By-products from methyl ester oil production and their thermal-emission properties

J. Bradna[1], **J. Malaťák**[2]

[1]*Research Institute of Agricultural Engineering, Prague-Ruzyně, Czech Republic*
[2]*Faculty of Engineering, Czech University of Life Sciences in Prague, Prague, Czech Republic*

Abstract: With the exhaustion of fossil energy sources in sight, the importance of the renewable sources of energy becomes one of the major conditions for permanently sustainable development not only in agriculture, but also in the society as a whole. The growing use of biodiesel has opened other areas of utilising the by-products from the manufacture of rape seed oil methyl ester (FARME) as an energy source, used in the combustion equipment designed for these alternative fuels. The aim of this paper is to assess the feasibility of utilising the by-products from the production of rape seed methyl ester as a source of energy, from ecology and economy aspects of the combustion equipment used. Therefore, the study is focused on the concentration of emissions generated by burning FARME, and distillation of residuals from FARME production plants. An important objective of this study lies in the determination of the stoichiometry characteristics of rape seed oil methyl esters and distillation residuals from FARME production plants. The following parameters are set by calculations: fuel heating power, oxygen amount (air) necessary for ideal combustion, flue gases amount and composition, and flue gases specific weight.

Keywords: rape seed oil methyl ester; FARME; a liquid fuel; stoichiometry; combustion equipment; emissions; heating value; caloric value

The material of plants and animals, including their wastes and residues, is called biomass. It is organic, carbon-based, material that reacts with oxygen in combustion and natural metabolic processes to release heat. Such heat, especially at temperatures > 400°C, may be used to generate work and electricity. The initial material may be transformed by chemical and biological processes to produce biofuels, i.e. biomass processed into a more convenient form, particularly liquid fuels for transport. Examples of biofuels include methane gas, liquid ethanol, methyl esters, oils, and solid charcoal. The term bio-energy is sometimes used to cover biomass and biofuels together. Bio-energy is now accepted as having the potential to provide a major part of the projected renewable energy provisions of the future as biofuels in the form of gas, liquid or solid fuels, or electricity and heat. There are three main routes to providing these biofuels: thermal conversion, biological conversion and physical conversion, (Bridgwater 2006).

When released in combustion the bio-fuel energy is dissipated but the elements of the material should be available for recycling in natural ecological or agricultural processes. Thus the use of industrial biofuels, when linked carefully to natural ecological cycles, may be non-polluting and sustainable (Malaťák *et al.* 2004a).

Biofuels offer one method for the reduction of carbon dioxide (CO_2) emissions from fossil fuels, thus helping to meet UK and EU targets for mitigating the climate change. They also provide a rational option for land use within the EU that could be economically viable, provided that an appropriate financial and policy environment is developed. If 80% of the current set-aside land in the UK were used for the production of biomass crops for electricity generation, about 3% of the current UK electricity demand could be met from this source. (Powlson *et al.* 2005)

Biofuels are important because they replace petroleum fuels. There are many benefits for the

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environment, economy, and consumers in using biofuels. Bio-oil can be used as a substitute for fossil fuels to generate heat, power, and/or chemicals. Upgrading of bio-oil to a transportation fuel is technically feasible but it needs further development. Biofuels are made from biomass through thermochemical processes such as pyrolysis, gasification, liquefaction, and supercritical fluid extraction or biochemical ones. Biochemical conversion of biomass is completed through alcoholic fermentation to produce liquid fuels, and anaerobic digestion or fermentation, resulting in biogas (Demirbas & Balat 2006).

Within next 50 years, the share of energy generated from the renewable sources should reach 30% of the total energy consumed. In the European Union countries, the average share should double in 2010 to increase to 12% from the current 6%. Of the total renewable sources, biomass should account for 60%, with the anticipated increase to 80%. According to EU plans, one fifth of the fuels consumed should have been substituted by alternative fuels by 2020. Thus, the EU wants to reduce the dependency on fossil fuels and improve the quality of air. Five to eight percent of these twenty percent should be represented by the so called biofuels or rape seed oil methyl ester (FARME), or bio-alcohol (Jevič *et al.* 2006).

Such systems are called agro-industries, of which the most established are the sugarcane and forest products industries; however, more examples occur of commercial products for energy and materials made from crops as means of both diversifying and integrating agriculture. The term “modern biomass” is thus coming out. This term is generally used to describe the traditional biomass use through efficient and clean combustion technologies and sustained supply of biomass resources, environmentally sound and competitive fuels, heat and electricity using modern conversion technologies. Modern biomass can be used for the generation of electricity and heat. Bio-ethanol and biodiesel as well as diesel produced from biomass by Fischer-Tropsch synthesis are the most modern biomass-based transportation fuels. Bio-ethanol is a petrol additive/substitute. It is possible that wood, straw, and even household wastes may be economically converted to bio-ethanol. Bioethanol is derived from alcoholic fermentation of sucrose or simple sugars, which are produced from biomass by hydrolysis. Currently crops generating starch, sugar or oil are the basis for the transport fuel production. Renewed interest takes place in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature compared to the conventional petroleum diesel fuel. Biodiesel is a renewable replacement of petroleum-based diesel. Biomass energy conversion facilities are important for obtaining bio-oil. Pyrolysis is the most important process among the thermal conversion processes of biomass. The percentage share of biomass was 62.1% of the total renewable energy sources in 1995. The reduction of greenhouse gases pollution is the main advantage of utilizing biomass energy (Demirbas 2007).

Alternative liquid fuels – biodiesel

Rape seed oil methyl ester was the first type of biodiesel fuel produced commercially in 1988, characterised as a single-feed-stock product of then questionable quality. A huge progress has been made in the past 19 years by broadening the feedstock basis, improving technology through high flexibility in processing multi-feed-stocks at highest yield levels, developing sophisticated fuel standards thus assuring highest fuel quality, establishing biodiesel production capacities in many countries, intelligent product positioning in defined fuel market segments, obtaining numerous diesel engine warranties, and implementing a number of different supportive legal measures and voluntary regulations.

Under the standard name biodiesel, as a renewable fuel, produced either by esterification or reesterification of vegetable oils (rape, sunflower, soya beans), this fuel has been manufactured on an industrial scale in the EU and the Czech Republic since 1992. The reform of the common agricultural policy and the legislation on the utilisation of uncultivated land for non-food purposes were the key factors in starting up this production. The increased demand for biodiesel – and the permanent restriction imposed by the Blair House Treaty-have led to a gradual elimination of the obligation to use rape only from the land designated to rest, and gradually resulted in the use in the production of biomass also of vegetable oils obtained on an open market. Various EU programmes and legislation boosted the growth of the biodiesel industry. EU directives enabled member states to exempt biodiesel partially or wholly from taxes for the verification and assessment of a number of pilot projects.

The present market is simply dominated by fossil diesel in 100% and this is a competitive product to be replaced. With biodiesel being on one hand a product which can grow to approximately 8% of the market share at the best but on the other hand being an environmentally friendly fuel which shows clear and substantial differential advantages, it is a job for professional marketing to screen all the market segments carefully and define those niches in which the distinctive benefits of biodiesel are most needed and fully recognised and valued by the customers. Additional environmentally driven regulations, e.g. limitations on certain emissions, regulations for minimum biodegradability, laws for zero-toxicity to water-life, can carve out specific market segments in which only biodiesel will fulfill the rules and can obtain a dominant market position. In spite of these market opportunities, strategies exist of blending biodiesel with fossil Diesel (e.g. France), where the end user is not able to recognise the product and consequently all its differential advantages either.

Combustion equipment designed for alternative liquid fuels

The growing use of biodiesel has opened areas of utilising liquid by-products coming from the manufacture of rape seed oil methyl ester as an energy source, used in the combustion equipments designed for these alternative liquid fuels (Malaťák *et al.* 2005a).

The solution of the problem "The evaluation and higher efficiency of the production and utilisation of biofuels from the agricultural and manufacturing production" has a worldwide importance due to the rapid increase of the fuels use, renewable energy sources, and biomass. The solution will bring a definite classification and specific principles of agricultural products use. Their classification and specification will provide them acceptability at the fuels market and a public confidence increase, and will also precipitate compulsory approved procedures, information exchange about solid biofuels use and alternative fuels from renewable sources and related environmental problems.

The solution of the study is coming out of three domains of thermal-emissions properties of the chosen samples of methyl ester oil production line. The main task is to set particle analyses of the samples tested. Stoichiometric analyses follow and the last step of the whole procedure is an experimental combustion in a laboratory combusting equipment (Malaťák *et al.* 2004b).

The elementary analysis has been done of the selected liquid materials in order to set basic parameters of fuels, and was focused mainly on: water content (weight %), ash matter (weight %), volatile and nonvolatile combustibles (weight %), combustion heat (MJ/kg), carbon (C, weight %), hydrogen (H, weight %), nitrogen (N, weight %), sulphur (S, weight %), oxygen (O, weight %) and chlorine (Cl, weight %).

The concentrations of the following substances are monitored during the measurement using laboratory combustion equipment: carbon di-oxide (CO_2) and carbon mono-oxide (CO), oxygen (O_2), nitrogen mono-oxide (NO) and nitrogen di-oxide (NO_2), sulphur di-oxide (SO_2), hydrogen chloride (HCl) and excess-air coefficient (n). In the following steps, the particular values of the combustion characteristics are defined.

The amounts of sulphur and nitrogen, contained in fuel are the most determining property of emission concentrations sought by particle analysis. The high increase of nitrogen emissions of FARME distillation residues is caused by its high content in energy plants. It leads to a limited use of such plants (Malaťák *et al.* 2005b).

The stoichiometry analysis results have shown very satisfactory thermal-emission parameters of the tested liquid materials coming from FARME.

The tested liquid samples from FARME production showed good emission parameters and effec-

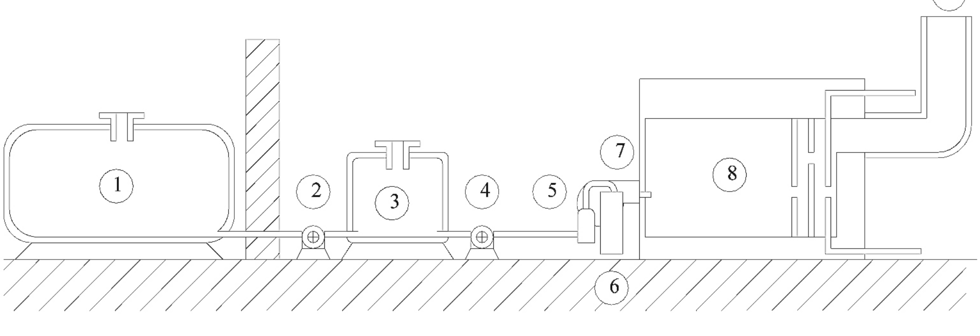

Figure 1. Scheme line on power used the rest of distillation

1 – tank (warming-up on 30°C), 2–4 – pump, 3 – tank (warming-up 30–35°C), 5 – filter, 6 – preheating 80–90°C, 7 – high pressure burner VH 60, 8 – boiler, 9 – smoke flue

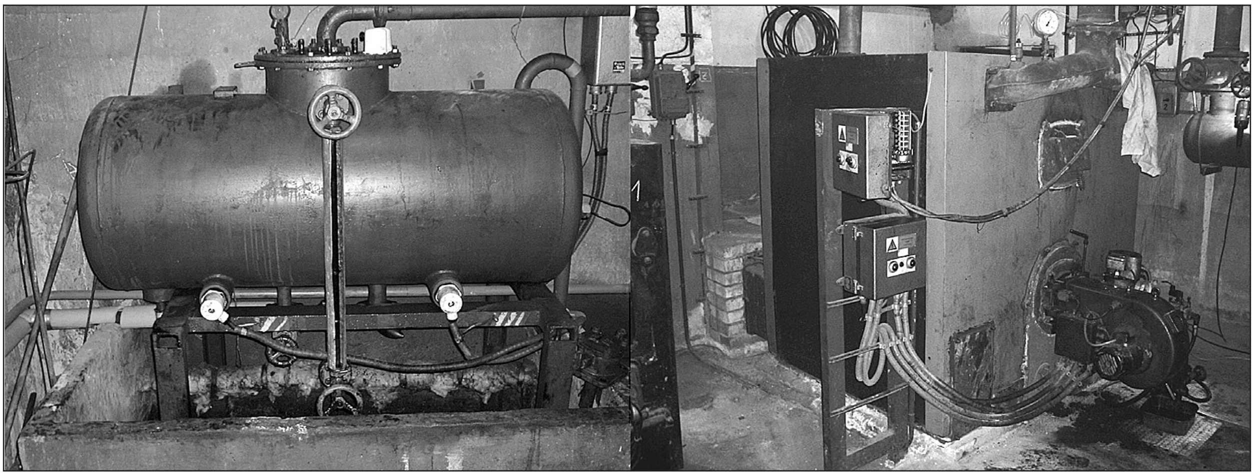

Figure 2. Tank (warming-up 30–35°C) and combustion equipment for liquid fuels about nominal heat output 460 kW and VH 60 high-pressure burner (25 kg/h)

tiveness. These samples may be used for some kind of liquid combustion equipments if certification requirements are completely met.

MATERIAL AND METHODS

In liquid fuel combustion equipment of nominal thermal output 460 kW fitted with a VH 60 high-pressure burner (25 kg/h), on an experimental basis were burnt rape seed oil methyl esters, their distillation residuals, and a mix of light heating oil with distillation residuals. The tank, the combustion equipment for liquid fuels, the measuring gauge with an analysator GA-60, and the combustion space VH 60 high-pressure burner are presented in Figures 1–3.

The prerequisite for implementing the research task was the elementary analysis carried out for each liquid fuel, with the subsequent determination of the combustion process stoichiometry, which complements the fuel characteristic and constitutes the base for any thermal calculations and determination of the emission concentrations of SO_2, CO, CO_2, NO and NO_x. It is very important to solve the essential condition as ecology operation of these equipments in usage of the agricultural liquid materials for energy recuperation. It is necessary then to issue the chemical composition analyses, operation parameters, ash matter, and stoichiometric calculations of the combustion equipment.

All kinds of liquid fuels, occurring in natural (raw) state are composed of three main components: total water content, ash matter, and combustibles. This composition can be expressed by following formula:

$$\sigma(W_t^r) + \sigma(C_t^r) + \sigma(H_t^r) + \sigma(O^r) + \sigma(S_t^r) + \sigma(N^r) + \sigma(A_t^r) = 100\% \qquad (1)$$

where:

$\sigma(W_t^r)$, $\sigma(C_t^r)$, $\sigma(H_t^r)$, $\sigma(O^r)$, $\sigma(S_t^r)$, $\sigma(N^r)$, $\sigma(A_t^r)$ – weight parts of total water, oxygen, carbon, hydrogen, sulphur, nitrogen and ash amounts in the original sample (% weight)

Water and ash matter are contained ino the non flammable part of fuel, described as ballast or deadwood. Both of them reduce the fuel heating power. Their presence influences the combustion equipment construction, and they are sources of frequent problems occurring during operations (Malaťák *et al.* 2006).

The flammable part of the fuel is composed of carbon, hydrogen, sulphur, and nitrogen. Merely carbon, hydrogen, and sulphur are involved in the exothermic reaction with air oxygen-autogenous burning. Oxygen involved in fuels works as an oxidant and nitrogen is the only part which is not involved in burning.

All of the main three fuel components (water, ash, and flammables) are very important factors in the combustion process. Their properties highly influence the construction of the combustion equipment as well as its operation regime.

The particle analysis of the selected liquid fuels was done in the framework of the research project, concerned with selected liquid fuels. The material liquid samples are provided by methyl ester oil production. The samples in the framework of the project were represented by:

- diesel fuels, as a reference fuel
- light fuel oil (LFO), as a reference fuel
- pure rape seed oil (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun)
- rape seed oil methyl ester (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun)

Figure 3. A measuring gauge with an analysator GA-60 and combustion space of VH 60 high-pressure burner

- distillation residues from FARME production (water-free sample and flammable substance), (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun)

The elementary analysis was done with the selected samples in order to set the basic parameters of fuels. It was mostly focused on the water content (weight %), ash matter (weight %), combustion heat (MJ/kg), C (weight %), H (weight %), N (weight %), S (weight %), O (weight %) and Cl (weight %). The fixed elementary analysis was set by the elementary analyser multi-EA for the determination of C, N, S, and Cl (producer ChromSpec), by chromatograph GC-MS for the detection of the combustible components (producer Perkin Elmer), and calorimeter IKA-2000 (producer IKA Laboratory and Analytical Equipment) for the determination of combustible heat and the samples heating power. The final values are pictured in Table 1. The elementary analysis is a necessary part of measurements to set basic stoichiometric and heat properties of the tested samples.

The results of the elementary analysis of the liquid samples were converted into the values under normal conditions (temperature t = 0°C and pressure p = 101.325 kPa). Table 1 shows that the most determining factor is the emissions concentrations of sulphur, chlorine, and nitrogen contained in fuels. In the case of FARME residues is an obvious increase of nitrogen emissions, because of its natural high content in the energy plants. This causes a limited use of these fuels.

Chlorine proceeds to gas phases during the combustion, in most of its volume. There is a tiny amount of chlorine in the tested samples. Its importance comes from HCl emissions and their possible influence on polychloride dibenzo/dioxines and furanes (PCDD/F). The mentioned elements may be also

Table 1. Elementary analysis of choice liquid samples (weight %)

Samples	Diesel fuel	Light fuel oil	Rape oil	Methylester	Distillation residues from FARME (water-free sample)	Distillation residues from FARME (combustible)
Carbon	86.50	85.60	77.70	76.900	78.66	78.70
Hydrogen	13.00	12.30	11.60	12.200	11.86	11.87
Oxygen	0.00	0.10	10.60	0.010	9.38	9.38
Sulphur	0.11	1.40	0.001	0.001	0.01	0.01
Nitrogen	0.00	0.05	0.00	0.000	0.04	0.04
Chlorine	0.00	0.08	0.06	0.060	0.04	0.04
Water content	0.01	0.01	0.00	0.000	0.00	0.00
Ash	0.01	0.05	0.10	0.000	0.05	0.00

involved in the formation of other compounds, and they have strong corrosive impacts on the construction materials.

Sulphur is also mostly changed to gas phases during combustion in the form of SO_2 or SO_3. Normally, sulphur emissions do not mean a real problem in the case of thermal devices using liquid fuels originating in renewable sources. The limiting factors are the corrosive qualities of sulphur and its compounds. Other parameters of the particle analyses meet the requirements for the use of these samples in the combusting equipment.

The most determining factors of the thermal use of fuels are the water and ash contents. The water content is relatively low in the tested samples, which has a positive impact on the fuel heating power. Another in flammable component is ash. The amount of ash is low, as obvious from Table 1. The amount of ash can significantly influence the thermal properties and these properties then affect the choice and adjustment of the combustion equipment.

Next essential task is to determine stoichiometry of the liquid fuels studied. Stoichiometric calculations of the combustion processes are important particularly for solving a number of the design practice problems, and for checking the work done by the existing combustion aggregates. Stoichiometric calculations of the combustion processes supplement the fuel characteristics and are also the basis for any heat calculation. These are very important for solving the heat system design problems and during the heat equipment control. The following parameters are set by calculations:

- fuel heating power,
- oxygen amount (air) necessary for ideal combustion,
- flue gases amount and composition,
- flue gases specific weight.

The samples heating power is determined by calculation based on the combustion heat measured and the elementary analyses. The combustion heat is measured by calorimeters (according to ČSN 44 1352 1999). The sample stoichiometry is assessed for the mass combusting as well as for the voluminous combusting.

The final stoichiometric calculations for these fuels are presented in Table 2. The stoichiometric calculations for the liquid fuels were converted to the values under normal conditions (temperature $t = 0°C$ and pressure $p = 101.325$ kPa). The concentrations of individual combustion products were subsequently converted to the reference level of oxygen in the combustion gas (O_r). Its value in these liquid fuels was defined in accordance with the applicable standards as $O_r = 3\%$. The final stoichiometry analyses values (see Table 2) indicate very good thermal-emission parameters of the tested samples of liquid materials coming from methyl ester rape seed oil.

For another possible thermal utilisation of rape seed oil, it is necessary to adjust the combustion equipment to higher fuel inputs and also to pre-set other operation parameters of the device. An other possibility with rape seed oil is to form a mixture with a fuel with higher value of heating power. In the following part of the work, the analysis was done of flue gases thermal-emission concentrations and thermal-technical efficiency of the laboratory tested samples. In the liquid fuel burning combustion equipment of nominal thermal output of 460 kW fitted with a VH 60 high-pressure burner (25 kg/h), the following samples from the production of rape seed oil methyl esters (FARME) were burnt on an experimental basis burnt samples from production rape seed oil methyl esters (FARME):

- distillation residues from FARME production (10%) + LFO (90%) (samples from methyl ester oil production –Agrochem, joint-stock company, Lanškroun),
- distillation residues from FARME production (100%) (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun),
- FARME (100%) (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun),
- pure rape seed oil (100%) (samples from methyl ester oil production – Agrochem, joint-stock company, Lanškroun).

The prerequisite for implementing the research task was the elementary analysis carried out for each liquid sample, with the subsequent determination of the combustion process stoichiometry, which complements the fuel characteristic and constitutes the basis for any thermal calculation and determination of the emission concentrations of SO_2, CO, CO_2, NO, and NO_x.

The actual observation is focused on the concentration of emissions generated by the combustion of these liquid fuels. The contents of carbon oxides (carbon dioxide and carbon monoxide), nitrogen oxides (nitrogen oxide and nitrogen pentoxide), oxides of sulphur and hydrogen chloride were determined. Carbon dioxide was determined from the measured concentration of oxygen and the fuel characteristics. These measurements were used to assess the fuel as well as the combustion equipment as far as its thermal parameters and emissions are

Table 2. Final stoichiometry calculations of liquid fuels

Stoichiometry calculations		Diesel fuel	Light fuel oil	Rape oil	Methylester	Distillation residues from FARME (water-free sample)	Distillation residues from FARME (combustible)
Q_n	heating value – ČSN 44 1352 (1999) (MJ/kg)	42.49	40.01	37.05	37.03	37.64	37.66
Q_v	calorific value (MJ/kg)	45.33	42.70	39.24	39.70	40.23	40.25
Setting of mass combustion							
$O_{\min}$	theoretical quantity of oxygen for ideal combustion process (kgN/kg)	3.35	3.28	2.89	3.027	2.95	2.95
$L_{\min}$	theoretical air quantity for ideal combustion process (kgN/kg)	14.43	14.13	12.47	13.05	12.72	12.73
n	overflow of the air (O_2 = 3%)	1.20	1.20	1.20	1.20	1.20	1.20
m^{s}_{spmin}	theoretical mass quantity of dry combustion gas (kgN/kg)	16.06	15.82	14.26	14.67	14.49	14.49
$CO_{2\max}$	theoretical mass concentration of oxide carbonic in dry combustion gas (% mass.)	19.74	19.83	19.97	19.22	19.90	19.90
CO_2	carbon dioxide (weight %)	16.91	17.06	17.42	16.63	17.30	17.30
SO_2	sulfur dioxide(weight %)	0.01	8.15	0.0	0.013	0.002	0.001
H_2O	water (weight %)	9.90	9.68	1.02	10.14	10.04	10.05
N_2	nitrogen (weight %)	69.49	69.43	68.91	69.53	68.99	68.99
O_2	oxygen (weight %)	3.56	3.56	3.53	3.56	3.53	3.53
Setting of cubical combustion (values of real molecular gas mass)							
$O_{\min}$	theoretical quantity of oxygen for ideal combustion process (m^3N/kg)	2.335	2.29	1.298	2.112	2.06	2.06
$L_{\min}$	theoretical air quantity for ideal combustion process (m^3N/kg)	11.120	10.89	6.182	10.056	9.81	9.81
n	overflow of the air (O_2 = 3 %)	1.20	1.20	1.20	1.20	1.20	1.20
v^{s}_{spmin}	theoretical cubical quantity of dry combustion gas (m^3N/kg)	10.284	10.10	3.725	9.276	9.11	9.12
$CO_{2\max}$	theoretical cubical concentration of oxide carbonic in dry combustion gas (% vol.)	15.60	15.71	16.11	15.37	16.00	16.00
CO_2	carbon dioxide (% vol.)	11.02	11.15	8.58	10.81	11.28	11.28
SO_2	sulfur dioxide (% vol.)	0.01	0.07	0.01	0.01	0.0005	0.0005
H_2O	water (% vol.)	13.56	13.24	11.30	13.91	13.81	13.81
N_2	nitrogen (% vol.)	71.37	71.49	69.47	71.23	70.89	70.89
O_2	oxygen (% vol.)	3.20	3.21	9.83	3.19	3.17	3.18

Table 3. Technical parameters of GA-60 analyzer

	Range	Resolution	Indicator accuracy (%)
Surrounding temperature/indicator Pt 500	0–100°C	1°C	± 2
Combustion gases temperature	0–1300°C	1°C	± 5
Indicator NiCr/Ni (or PtRh/Pt)	0–1600°C	1°C	± 2
Electrochemical converter/oxygen	0–20.95%	0.01%	± 2
Electrochemical converter/carbon monoxide	0–20 000 ppm	1 ppm	± 5
Electrochemical converter/nitrogen compounds	0–5000 ppm	1 ppm	± 5
Electrochemical converter/nitrogen dioxide	0–800 ppm	1 ppm	± 5
Electrochemical converter/sulphur dioxide	0–2000 ppm	1 ppm	± 5
Pressure	± 50 kPa	0.01 kPa	
Soot number by Bacharach	0–9	1	
Nitrogen compounds as NO_2/calculation from NO + NO_2	0–6000 ppm	1 ppm	
Carbon dioxide/calculation by fuel from CO_{2max} and O_2	0–25%	0.1%	
Thermal – technical efficiency/calculation by DIN/öNORM	0–100%	0.1%	
Stack loss and loss by imperfect combustion/calculation by DIN/öNORM	0–100%	0.1%	
Air surplus/calculation by DIN/öNORM	1–∞	0.01	

concerned. The emission concentration in the combustion gases and the technical thermal combustion efficiency were determined using a GA-60 device. The technical parameters of GA-60 are mentioned in Table 3.

The following formulas are used to recalculate the measured amounts of the wet combustion gases compounds at certain temperature (t) and pressure (p) to normal conditions (0°C; 101.325 kPa). These are recalculated to the reference oxygen amount in the combustion gases.

The emission factor calculation of normal condition of wet combustion gases:

$$E_v = \frac{273.15 + t}{273.15} \times \frac{101\,325}{101\,325 + p} \times E_n \tag{2}$$

The emission factor calculation of normal condition of dry combustion gases:

$$E_s = \frac{273.15 + t}{273.15} \times \frac{101\,325}{101\,325 + p} \times \frac{100}{100 - w} \times E_n \tag{3}$$

The emission factor calculation of normal condition of dry combustion gases and the reference oxygen amount in the combustion gases:

$$E_{sr} = \frac{273.15 + t}{273.15} \times \frac{101\,325}{101\,325 + p} \times \frac{100}{100 - w} \times$$

$$\times \frac{21 - O_r}{21 - O_p} \times E_n \tag{4}$$

where:

E_n – measured amount of derogatory compounds in 1 m^3 of combustion gases at operational conditions (mg/m),

E_v – amount of derogatory compounds in 1 m^3 of wet combustion gases at operational conditions (mg/m_N^3),

E_s – amount of derogatory compounds in dry combustion gases at operational conditions (mg/m_N^3),

E_{sr} – amount of derogatory compounds in 1 m^3 dry combustion gases at normal conditions and for the reference oxygen amount in combustion gases (mg/m_N^3),

t – operational temperature of combustion gases (°C),

p – pressure difference between the operational pressure and the normal pressure (Pa),

w – water vapor content in combustion gases (% vol.),

O_p – oxygen content in combustion gases corresponding to operational conditions (measured) (% vol.),

O_r – reference amount of oxygen in combustion gases (% ol.).

The emission limits are set for the normal conditions of combustion (0°C; 101.325 kPa; dry combustion gases) and a certain reference amount of oxygen in the combustion gases (in the case of this research work 3%, if not stated differently).

The test measurements were performed in accordance with ČSN 07 0240 (1993) "Hot water and low pressure steam boilers – basic provisions", with ČSN 124070 (1989) "Separation equipment – methods of measuring quantities", with ČSN 44 1310 (2001) "Marking analytical indicators and formula for converting the results of analyses to different fuel conditions" and with ČSN 38 5509 (1991) (the values of molecular mass and molecular volume).

Besides testing chemical combustion gases parameters the GA-60 device provides the calculations of the burning characteristics. The main characteristic is undoubtedly the thermal loss, caused by the physical heat of the combustion gases led to the air (stack loss q_a). This loss is calculated by the following empiric formula:

$$q_a = (t_s - t_o) \times \left(\frac{A_2}{20.95 - O_{2M}} + B\right) \qquad (5)$$

where:
q_a – stack loss,
t_s – combustion gas temperature (°C),
t_o – surroundings temperature (°C),
A_2 – fuel constant,
B – fuel constant,
O_{2M} – measured oxygen amount.

The efficiency is then calculated by the formula:

$$eta = 100 - q_a \qquad (6)$$

Such calculated value of efficiency presumes that the only decrease is caused by the stack loss. Other kinds of losses such as imperfect combustion, radiations etc. are negligible. This simplification is possible only when the stack loss is multiple in comparison to the total sum of other losses. To get more accurate results, it is worthy to apply other calculations, including the chemical imperfect combusting loss or just the loss of imperfect combustion (%), assigned by formula:

$$q_{CO} = \frac{a \times CO}{CO + CO_2} \qquad (\%) \qquad (7)$$

where:
CO, CO_2 – measured or calculated contents of components of gas,
a – fuel parameter.

The calculation of this loss will provide a correlation (higher accuracy) of previously calculated efficiency *eta* by using the formula:

$$eta_{kor} = eta - q_{co} \qquad (\%) \qquad (8)$$

This efficiency is called thermal-technical efficiency of combustion. Consequential average values of thermal - emission analyses of flue gases concentrations as well as the thermal-technical efficiency of the tested samples are shown in Table 4.

The quality (efficiency) of the combusting process may be indicated by carbon dioxide (CO_2) (see Table 4). If the stoichiometric calculations of carbon dioxide are taken into account (see Table 2) and the measured air surplus (n) as well as the amount of the measured carbon monoxide (CO) are considered, the losses caused by combustion gases (at the same temperature of combustion gases) are optimal.

An other problematical part is presented by sulphur dioxides and hydrogen chloride. These emissions are caused mainly by the sulphur content in light fuel oil (Table 2).

Sulphur dioxide emissions produced by laboratory combustion of the distillation residues from

Table 4. Results of work measurement of gaseous emissions and thermal-technical parameters

Samples		Distillation residues from FARME (10%) + LFO (90%)	Distillation residues from FARME (100%)	Methylester from FARME (100%)	Rape seed oil from FARME (100%)
Temp. gas	°C	278.2	275.6	256.8	249.9
Oxygen	%	12.9	12.9	13.7	14.1
n from Oxygen	–	2.09	2.09	2.38	2.55
Carbon dioxide	%	9.1	10.0	8.5	8.2
Carbon monoxide	ppm	49	129	1	153
Carbon monoxide	mg/m^3	61	185	1	191
Carbon monoxide (O_r = 3%)	mg/m^3	135.2	381.4	2.1	498.4
Oxides of sulphur	ppm	177	25	3	0.0
Oxides of sulphur	mg/m^3	525	75	9	0.0
Oxides of sulphur (O_r = 3%)	mg/m^3	1165.1	166.5	22.3	0.0
Hydrogen chloride	ppm	40	24	29	26
Hydrogen chloride	mg/m^3	66	40	48	43
Hydrogen chloride (O_r = 3%)	mg/m^3	146.2	88.2	118.1	110.8
Nitrogen oxides	ppm	40	24	29	26
Nitrogen oxides	mg/m^3	83	50	60	53
Nitrogen oxides (O_r = 3%)	mg/m^3	183.3	110.7	148.2	138.7
Technical-thermal effect combustion	%	90.7	85.3	93.9	80.5

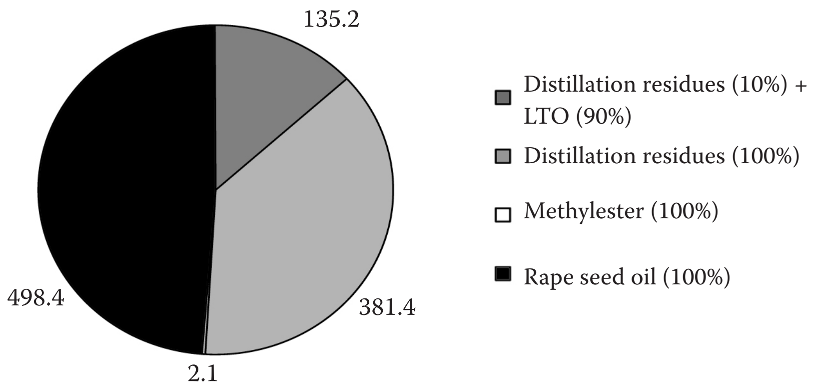

Figure 4. Results of work measurement of gaseous emissions CO mg/m (O_2 = 3%)

FARME (10%) and LFO (90%) showed higher concentrations in comparison with other samples. To decrease sulphur dioxide content in light fuel oil mixtures, further addition of distillation residues is recommended.

Hydrogen chloride emissions have reached standard, average values. Its importance comes from its HCl emissions – and their possible influence on polychloride dibenzo/dioxines and furanes (PCDD/F). The mentioned elements may be also involved in the formation of other compounds; they have strong corrosive impacts on the construction materials.

The results of the measurements indicate that the thermal use of by-products from methyl ester production is very favourable. An addition of distillation residues (10%) to light fuel oil will improve its emission parameters (see Figure 4 and 6), especially sulphur dioxide emissions (see Figure 5). The final average values are pictured in Table 4.

Burning pure rape seed oil and distillation residues is evaluated as an asset; however, the efficiency of the whole process decreases, due to the fuel quality. Especially in the combusting equipment it gives out to imperfect burning of material and losses caused by imperfect burning of fluid carbon dioxide are increased. This loss is also caused by not combusted flammable compounds contained in the combustion gases coming from the grate. The loss is caused by imperfect burning of fuel, which is brought about by the lack of air or an imperfect mixing of the combusting air with the fuel or flammable surroundings in the grate.

All the values obtained by measurements are recalculated to normal conditions (the temperature $t = 0°C$ and the pressure $p = 101.325$ kPa) using the referential amount of oxygen $O_r = 3\%$.

CONCLUSION AND DISCUSSION

Taking into account a longer-term perspective, biofuels can be seen as one of a number of stepping stones towards sustainability, introducing renewable components into the fuel pool. To achieve this, flexibility should be the goal, with engines increasingly able to operate effectively with the evolved mixtures of prospective biofuels, and with the fuel suppliers becoming increasingly adept at delivering fuels derived from a wider range of sources. To ensure that fuels and engines continue to operate at their optimum in the future, the same degree of attention must be paid to the potential bio-fuel components as has been paid to refinery streams over many decades. Appropriate controls and constraints will also be necessary to ensure that consumers continue to

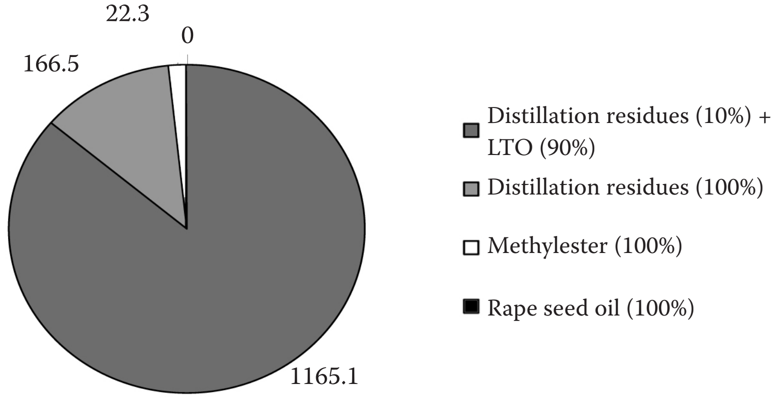

Figure 5. Results of work measurement of gaseous emissions SO_2 mg/m^3 (O_2 = 3%)

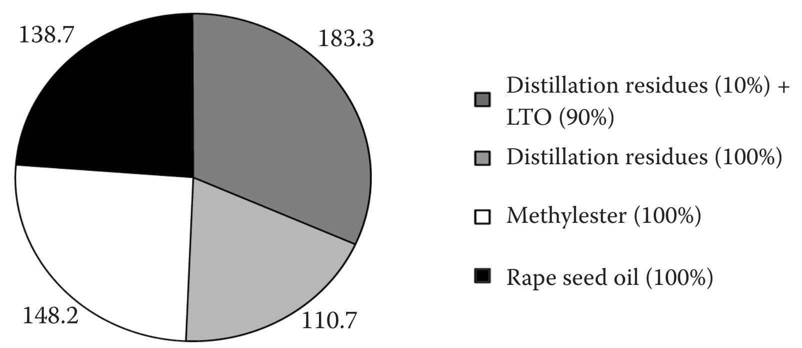

Figure 6. Results of work measurement of gaseous emissions NO_x mg/m^3 (O_2 = 3%)

enjoy confidence in the quality of fuels supplied by the oil industry.

Concentrated vegetable oils may be used directly as fuel in diesel engines, but difficulties arise from their high viscosity and from the combustion deposits, as compared with conventional (fossil) petroleum-based diesel oil, especially at low ambient temperatures (< 5°C). Both difficulties may be overcome by reacting the extracted vegetable oil with ethanol or methanol to form equivalent esters. Such esters, called biodiesel, have technical characteristics as fuels that are better suited for the diesel-engines than petroleum-based diesel oil.

The enormous boom in rape seed oil methyl esters (biodiesel) since its production started in the EU back in 1992, has been boosted also by the growing prices of crude oil and the so called ecological tax reform, connected with gradual increases of taxes imposed on mineral oils. Biodiesel has remained exempt from tax, increasing its ability to compete with standard motor diesel fuel. At the same time more and more vehicles produced by the automobile industry have been modified to run on rape seed methyl esters, even though the process gave rise to temporary stormy discussions about the biodiesel quality. The success of biodiesel sales in Germany and Austria, where this fuel is sold nationwide at about 1700 filling stations, is also the result of the gradually more stringent quality standards. The quality management covers producers, trading organisations and corporations, transportation and storage companies.

Different possibilities are considered to utilise the rapeseed oil methyl esters as fuel for the combustion equipments. Such problems are of significant importance in view of the continually increasing needs for the fuels, renewable sources of energy and biomass. Great emphasis must be put on meeting the stringent environmental standards of the combustion processes. The assessment starts from the chemical composition of the fuels employed, stoichiometric computations, and operational parameters of a given type of the combustion equipment (Vasudevan *et al.* 2005).

C, H, and O are the main components of liquid biofuels and are of special relevance for the gross caloric value, H in addition also for the net caloric value. The fuel N content is responsible for NO formation. NO emissions belong to the main environmental impact factors of solid biofuels combustion. Cl and S are responsible for the deposit formation and corrosion and are therefore relevant for the high plant availability. Furthermore, Cl causes HCl as well as PCDD/F, S, and SO emissions and both elements are involved in the formation of aerosols (submicron particle emissions). The ash content influences the choice of the appropriate combustion technology and influences the deposit formation, fly ash emissions, and the logistics concerning ash storage and ash utilisation/disposal (Obernberger *et al.* 2006).

The choice and design of the combustion equipment are influenced by the fuel stoichiometry and other fuel parameters, such as the heating power, water content and energy density. The analyses of the selected samples confirm a wide range of nitrogen, sulphur, and chlorine concentrations in the fuels. Oxygen is a problematic part of the fuel, because of hydrogen and partly carbon binding, creating hydroxides, water, and other oxides. Oxides are mainly connected with nitrogen (in the form of amines and proteins contained in fuels) and chlorine. Interactions occur of chlorine oxides with the conversion equipment, especially with the combusting equipment.

All water present in fuels and the excess air coefficients are primary factors which may significantly affect the combustion equipment thermal work. The calculated stoichiometric values are then inducted to the formulas of emission concentrations, thermal powers, and thermal equipment losses calculations.

Mass flows, emission factors, and characteristics of solid particles during thermal processing of liquid fuels cannot be determined without stoichiometric calculations. Stoichiometric calculations of combustion processes complement the liquid fuel characteristic and constitute the base for any thermal calculation. They are important especially for solving a whole series of the design practice problems, as well as when checking the work of the existing combustion equipment.

The combustion quality (efficiency) can be judged by the content of carbon dioxide (CO_2). When the maximum possible concentration of CO_2 is achieved with a small excess of air (perfect combustion), the losses caused by the combustion products (at the same temperature of the combustion products) are minimal. For any liquid and solid fuel, a maximum achievable proportion of carbon dioxide CO_2 exists (the so called CO_{2max}) in the combustion gases, given by the element composition of the fuel flammable components. Of course, this value is inachievable in the real combustion equipment.

Since hydrocarbons and other products of imperfect combustion behave identically as carbon monoxide, this emission component is an important indicator of the combustion process quality. The actual emissions generated during the combustion of the liquid fuels studied constitute no problem. All liquid fuels showed excellent parameters of thermal-technical efficiency during combustion.

The tested liquid fuels showed good emission parameters and efficiency and may be, if they meet other certification criteria, suitable also for similar liquid fuel powered appliances.

The support of this agricultural non-food production as a renewable source of energy is regarded as perspective not only from ecological aspects. Without this support, biofuels could not compete with classic sources of energy. The current agricultural policy of the European Union, and thus also of the Czech Republic, puts an emphasis on such a utilisation of agricultural production as the most important alternative to restrictions on agricultural production. The state support is essential for the renewable sources to penetrate into the market on a larger scale.

In order to be able to use rape seed oil methyl ester and distillation residuals (but other fuels as well) in the combustion equipments burning liquid fuels, it is necessary for the combustion process to take place under ideal conditions. Without meeting these assumptions, the combustion of distillation residuals is of no benefit. Therefore, it is important to burn in a particular equipment only such fuel which is by its type, texture, quality, etc., suitable for that equipment. These aspects require permanent attention.

Results of measurements indicate following conclusions in sum

The most determining factors of the thermal use of fuels are the water and ash contents. The range of the water content is relatively low in the tested samples, which has a positive impact on the fuel heating power. An other nonflammable component is ash. The amount of ash is low, as obvious from the elementary analysis of the samples tested. The amount of ash can significantly influences the thermal properties, and these properties then affect the choice of the combustion equipment as well as its adjustment.

Stoichiometric analysis values indicate very good thermal-emission parameters of the tested liquid samples. These come from methyl ester production. Other problematical parts are sulphur dioxide (SO_2) emissions as well as hydrogen chloride emissions (HCl). Sulphur emissions of the samples tested are not such a problem, because of the trace amounts. These emissions are caused mainly due to sulphur contained in the light fuel oil. Hydrogen chloride emissions have reached common average values. The results of the measurements indicate the use of by-products coming from methyl ester production as a benefit for the future.

An addition of distilling residues (10%) to light fuel oil will improve the emission properties, mainly sulphur dioxide emissions. The tested liquid samples coming from methyl ester rape seed oil production showed very good emission parameters and efficiency and may be, if they meet other certification criteria, suitable also for similar liquid fuel powered appliances. The solution leads to the emission reduction and in this way also to the reduction of environmental pollution. The definition of typical physical-chemical properties of the selected samples coming from methyl ester rape seed oil production, can be used as the initial data for the material and thermal-chemical use. By-products classification and specification will simplify the acceptability on the fuel market and an increase in public trust.

The definite determination of typical physical-chemical properties is necessary for designing, building, and checking the combusting equipments; the thermal use of liquid samples for burning by-products from methyl ester rape seed oil production is useless without meeting these premises.

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Abstrakt

BRADNA J., MALAŤÁK J. (2008): **Vedlejší produkty z výroby methylesteru řepkového oleje a jejich tepeně emisní vlastnosti.** Res. Agr. Eng., **54**: 9–21.

S dohlednou vyčerpatelností fosilních energetických zdrojů roste význam obnovitelných zdrojů energie a stává se jednou z hlavních podmínek trvale udržitelného rozvoje nejen zemědělství, ale i celé společnosti. V návaznosti na rozvoj využívání bionafty se otevírá další oblast energetického využití vedlejších produktů z výroby methylesteru řepkového oleje (MEŘO) pro spalovací zařízení určená pro tento typ alternativního paliva. Cílem tohoto článku je zhodnotit energetické využití vedlejších produktů z výroby methylesteru řepkového oleje s ohledem na ekologii a ekonomii použitého spalovacího zařízení. Měření je proto zaměřeno na koncentrace emisí vzniklé spalováním kapalných meziproduktů z výroby MEŘO a tepelné práce spalovacího zařízení. Významný cíl práce spočívá ve stanovení stechiometrie methylesterů řepkového oleje a destilačních zbytků z výrobny MEŘO. Při těchto výpočtech se stanoví: výhřevnost paliva, množství kyslíku (vzduchu) potřebného k dokonalému spalování paliva, množství a složení spalin a měrná hmotnost spalin.

Klíčová slova: methylester řepkového oleje; MEŘO; kapalné palivo; stechiometrie; spalovací zařízení; emise; výhřevnost paliva; spalné teplo

Corresponding author:

Ing. JIŘÍ BRADNA, Výzkumný ústav zemědělské techniky, v.v.i., Drnovská 507, P.O. Box 54, 161 01 Praha 6-Ruzyně, Česká republika
tel.: + 420 233 022 473, fax: + 420 233 312 507, e-mail: jiri.bradna@vuzt.cz