p. 13-26.
55. Conversion of Glycerol Stream in a Biodiesel Plant, 2006. Virent Energy Systems, Inc. [searched 2007-01-18]. Internet approach: http://www.virent.com/whitepapers/Biodiesel%20Whitepaper.pdf.
56. Cortright, R.D.; Davda, R.R.; Dumesic, J.A. “Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water”. *Nature 418*, 2002. p. 964-967.
57. Lee, C.S; Park, S.W.; Kwon, S.I. “An Experimental Study on the Atomization and Combustion Characteristics of Biodiesel-Blended Fuels”. Energy and Fuels. American Chemical Society: 2005, 19, p. 2201-2208.
58. Yong, K.C.; Dzulkefly, T.L.; Hazimah, W.Y. “Refining of crude glycerol recoevered from glycerol residue by simple vacuum distillation introduction”. *Journal of oil palm research* Vol. 13 No. 2, 2001. p. 39-44.
59. Pachauri, N.; He, B. Value-added Utilization of Crude Glycerol from Biodiesel Production: A Survey of Current Research Activities, 2006. An ASABE Meeting Presentation Paper Number: 066223 [searched 2007-01-25]. Internet approach: http://www.webpages.uidaho.edu/~bhe/pdfs/asabe066223.pdf.
60. List of UV filters which cosmetic products may contain. Part V – List of UV Filter Which Cosmetic Products May Contain [searched 2007-02-18]. Internet approach: http://www.aseancosmetics.org/docdocs/AppendixVIIPart5.pdf.

61. Atmospheric dispersion modeling. Wikipedia, the free encyclopedia [searched 2007-05-20]. Internet approach: http://en.wikipedia.org/wiki/Atmospheric_dispersion_modeling.
62. Aplinkos oro kokybės vertinimas naudojant modelius. Aplinkos apsaugos agentūra, 2005. p.11
63. Vyriausybės nutarimas 2001 m. rugsėjo mėn. 28 d. Nr. 486 „Dėl išmetamų teršalų ir didelių kurą deginančių įrengimų normų ir išmetimų teršalų iš kurą deginančių įrengimų normų LAND 43-2001 nustatymo“ (Žin., 2001, Nr. 88-3100).
64. Hanawal Search Manual, Inorganic Phases, International Centre for Diffraction Data Sets 1-48,1998.
65. Diffraction analysis equipment, PDWIN software package, 2006. BOUREVESTNIK Inc. [searched 2006-12-21]. Internet approach http://www.bourevestnik.com/products/rproduct015.htm.
66. Karademir, A. Evaluation of the potential air pollution from fuel combustion in industrial boilers in Kocaeli, Turkey, 2006. Environment Technical Information Service [searched 2007-05-20]. Internet approach: http://www.aseanenvironment.info/Abstract/41012986.pdf.
67. Shepard, W.L. Corrosion and chemical resistant masonry materials handbook. New Jersey: Noyes Publications, 1986. p. 8-15.
68. Datez, D.; Pantel, R.H. Environmental modeling: analysis and management, Dowden, Hutchinson & Ross, 1974. p. 156-163
69. Hemond, H.F.; Fechner. E.J. Chemical fate and transport in the environment, Academic press, 1994. p. 273-278.
70. Henry, J.G.; Heinke, G.W. Environmental science and engineering, Prentice Hall, 1989. p. 525-529.

ANNEXES

PUBLISHED ARTICLES

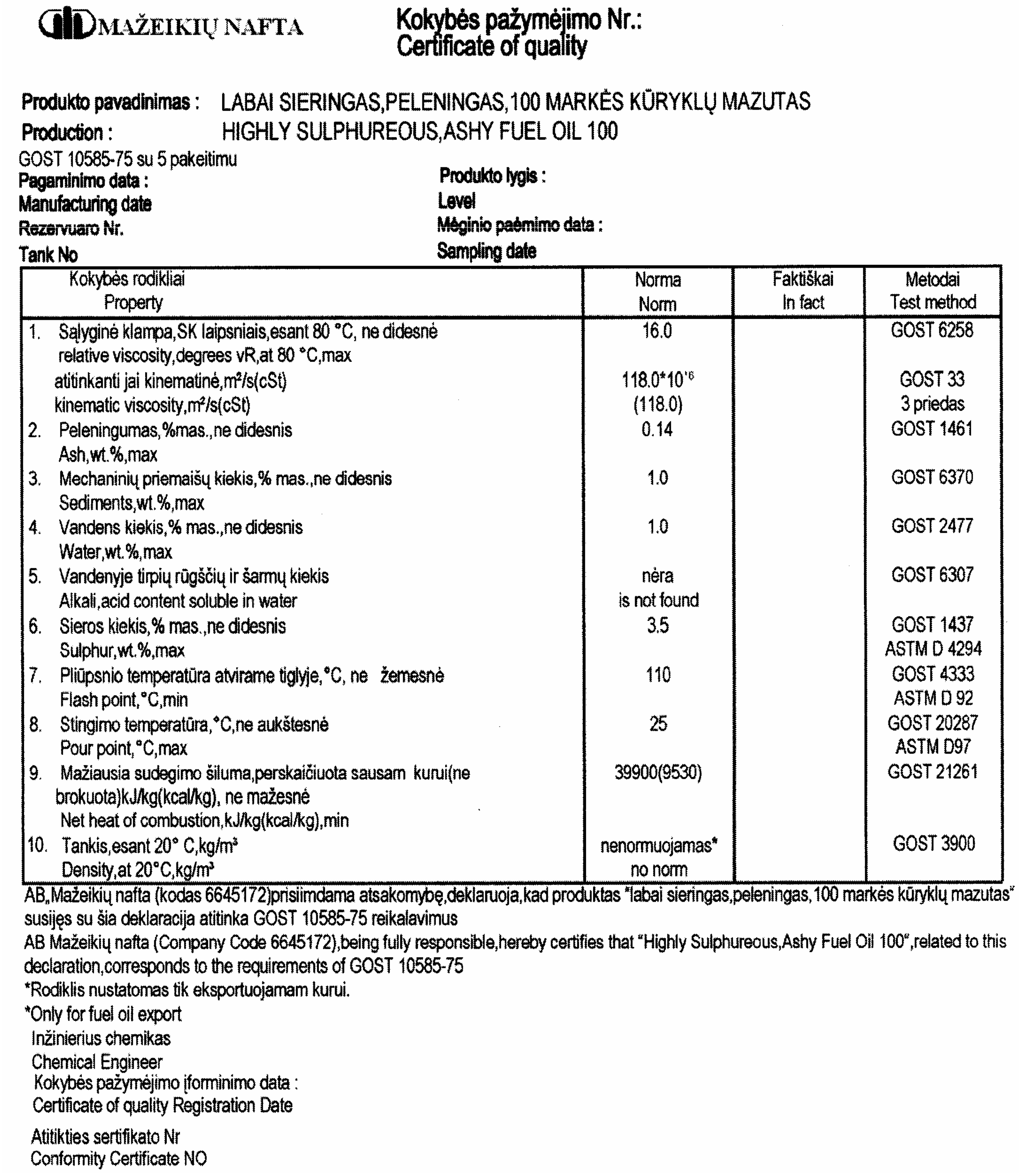
Articles

1. D.Stepanonytė, J.J.Blynas. „A thermodynamical assessment of carbamide use for reduction of boiler NO_x, CO flue gas emissions“ („Termodinaminis katilinių išmetamųjų dujų NO_x ir CO taršos nukenksminimo proceso su karbamidu įvertinimas“). Presented for publishing in *Journal of environmental engineering and landscape management.*
2. D.Stepanonytė, J.J.Blynas. „Analysis of biodiesel production process by-product utilization in Europe“ („Biodyzelino gamybos proceso šalutinių produktų panaudojimo Europoje analizė“). Aplinkos apsaugos inžinerija (2006 m. kovo 30 d.). 9-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ pranešimų medžiaga. Vilnius: Technika, 2006. p. – 468-474.
3. D.Stepanonytė, A.Zigmontienė. „A thermodynamical assessment of carbamide usage for reduction of boiler NO_x flue gas emissions“ („Termodinaminis katilinių išmetamųjų dujų NO_x taršos kenksmingumo naikinimo proceso karbamidu įvertinimas“). 10 -osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ pranešimų medžiaga 2007 m. kovo 29 d.

Presented articles

1. D.Stepanonytė, J.J.Blynas. „Analysis of biodiesel production process by-product utilization in Europe“ („Biodyzelino gamybos proceso šalutinių produktų panaudojimo Europoje analizė“). 9-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ pranešimų medžiaga
2. D.Stepanonytė, A.Zigmontienė. „A thermodynamical assessment of carbamide usage for reduction of boiler NO_x flue gas emissions“ („Termodinaminis katilinių išmetamųjų dujų NO_x taršos kenksmingumo naikinimo proceso karbamidu įvertinimas“). 10 -osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ pranešimų medžiaga 2007 m. kovo 29 d.

ANNEX 2



MAŽEIKIŲ NAFTA

Kokybės pažymėjimo Nr.:
Certificate of quality

Produkto pavadinimas : LABAI SIERINGAS,PELENINGAS,100 MARKĖS KŪRYKLŲ MAZUTAS
Production : HIGHLY SULPHUREOUS,ASHY FUEL OIL 100
GOST 10585-75 su 5 pakeitimu

Pagaminimo data :
Manufacturing date
Rezervuaro Nr.
Tank No

Produkto lygis :
Level
Mėginio paėmimo data :
Sampling date

Kokybės rodikliai Property	Norma Norm	Faktiškai In fact	Metodai Test method
1. Sąlyginė klampa,SK laipsniais,esant 80 °C, ne didesnė relative viscosity,degrees vR,at 80 °C,max	16.0		GOST 6258
atitinkanti jai kinematinė,m^2/s(cSt) kinematic viscosity,m^2/s(cSt)	118.0*10^{-6} (118.0)		GOST 33 3 priedas
2. Peleningumas,%mas.,ne didesnis Ash,wt.%,max	0.14		GOST 1461
3. Mechaninių priemaišų kiekis,% mas.,ne didesnis Sediments,wt.%,max	1.0		GOST 6370
4. Vandens kiekis,% mas.,ne didesnis Water,wt.%,max	1.0		GOST 2477
5. Vandenyje tirpių rūgščių ir šarmų kiekis Alkali,acid content soluble in water	nėra is not found		GOST 6307
6. Sieros kiekis,% mas.,ne didesnis Sulphur,wt.%,max	3.5		GOST 1437 ASTM D 4294
7. Pliūpsnio temperatūra atvirame tiglyje,°C, ne žemesnė Flash point,°C,min	110		GOST 4333 ASTM D 92
8. Stingimo temperatūra,°C,ne aukštesnė Pour point,°C,max	25		GOST 20287 ASTM D97
9. Mažiausia sudegimo šiluma,perskaičiuota sausam kurui(ne brokuota)kJ/kg(kcal/kg), ne mažesnė Net heat of combustion,kJ/kg(kcal/kg),min	39900(9530)		GOST 21261
10. Tankis,esant 20° C,kg/m^3 Density,at 20°C,kg/m^3	nenormuojamas* no norm		GOST 3900

AB„Mažeikių nafta (kodas 6645172)prisiimdama atsakomybę,deklaruoja,kad produktas "labai sieringas,peleningas,100 markės kūryklų mazutas" susiję su šia deklaracija atitinka GOST 10585-75 reikalavimus

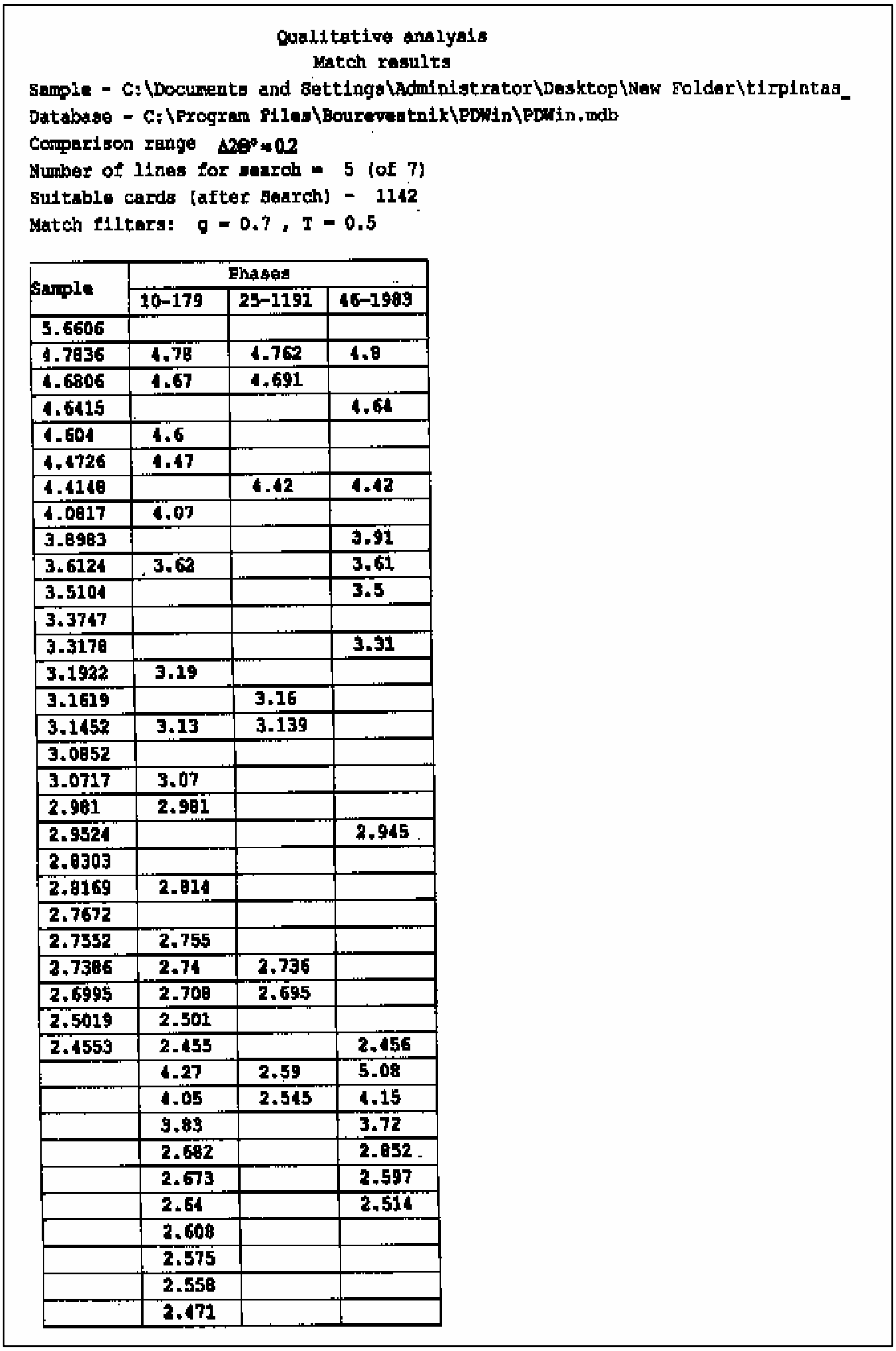
AB Mažeikių nafta (Company Code 6645172),being fully responsible,hereby certifies that "Highly Sulphureous,Ashy Fuel Oil 100",related to this declaration,corresponds to the requirements of GOST 10585-75

*Rodiklis nustatomas tik eksportuojamam kurui.
*Only for fuel oil export

Inžinierius chemikas
Chemical Engineer
Kokybės pažymėjimo įforminimo data :
Certificate of quality Registration Date

Atitikties sertifikato Nr
Conformity Certificate NO

ANNEX 3



Qualitative analysis

Match results

Sample - C:\Documents and Settings\Administrator\Desktop\New Folder\tirpintas_

Database - C:\Program files\Bourevestnik\PDWin\PDWin.mdb

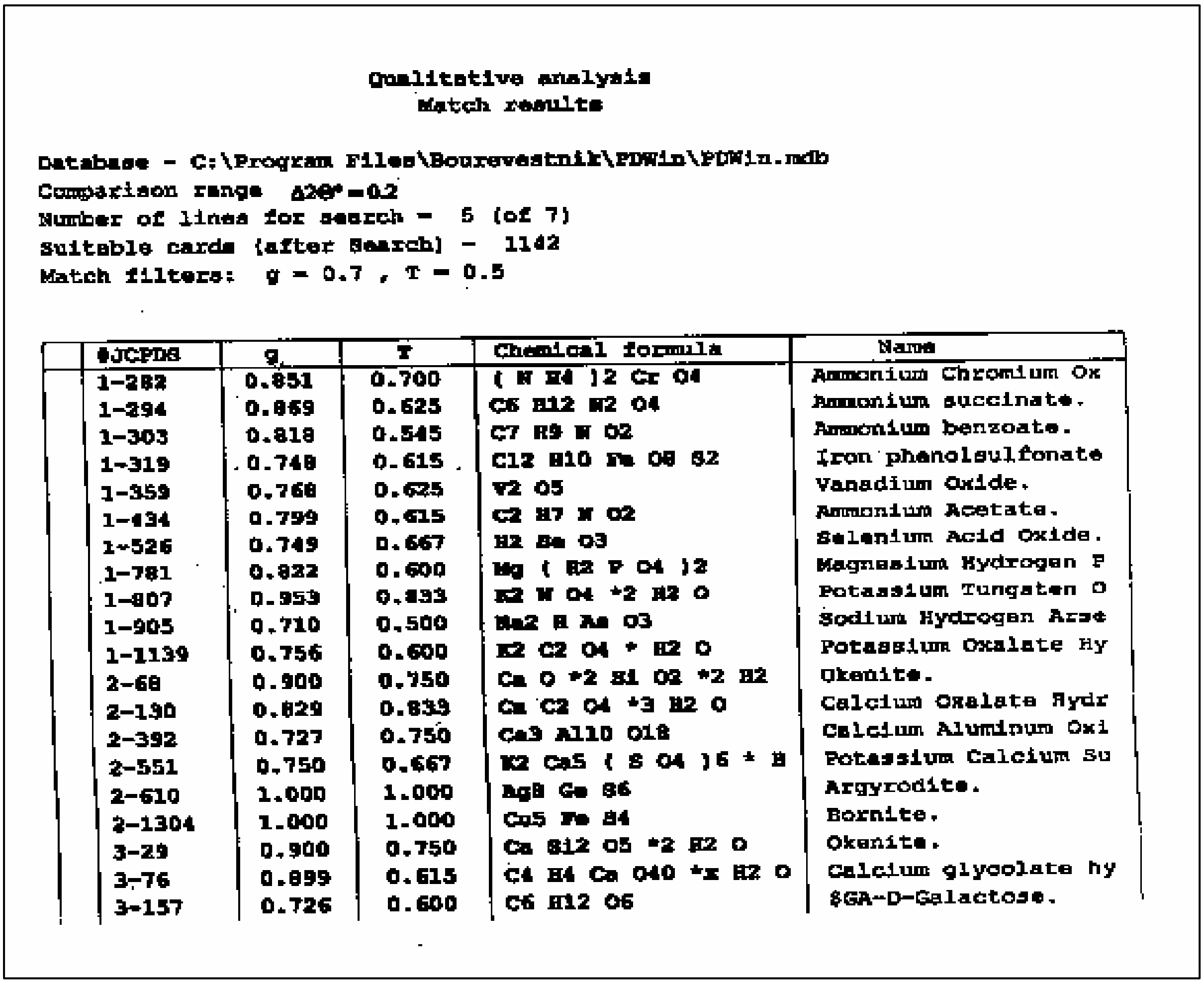
Comparison range $\Delta 2\theta^\circ = 0.2$

Number of lines for search = 5 (of 7)

Suitable cards (after Search) - 1142

Match filters: g - 0.7 , T - 0.5

Sample	Phases		
	10-179	25-1191	46-1983
5.6606			
4.7836	4.78	4.762	4.8
4.6806	4.67	4.691	
4.6415			4.64
4.604	4.6		
4.4726	4.47		
4.4148		4.42	4.42
4.0817	4.07		
3.8983			3.91
3.6124	3.62		3.61
3.5104			3.5
3.3747			
3.3178			3.31
3.1922	3.19		
3.1619		3.16	
3.1452	3.13	3.139	
3.0852			
3.0717	3.07		
2.981	2.981		
2.9524			2.945
2.8303			
2.8169	2.814		
2.7672			
2.7552	2.755		
2.7386	2.74	2.736	
2.6995	2.708	2.695	
2.5019	2.501		
2.4553	2.455		2.456
	4.27	2.59	5.08
	4.05	2.545	4.15
	3.83		3.72
	2.682		2.852
	2.673		2.597
	2.64		2.514
	2.608		
	2.575		
	2.558		
	2.471		



Qualitative analysis
Match results

Database - C:\Program Files\Bourevestnik\PDWin\PDWin.mdb
Comparison range $\Delta 2\theta^{\circ} = 0.2$
Number of lines for search - 5 (of 7)
Suitable cards (after Search) - 1142
Match filters: g - 0.7 , T - 0.5

	#JCPDS	g	T	Chemical formula	Name
	1-282	0.851	0.700	(N H4)2 Cr O4	Ammonium Chromium Ox
	1-294	0.869	0.625	C6 H12 N2 O4	Ammonium succinate.
	1-303	0.818	0.545	C7 H9 N O2	Ammonium benzoate.
	1-319	0.748	0.615	C12 H10 Fe O8 S2	Iron phenolsulfonate
	1-359	0.768	0.625	V2 O5	Vanadium Oxide.
	1-434	0.799	0.615	C2 H7 N O2	Ammonium Acetate.
	1-526	0.749	0.667	H2 Se O3	Selenium Acid Oxide.
	1-781	0.822	0.600	Mg (H2 P O4)2	Magnesium Hydrogen P
	1-807	0.953	0.833	K2 W O4 *2 H2 O	Potassium Tungsten O
	1-905	0.710	0.500	Na2 H As O3	Sodium Hydrogen Arse
	1-1139	0.756	0.600	K2 C2 O4 * H2 O	Potassium Oxalate Hy
	2-68	0.900	0.750	Ca O *2 Si O2 *2 H2	Okenite.
	2-130	0.829	0.839	Ca C2 O4 *3 H2 O	Calcium Oxalate Hydr
	2-392	0.727	0.750	Ca3 Al10 O18	Calcium Aluminum Oxi
	2-551	0.750	0.667	K2 Ca5 (S O4)6 * H	Potassium Calcium Su
	2-610	1.000	1.000	Ag8 Ge S6	Argyrodite.
	2-1304	1.000	1.000	Cu5 Fe S4	Bornite.
	3-29	0.900	0.750	Ca Si2 O5 *2 H2 O	Okenite.
	3-76	0.899	0.615	C4 H4 Ca O40 *x H2 O	Calcium glycolate hy
	3-157	0.726	0.600	C6 H12 O6	$GA-D-Galactose.

ANNEX 5

MAZUTO EMULSIJOS MODIFIKUOTOS GLICEROLIO PRIEDU

TECHNINIS

REGLAMENTAS

Šis reglamentas skirtas modifikuotai mazuto emulsijai paruošti ir sudeginti UAB „Rietavo veterinarinė sanitarija“ katilinėje. Atsižvelgiant į katilų konstrukcijas, naudojamus degiklių tipus ir katilų galią. Kitiems vartotojams techninės sąlygos bus koreguojamos.

I.BENDROSIOS NUOSTATOS

1. **Mazuto emulsijos modifikuotos** glicerolio priedu techninis reglamentas (toliau modifikuotas mazutas) skirtas Lietuvos biokuro gamintojams ir naudotojams sudaryti galimybę pasigaminti ir deginti tokį kurą, prekiauti, užtikrinant jo kokybę ir jos kontrolę bei saugų vartojimą.
2. **Reglamentas atitinka** Nacionalinės energetikos strategijos 2002 m. spalio 10 d., patvirtintos Lietuvos Respublikos Seimo nutarimu Nr. IX-1130 „Dėl Nacionalinės energetikos strategijos patvirtinimo“ (Žin., 2002, 99-4397), Nacionalinės energijos vartojimo efektyvumo didinimo programos, 2001 m.rugsėjo 19 d. patvirtintos Lietuvos Respublikos Vyriausybės nutarimu Nr. 1211 „Dėl patikslintos ir atnaujintos Nacionalinės energijos vartojimo efektyvumo didinimo programos santraukos ir pagrindinių šios programos įgyvendinimo 2001-2005 m. krypčių“ (Žin., 2001, Nr.82-2856), Jungtinių Tautų Bendrosios klimato kaitos konvencijos įgyvendinimo nacionalinės strategijos, kuriai 1993 m. spalio 25 d. pritarė Lietuvos Respublikos Vyriausybės nutarimu Nr.1236 (Žin., 1996, Nr.105-2409), ir Nacionalinės aplinkos sveikatinimo veiksmų 2003-2006 m. programos, patvirtintos Lietuvos Respublikos Vyriausybės 2003 m. sausio 21 d. nutarimu Nr. 66 (Žin., 2003, 8-288), LR Vyriausybės nutarimas „Dėl nacionalinės darnaus vystymosi strategijos patvirtinimo ir įgyvendinimo“, 2004 m. rugsėjo mėn. 11 d. Nr.1160, nuostatos.

3. Pagrindinės Reglamento sąvokos:

GLICEROLIS – tai priedas modifikuoto biokuru mazuto emulsijai gauti ir yra tankioji biodyzelino gamybos frakcija (tankis ~ 1200 kg/m^2 netinkanti modifikuoti iš mineralinės naftos gautam dyzelinui.

MAZUTAS – tai naftos frakcija, vartojama kaip katilinių kuras.

II.MAZUTO MODIFIKUOTO GLICEROLIU APRAŠYMAS

4. Modifikuota glicerolio priedu mazuto emulsija yra kompleksinė medžiaga, susidedanti iš mazuto ir glicerolio mišinio santykiu <1:1 emulguota prie t >70°C. Mazutas – tai naftos frakcija, liekanti nudistiliavus benziną, ligroiną, žibalą ir dyzelinius degalus. Tankis nuo 890-1000 kg/m^3, o degimo šiluma 38-41 MJ/kg, be angliavandenilių mazute yra iki 60% dervų, sieros (0,8-3,5%), peleningumas 0,1-0,5%. Kai kurios mazuto (aukšto, vidutinio ir mažo sieringumo) fizinės ir cheminės savybės pateiktos 1 lentelėje.

1 lentelė. Įvairaus sieringumo mazuto fizinės ir cheminės savybės

Savybės	Daug S	Vidut. S	Mažai S
Siera, masės %	2,2	0,96	0,50
Anglis, masės %	86,25	87,11	87,94
Vandenilis, masės %	11,03	10,23	11,85
Azotas, masės %	0,41	0,26	0,16
Klampa cSt, 38°C	690	129	49
Netirpi heksane dalis, %	10,33	4,72	2,25
Pelenai, %	0,08	0,04	0,02
Metalai, ppm			
Vanadis	350	155	70
Nikelis	41	20	10
Natris	25	10	<5
Geležis	13	9	<5

Glicerolis – tai tankioji biodyzelino gamybos frakcija, gaunama vykdant transesterifikacijos procesą, taip pat žinomas kaip techninis glicerinas arba 1, 2, 3 propantriolis. Glicerinas turi daug įvairių panaudojimo sričių: maisto pramonėje, kosmetikoje, dantų pastose, vaistuose ir t.t.

Atlikus tyrimus nustatyta, kad tankioji biodyzelino frakcija glicerolio, po vandens ir metanolio išgarinimo frakcijos, klampa esant 70°C yra 250±21 mm^2/s. Po to, toliau kaitinant glicerolį, iš jo pašalinama daugiau vandens ir per 30 min. jo klampa padidėja iki 605±25 mm^2/s. Iš to galima padaryti išvadą, kad naudojant glicerolį mazuto emulsijai gauti: paduodamas į emulgavimą mazutas turi būti pakaitintas iki >70°C.

Glicerolio (tankiosios biodyzelino frakcijos) sudėtis, po metanolio ir dalinio vandens netinkamo mazuto emulgavimui priedų medžiaginės sudėties pateikta 2 lentelėje.

2 lentelė. Glicerolio frakcijos sudėtis

Rodikliai	Glicerolis (tankioji biodyzelino frakcija)
Vanduo, proc.	12,5±0,6
Glicerolis, proc.	86,8±3,6
Metanolis, proc.	0,3±0,03
RME likučiai, proc.	0,4±0,08
Tankis prie 20°C, g/cm^3	1,18±0,11

Sausai glicerolio masei bandymais nustatytas šilumingumas, sudaro 22,1±1,7 MJ/kg.

Mazuto modifikuoto gliceroliu degiosios masės tūrio, procentai:

- anglies – 63,12;
- vandenilio – 4,80;
- azoto – 0,13;
- deguonies – 27,151;

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* terminas "Žalias glicerolis" - pakeista į tankioji biodyzelino gavimo iš rapsų aliejaus, sutrumpintai - glicerolis

Pelenų kiekis apytikriai yra 1,30%

Metalų koncentracija, %

- kalis – 0,1;
- natris – 0,195;
- vanadis – 0,015;
- nikelis – 0,002;
- geležis – 0,0009.

5. Gliceroliu modifikuotas mazutas yra nesprogus, neradioaktyvus, chemiškai mažai aktyvus, jo pliūpsnio temperatūra 152°C.

III.PARUOŠIMAS

6. Modifikuotas glicerolio priedu mazuto emulsija ruošiama pakaitinus mazutą iki > 70°C temperatūros, pridėjus glicerolį emulguojamas su emulgavimo įrenginiu iki pilno homogeniškumo. Homogeniškumo laipsnis nustatomas vizualiai, žiūrint pro mikroskopą.

IV.MAZUTO MODIFIKUOTO GLICEROLIO PRIEDU KOKYBĖS RODIKLIAI

7. Kokybės rodikliams patikrinti iš deginamo modifikuoto mazuto produkcijos partijos sudaromos vidutinis bandinys (ne mažiau kaip 2 kg): Pusė vidutinio bandinio analizuojama laboratorijoje, kita pusė nustatyta tvarka įforminama ir paliekama galimiems arbitražiniams tyrimams.
8. Pagrindiniai kokybės rodikliai pateikti 3 lentelėje, o išlakų į atmosferą normos priede

3 lentelė. Pagrindiniai kokybės rodikliai

Rodiklis	Norma
Drėgmės kiekis, ne didesnis kaip, proc.	10%
Didžiausias dalelių dydis, μm	20
Modifikuoto mazuto sausosios masės:	
- šiluminė vertė, ne mažesnė kaip kcal/kg	6800
- peleningumas, ne didesnis kaip, proc.	2,0
- sieros kiekis, ne didesnis kaip, proc.	1,0
Kinetinė klampa, mm^2/s prie 80°C	2,10
- pliūpsnio temper., °C	152-159
- tankis, 20°C, kg/m^3	1,11

V.LAIKYMAS IR GABENIMAS

9. Mazuto modifikavimo priedas ir modifikuotas mazutas laikomi pagal GOST 10585-75 su 5 pakeitimu: „Labai sieringas, peleningas 100 markės kūryklų mazutas“, bei esant reikalui gabenamas.
10. Kokybės kontrolės ir kokybės rodiklių tikslumas bei vartojimas taikomuose metoduose turi atitikti Lietuvos Standarto LST EN 180 4259:1999 „Naftos produktai. Tikslumo duomenų nustatymas ir vartojimas bandymo metoduose reikalavimus.“
11. Modifikuoto mazuto kuro ir glicerolio priedo kokybę kontroliuoja ir už kokybę atsako gamintojas.

VI.PAVOJINGUMO NUSTATYMO IR PIRMOSIOS PAGALBOS PRIEMONĖS

12. Ruošiant modifikuotą mazutą ir dirbant su juo, turi būti laikomasi Lietuvos respublikos darbuotojų saugos ir sveikatos įstatymo (Žin., 2003, Nr.30-3170), kitų sveikatos apsaugą reglamentuojančių teisės aktų bei šio Reglamento reikalavimų.
13. Įkvėpus modifikuoto mazuto garų, nukentėjusįjį išvesti į gryną orą, o jeigu kvėpavimas pasunkėjęs, kreiptis į gydytoją. Patekus ant odos, plauti odą tekančiu vandeniu su muilu. Patekus į akis, akis plauti tekančiu vandeniu 10-15 min. Jeigu dirginimas nepraeina, kreiptis į gydytoją. Prarijus pirmiausia skalauti burną, stengiantis nesukelti vėmimo, ir kreiptis į gydytoją.

14. Priešgaisrinės priemonės:

vadovaujantis Bendrosiomis priešgaisrinės saugos taisyklėmis, patvirtintomis Lietuvos respublikos vidaus reiklų ministerijos 1997 m. vasario 14 d. įsakymu Nr. 59 (žin., 1997, Nr.102-2577), ir kitais priešgaisrinę saugą reglamentuojančiais teisės aktais;

modifikuoto mazuto absoliučiai sausos masės uždegimo temperatūra – 155°C, savaiminio užsidegimo – 393°C;

Modifikuoto mazuto gesinimas vandeniu, smėliu ir putomis;

asmenims, dalyvaujantiems gesinant modifikuotą mazuto kurą, rekomenduojama naudoti autonomines kvėpavimo organų apsaugos priemones.

15. Saugos priemonės:

naudoti pirštines, respiratorius ir kitas asmenines apsaugos priemones, atitinkančias Darbuotojų aprūpinimo asmeninėmis apsaugos priemonėmis nuostatų reikalavimus, patvirtintus Lietuvos Respublikos socialinės apsaugos ir darbo ministerijos 1998 m. balandžio 20 d. įsakymu Nr.77 (Žin., 1998, Nr. 43-1188);

aprūpinti darbuotojus tinkamais drabužiais, skirti jiems gamybines buities patalpas pagal Buities, sanitarinių ir higienos patalpų įrengimo reikalavimus, patvirtintus Lietuvos Respublikos Vyriausybės 2003 m. balandžio 24 d. nutarimu Nr. 501 (Žin., 2003, Nr.40-1820).

VII. PANAUDOJIMAS

16. Modifikuoto mazuto emulsijos paskirtis ir naudojimo sąlygos:

Modifikuotas mazutas naudojamas šilumos gamybai, deginant specialiai tam pritaikytuose skystojo kuro įrenginiuose, laikantis technologinių ir teisės aktais nustatytų aplinkosaugos reikalavimų;

Modifikuotas mazutas gali būti maišomas ir su kitomis skystojo kuro rūšimis. Modifikuoto mazuto priedo - glicerolio kiekis kure negali viršyti 50 %.

PRIEDAS 1

Mazuto modifikuoto gliceroliu (1:1) išlakų ribinės vertės skaičiavimas, taikant biokuro skirtas normas*

Eil. Nr.	Teršalo pavadinimas	Mazuto ribinė vertė, mg/Nm^3	Biokuro ribinė vertė*	GMK santykio 1:1 ribinė vertė	Pastabos
1	Anglies monoksidas (CO)	500	4000	2250	
2	Azoto oksidai (NO$_x$)	650	750	700	
3	Sieros dioksidas (SO$_2$)	1700	1700	1700	
4	Kiekinės dalelės (aukšto tankumo biokuras, mediena)	-	800	800	

*Vyriausybės nutarimas 2001 m. rugsėjo mėn. 28 d. Nr. 486 „Dėl išmetamų teršalų ir didelių kurą deginančių įrengimų normų ir išmetimų teršalų iš kurą deginančių įrengimų normų LAND 43-2001 nustatymo“ (Žin., 2001, Nr. 88-3100).