Original Research

Influence of Composition of Fatty Acid Methyl Esters on Smoke Opacity and Amount of Polycyclic Aromatic Hydrocarbons in Engine Emissions

E.Sendzikiene, V.Makareviciene*, P.Janulis

Institute of the Environment, Lithuanian University of Agriculture, Studentu 11, LT-53361 Akademija, Kaunas r., Lithuania

Abstract

Soot and hydrocarbons are usually found in diesel exhaust gases. They are formed when the fuel is burnt out incompletely. Polycyclic aromatic hydrocarbons (PAH) are sorbed on the soot, and may cause cancerous diseases, asthma and other diseases. The purpose of this work was to evaluate the dependence of smoke opacity and amount of polycyclic aromatic hydrocarbons in engine emissions on multi-component biodiesel fuel composition.

We analyzed the composition of exhaust gases when diesel engine was fuelled with rapeseed oil methyl esters (RME), RME mixtures with linseed oil methyl esters (LSME) and fatty acid methyl esters (FAME) of animal origin, assessing the smoke opacity and qualitative and quantitative composition of PAH. It was determined that smoke opacity of exhaust gases decreases at different rotation speeds (1200 and 2000 min^{-1}) when the amount of FAME, containing a greater amount of saturated fatty acids, is increasing. Total PAH concentration in exhaust gases of biofuel mixtures with pork lard fatty acid methyl esters (LME) is lower than in the case of mixtures with beef tallow fatty acid methyl esters (TME). The amount of PAH at a rotation speed of 1200 min^{-1} reduced down to 57%, if compared to pure RME, and down to 30%, when the rotation speed was 2000 min^{-1}. In the exhaust gases of biofuel mixtures with pork lard fatty acid methyl esters there are fewer PAHs with highly expressed mutagenic and carcinogenic effects if compared to pure RME and its mixtures, containing tallow fatty acid methyl esters. The most effective from an environmental point of view is use of a fuel mixture containing 80% RME, 4% LSME and 16% LME.

Keywords: polycyclic aromatic hydrocarbons, smoke opacity, fatty acid methyl esters, multi-component biodiesel fuel, exhaust gases

Introduction

The global problems of atmospheric pollution are the following: greenhouse effect, acid rain, ozone layer depletion, inversion of temperature and smog formation. The main sources of air pollution in Lithuania are transport (68%) and industry (20–25%). The majority (i.e. approx. 98%) of atmospheric pollutants from the transport sector consist of contaminants emitted by motor vehicles, and only 2% are contaminants of other transport means (trains, ships, planes). Transport pollution is more difficult to control than industrial pollution as it is rather difficult to apply effective cleaning devices. Therefore, it is predicted that the load of transport emissions compared with the total emission of environmental pollutants is going to increase in the future, as the number of cars is constantly increasing.

*Corresponding author; e-mail: agrotech@lzuu.lt

The pollution level and composition of emissions of motor vehicles depend on the type of fuel, type of engine, lifetime of car and other factors. According to the Lithuanian environmental normative document, only the smokiness of exhaust gases is regulated for cars with diesel engines [1]. However, having in mind the experience of other countries, it is also important to determine the amount of CO and NO_x, as well as solid particles in exhaust gases [2].

The solid particles consist of various organic and inorganic compounds. The biggest part of organic compounds is defined as soot (carbonic compounds) – not burnt out or partially burnt out fuel and oil. Soot appears when the fuel gets into an environment where the temperature is high and the concentration of oxygen is low, though reactions of soot formation have not yet been fully explained. The composition of solid particles depends on many parameters: character of combustion, operation conditions of engine (rotation speed and torque), quality of fuel and oil, and engine wear [3]. Solid particles are of various sizes, and that is on what the effect on the human organism depends. Wichman has analyzed the fractions of solid particles in exhaust gases of diesel engines that have the strongest toxic effect on humans and increase the risk of cancerous diseases: small particles – <2.5 µm and ultra small – <0.1 µm [4]. These particles get into the lungs together with air inhalation. Ultra small particles are even more toxic than the small ones, especially for elderly people [4-6].

Hydrocarbons in exhaust gases are formed when the fuel is burnt out incompletely. Their emissions may have both toxic (alkanes and alkenes) and carcinogenic (polycyclic aromatic hydrocarbons) effects [7, 8]. Polycyclic aromatic hydrocarbons (PAH) are formed when acetylene is polymerized and sorbed on soot. They cover several hundred separate compounds which consist of two or more aromatic rings [9, 10]. The U.S. Environmental Protection Agency suggests analyzing 16 PAHs, in dust and air, which are highly carcinogenic and are found often in the environment. From the air, PAH can easily migrate to water bodies, soil and plants [11, 12].

Some PAHs may cause cancerous diseases and disorders of the haematic system [13-18]. The most explored PAH is benzo(a)pyrene, which is selected as the main index when determining PAH pollution [19].

Comprehensive studies of PAH content in exhaust gases when engine was fuelled with fossil diesel fuel and ordinary biodiesel fuel (RME, SME) were performed by different researchers. The results proved that exhaust gases of fatty acid methyl esters contain only negligible amounts of PAH if compared with low-sulfur fossil diesel fuel [20-23]. The vast majority of studies have resulted in a clear advantage of conventional biodiesel fuel over fossil diesel fuel if carcinogenic potential of exhaust particulate matter is concerned. Some authors showed that PAH concentration depends on the nature of fatty acid methyl esters: PAH concentration in exhaust gases of SME was higher than those of RME [23]. Currently interest is growing on the production of fatty acid methyl esters using

other raw materials such as animal fat and waste vegetable oil, but influence of new kinds of biodiesel fuel on the composition of diesel engine emissions (including PAH content and composition) was little analyzed. In order to prove that environmental properties of fatty acid methyl esters (and their mixtures with RME) produced from animal fat and waste vegetable oil is not worse than those of an ordinary biodiesel fuel, it is necessary to perform comparative analysis of harmful components in exhaust gases of a diesel engine.

The aim of our work was to evaluate the dependence of smoke opacity and amount of polycyclic aromatic hydrocarbons in the engine emissions on the composition of multi-component biodiesel fuel containing fatty acid methyl esters of animal and vegetable origin.

Experimental Procedures

The materials used for research are:
– Rapeseed oil fatty acid methyl esters (RME), which was produced when the refined rapeseed oil was transesterified twice by rectified methanol of 99.9%, using an alkaline catalyst (KOH). RME met the requirements of the standard LST EN 14214:2001.
– Linseed oil fatty acid methyl ester (LSME) was produced from linseed oil applying the same alkaline transesterification method as in the case of RME. The transesterification yield was 98.1%.
– Tallow fatty acid methyl esters (TME) was produced from beef tallow applying the same alkaline transesterification method than in the case of RME. The transesterification yield was 97.8%.
– Lard fatty acid methyl esters (LME) was produced from pork lard applying the same alkaline transesterification method as in the case of RME. The transesterification yield was 97.2%.
The following biofuel mixtures were used for analysis of engine emissions:
– 100% RME;
– 90% RME, 2% LSME, 8% LME;
– 80% RME, 4% LSME, 16% LME;
– 70% RME, 6% LSME, 24% LME;
– 90% RME, 2% LSME, 8% TME;
– 80% RME, 4% LSME, 16% TME;
– 70% RME, 6% LSME, 24% TME.
Short-term engine tests were conducted using a direct injection 1 cylinder AVL test engine, type 502.019, placed on the test stand. The following test conditions were chosen:
a) rotation speed 2000 min^{-1}, torque 42.42 Nm,
b) rotation speed 1200 min^{-1}, and torque 9.7 Nm.

The torque was measured using a dynamometer (HBM U1) and the rotation speed – by an impulse meter (Vibro-Meter JP 1412).

The PAH analysis was carried out using two different methods: 1) laser-induced fluorescence spectrometry (LIF, Optimare) and 2) liquid chromatography (HPLC, Varian, diode detector). Average values of PAH concentration to

determine applying the above-mentioned methods were calculated.

PAH samples were collected on Pall membrane filters (T60A20). The loaded filters were heated at 300°C for 8 h and kept in a desiccator before analysis. Samples for spectrometry were prepared by extraction from filters (toluene; 25 min) using an ultrasonic bath. PAH content was measured at wavelength 355 nm. Samples for liquid chromatography were prepared by applying PAH extraction with toluene for 90 min. The excess of toluene was removed using a rotary separator Rotavac (by rotary evaporation). Polar compounds were separated from a solution applying conventional column chromatography (Sorbent Strata S1-1 from Phenomenex). Finally, the PAH phase was extracted using a mixture of cyclohexane and dichloromethane (9:1). Smoke opacity was measured using a Bosch smoke meter.

Mainly all analysis has been performed using triplicates. Values of the experiments have been evaluated using MS Excel 2003 software, calculating mean value of parallel measurements. Standard deviations of repeatability in PAH analysis applying HPLC method was between 2.5 to 9.8%. Standard deviation of repeatability in laser-induced fluorescence spectrometry analysis was between 3.8 to 12.1%.

Results and Discussions

We chose multi-component biofuel mixtures consisting of animal and vegetable methyl esters, which met the quality parameters of standard EN 14214 for iodine value, linolenic acid methyl ester content and oxidation stability [24, 25].

We determined the smoke opacity that characterizes the pollution by solid particles. Content of polycyclic aromatic hydrocarbons, which accumulate on soot and which are dangerous for human health was also analyzed.

Analyses were carried out while the engine was running at various rotation speeds.

Table 1 shows dependence of smoke opacity on the composition of multi-component biofuel.

The results showed that at rotation speed 1200 min^{-1}, Bosh number in all cases is below one. The bigger amount of LSME and LME or TME in fuel mixtures, the lower is the value of the Bosch number of exhaust gases. Smokeness almost does not differ in the case of the same content of fatty acid methyl esters of animal origin (LME or TME) in fuel mixtures. When the engine rotation speed is 2000 min^{-1}, the Bosh number varies between 3.65 and 3.8. When fuelled with mixtures of linseed oil, fatty acid methyl esters and fatty acid methyl esters of animal origin, the Bosch number of exhaust gases is lower than that of pure RME and decreases when the amount of waste fatty acid methyl esters is increased in the fuel mixture. The results show that biofuel mixtures containing fatty acid methyl esters produced from fatty waste have equal or slightly better environmental properties concerning soot content in exhaust gases.

Special attention was paid to the analysis of polycyclic aromatic hydrocarbons, thus their composition and concentration was investigated using different equipment – high-performance liquid chromatography and laser–induced fluorescence spectrometer (LIF). Fig. 1 shows mean values of total PAH content in exhaust gases.

PAH alternation tendencies were different at different rotation speeds. Total PAH amount in exhaust gases of the biofuel mixtures containing fatty acid methyl esters of animal origin and linseed oil methyl esters reduced down to 57% at the rotation speed of 1200 min^{-1}, and down to 30% at the rotation speed of 2000 min^{-1}, if compared with pure RME.

When the engine was working at the rotation speed of 2000 min^{-1}, we encountered 820μg/m³ of total PAH in engine emissions when fuelled with pure RME. In engine emissions of biofuel mixtures (RME-LSME-LME and RME-LSME-TME), which contained waste fat and oil methyl esters, PAH concentration was lower. Total PAH amount in exhaust gases when fuelled with biofuel mixtures containing pork lard fatty acid methyl esters were

Table 1. Smoke opacity (Bosch number) of exhaust gases of three-component biofuel mixtures RME-LSME-LME and RME-LSME-TME.

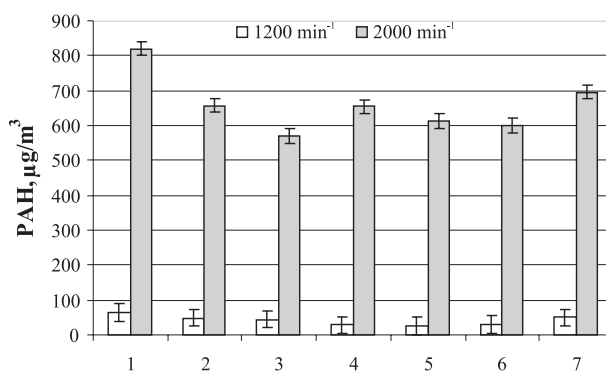| Fuel composition,%				Smoke opacity (Bosch)	
RME	LSME	LME	TME	Rotation speed, min[-1]	
				1200	2000
100				0.07	3.8
90	2	8		0.06	3.75
80	4	16		0.05	3.7
70	6	24		0	3.7
90	2		8	0.09	3.75
80	4		16	0.06	3.7
70	6		24	0.06	3.65

Fig. 1. Dependence of PAH total concentration on fuel composition: 1 – RME, 2- RME90-LSME2-LME8, 3- RME80-LSME4-LME16, 4- RME70-LSME6-LME24, 5- RME90-LSME2-TME8, 6- RME80-LSME4-TME16, 7- RME70-LSME6-TME24 (n=3).

smaller than in the case of mixtures containing tallow fatty acid methyl esters. The greatest decrease in total PAH concentration was observed when fuel composition was 80% RME, 4% LSME and 16% LME. In this case at the rotation speed of 2000 min^{-1}, we encountered 570μg/m^3 of total PAH amount in engine emissions.

It causes a problem to explain the received minimal PAH amounts, when the composition of fuel is the following: 80% RME, 4% LSME, 16% LME or TME. The formation of PAH is influenced by two main factors related to the composition of fuel: amount of unsaturated fatty acids, due to which oxidation occurs and PAHs are formed, and calorific value of fuel, which determines higher combustion temperature and more intensive PAH formation.

When the amount of fatty acid methyl esters of animal origin in fuel is increased up to 16%, the first factor has a bigger influence, i.e. the amount of unsaturated fatty acids decreases, and fewer PAHs are formed in exhaust gases. With the further increase of the fatty acid methyl esters of animal origin, the influence of the second factor becomes more evident, i.e. the higher combustion temperature determines the increase of PAH formation in the engine emissions.

At the rotation speed of 1200 min^{-1} PAH concentration was much more lower (more than 10 times) if compared with the rotation speed of 2000 min^{-1}. When engine was fuelled with pure RME, total PAH concentration in engine emissions was 65μg/m^3. In the case of fuel mixture RME-LSME-LME, PAH concentration decreased with increase of LSME and LME percentage in fuel. The low-est PAH concentration (28.1μg/m^3) was observed when the engine was fuelled with a mixture containing 70% RME, 6% LSME and 24% LME. On the contrary, when biofuel mixtures contained TME, total PAH concentration in exhaust gases increased with an increase of TME content in fuel. The lowest PAH amount (25.0μg/m^3) was determined when fuel contained 90% RME, 2% LSME and 8% TME.

Summarizing the obtained results it could be stated that fuel mixtures containing fatty acid methyl esters of animal origin and linseed oil have even better environmental properties regarding the smokiness of exhaust gases and total PAH content not only if compared with conventional biodiesel fuel – rapeseed oil methyl esters but also compared with fossil diesel fuel: research results of other authors showed that RME had better properties concerned with carcinogenic potential of exhaust particulate matter if compared with fossil diesel fuel [20-23].

Fuel mixtures containing pork lard fatty acid methyl esters showed better properties than those containing tallow fatty acid methyl esters.

Individual PAH compounds have different properties and their toxic effects on human also differ. As PAHs are lipophylic compounds, they resolve well through lungs and skin. Six of them are characterized by mutagenic and carcinogenic effects: chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene (all of which have 4-6 condensed aromatic rings). When the number of condensed rings increases, the solubility

Table 2. Concentration of PAH (μg/m^3) in engine emissions at a rotation speed of 1200 min^{-1} when fuelled with different biofuel mixtures.

PAH	RME, %	RME-LSME-LME, %			RME-LSME-TME, %		
	100	90-2-8	80-4-16	70-6-24	90-2-8	80-4-16	70-6-24
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND
Acenaphthene	ND	ND	1.06	ND	ND	ND	ND
Fluorene	6.65	ND	16.33	ND	ND	0.86	ND
Phenanthrene	32.03	42.27	18.03	12.91	18.53	22.33	26.88
Anthracene	9.36	1.19	3.76	0.85	ND	1.40	9.86
Fluoranthene	1.37	3.05	1.58	3.81	1.11	1.70	2.81
Pyrene	3.34	ND	ND	0.90	1.86	1.92	5.71
Benz(a)anthracene	1.54	ND	0.30	0.94	0.64	ND	ND
Chrysene	7.85	2.29	3.94	8.69	0.32	0.17	1.39
Benzo(b)fluoranthene	0.52	ND	ND	ND	0.60	0.84	1.44
Benzo(k)fluoranthene	2.34	ND	ND	ND	1.93	0.27	1.92
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND	ND	ND	0.02	ND

ND – Non-detectable ≤ 0.05%

in water decreases; however, these compounds dissolve well in organic solvents and fats. In the atmosphere PAHs are sorbed on dust particles of 0.1-2 μm and remain in the air for several days or even weeks, and can travel for long distances.

Benzo(a)pyrene and dibenz(a,h)anthracene are characterized by the strongest mutagenic and carcinogenic effect [18, 26]. They are characterized as the most dangerous among 16 PAHs suggested for environmental analysis by the U.S EPA. Their carcinogenic effect is more than 6 thousand times stronger than that of other polycyclic aromatic hydrocarbons, thus even a very low concentration in the environment is highly dangerous.

HPLC helped to determine both qualitative and quantitative PAH composition (Tables 2 and 3). PAH composition differs depending on engine rotation speed. When rotation speed was 2000 min^{-1}, the emitted total PAH amount was bigger and the diversity of PAH species was higher if compared with engine test results performed at the rotation speed of 1200 min^{-1}.

Quantitative analysis of PAH composition showed that at low rotation speed (1200 min^{-1}) most hazardous PAH representatives (benzo(a)pyrene and dibenz(a,h)anthracene) were not detected in engine emissions when an engine was fuelled with all kinds of the investigated fuel mixtures as well as with pure RME.

At the rotation speed of 2000 min^{-1} benzo(a)pyrene was detected in all cases with the exception of fuel mixture containing 80% RME, 4% LSME and 16% LME. Concentrations of benzo(a)pyrene was lower when an engine was fuelled with biofuel mixtures if compared with pure RME. Dibenz(a,h)anthracene was detected only in one case, when fuel contained LME (70% RME, 6% LSME, 24% LME) and in all cases when fuel contained TME. However, concentrations of dibenz(a,h)anthracene in exhaust gases when an engine was fuelled with biofuel mixtures was also lower if compared with pure RME.

Other hazardous PAHs – benzo(b)fluoranthene and benzo(k)fluoranthene – were not detected in exhaust gases when an engine was fuelled at 1200 min^{-1} rotation speed with biofuel mixtures containing LME. In the case of fuel mixtures containing TME, the increase of tallow fatty acid methyl ester content in the mixture caused an increase of benzo(b)fluoranthene concentration. In all cases this concentration was higher than that of pure RME. Concentrations of benzo(k)fluoranthene in emissions when an engine was fuelled with mixtures containing TME was lower than that when pure RME was used. A comparison of concentrations of the two above mentioned PAHs at the rotation speed of 2000 min^{-1} showed that slightly better results were obtained when an engine was fuelled with biofuel mixtures containing LME. The benzo(k)fluoranthene was not detected when an engine was fuelled with a mixture containing 80% RME, 4% LSME and 16% LME.

Table 3. Concentration of PAHs (μg/m^3) in engine emissions at the rotation speed of 2000 min^{-1} when fuelled with different biofuel mixtures.

PAH	RME,%	RME-LSME-LME, %			RME-LSME-TME, %		
	100	90-2-8	80-4-16	70-6-24	90-2-8	80-4-16	70-6-24
Acenaphthylene	ND	ND	ND	0.26	15.73	ND	ND
Acenaphthene	ND	20.88	ND	15.46	ND	10.96	ND
Fluorene	29.10	318.79	310.86	259.54	46.41	282.90	ND
Phenanthrene	396.65	66.79	55.64	65.48	257.27	80.68	368.94
Anthracene	122.03	64.23	57.02	90.92	34.73	83.28	75.20
Fluoranthene	106.35	56.15	46.92	104.81	49.73	4.24	92.83
Pyrene	65.19	14.85	12.22	9.71	24.66	45.02	72.82
Benz(a)anthracene	47.94	15.01	12.77	16.41	46.09	40.30	40.40
Chrysene	18.71	66.23	69.32	75.03	10.50	19.16	22.93
Benzo(b)fluoranthene	7.75	1.77	5.24	4.22	48.75	2.78	6.05
Benzo(k)fluoranthene	6.88	31.46	ND	3.46	4.73	19.85	1.81
Benzo(a)pyrene	8.71	1.34	ND	6.26	0.79	4.21	7.96
Dibenz(a,h)anthracene	2.98	ND	ND	1.40	2.22	1.27	1.90
Benzo(ghi)perylene	2.81	ND	ND	ND	33.28	3.46	0.90
Indeno(1,2,3-cd)pyrene	2.97	ND	ND	ND	38.10	1.90	4.26

ND – Non-detectable ≤ 0.05%

Concentration of indeno(1,2,3-cd)pyrene was below the detection limits in exhaust gases at the rotation speed of 1200 min^{-1} (with the exception when fueled with a mixture containing 80% RME, 4% LSME and 16% TME). At the rotation speed of 2000 min $^{-1}$ indeno(1,2,3-cd)pyrene was detected only in the cases when biofuel mixtures contained TME as well as in the case of pure RME. Crysene was detected in all cases of this experiment. At the rotation speed of 1200 min^{-1} concentration of this PAH was higher when fuel mixtures contained pork lard fatty acid methyl esters if compared with fuel mixtures containing tallow fatty acid methyl esters. The increase of LME content caused an increase of crysene in exhaust gases. When the engine was fueled with a mixture containing 70% RME, 6% LSME and 24% LME, concentration of crysene was even higher than that when fueled with pure RME. At the rotation speed of 2000 min $^{-1}$ the same tendencies were observed. Mixtures containing TME showed better results than mixtures containing LME. However, this compound is not as harmful as benzo(a)pyrene or dibenz(a,h)anthracene, which are characterized by the strongest mutagenic and carcinogenic effects, and were found in engine emissions when fueled with pure RME and RME-LSME-TME mixtures.

To summarize, it is possible to state that more different PAH species were detected in exhaust gases when an engine was fuelled with RME and its mixtures with tallow fatty acid methyl esters. In engine emissions of biofuel mixtures with pork lard fatty acid methyl esters there are fewer PAHs with highly expressed mutagenic and carcinogenic effects, if compared with pure RME and its mixtures, containing tallow fatty acid methyl esters. Quantitative and qualitative analysis of PAH in exhaust gases allow us to state that the most effective from an environmental point of view is usage of biofuel mixtures containing 80% RME, 4% LSME and 16% LME. It was observed that when an engine was fuelled with the above-mentioned mixture, not only total amount of PAH was the lowest (especially at the rotation speed of 2000 min^{-1}), but also fewer of the most hazardous PAHs (benzo(a)pyrene and dibenz(a,h)anthracene) were detected in engine emissions.

Conclusions

1. It was determined that the Bosch number of exhaust gases at the rotation speed of 1200 min^{-1} as well as 2000 min^{-1} decreases when the amount of waste fatty acid methyl esters in biofuel increases.
2. Fuel mixtures containing fatty acid methyl esters of animal origin and linseed oil have even better environmental properties regarding smokiness of exhaust gases and total PAH content if compared with conventional biodiesel fuel – rapeseed oil methyl esters. Taking into account comparative research results of other authors, the investigated fuel mixtures are also less polluting than fossil diesel fuel.

3. Total PAH concentration in exhaust gases is lower when fueled with biodiesel fuel mixtures containing pork lard fatty acid methyl esters if compared with mixtures containing tallow fatty acid methyl esters. Total PAH amount in exhaust gases of the above-mentioned mixtures reduced down to 57% at the rotation speed of 1200 min^{-1}, and down to 30%, at the rotation speed of 2000 min^{-1}, if compared to pure RME.
4. Concentration of PAH with highly expressed mutagenic effect in exhaust gases when fuelled with biofuel mixtures containing pork lard fatty acid methyl esters was lower if compared with the results when fuelled with pure RME and its mixtures with tallow fatty acid methyl esters.
5. The most effective from an environmental point of view is usage of biofuel mixture containing 80% RME, 4% LSME and 16% LME. When an engine was fuelled with the above-mentioned mixture, not only total amount of PAH was the lowest (especially at the rotation speed of 2000 min^{-1}), but also fewer of the most hazardous PAHs (benzo(a)pyrene and dibenz(a,h)anthracene) were detected in engine emissions.

Acknowledgements

References

1. LAND 15-2000. Vehicles with diesel engines. Smokeness of exhaust gases. Ministry of Environment of the Republic of Lithuania. **2000.03.08.**
2. TSCHÖKE H., SCHULZE L., BRAUNGARTEN G. Motoruntersuchungen mit Abgasnachbehandlungssystemen: Magdeburg, **2002.**
3. WACHTER F., CARTELLIERI W.P. Wege zukünftiger Emissionsgrenzwerte bei LKW-Dieselmotoren. 8. Int. Wiener Motorensymposium, VDI-Bericht nr. **86**, VDI-Verlag: Düsseldorf, pp 206-239, **1987.**
4. WICHMANN H.E. Dieselruß und andere Feinstäube – Umweltproblem nr.1 Gefahrstoffe – Reinhaltung der Luft **62**, 1, **2002.**
5. HEINRICH U. Feine und Ultrafeine Partikel. Gefahrstoffe – Reinhaltung der Luft **58**, 377, **1998**.
6. http://www.amtsgerichtwinsen.niedersachsen.de/AG/Akt/ Kbs/GA/hauptteil ga.html.
7. MUNACK A., SCHRÖDER O., STEIN H., KRAHL J., BÜNGER J. Systematische Untersuchungen der Emissionen aus der motorischen Verbrennung von RME; MKI und DK: Landbauforschung Völkenrode FAL Agricultural Research, **2003.**
8. KASCHANI D.T., BRAUNS A. Bestimmung von PAH's in Kraftfahrzeugabgasen durch HPLC. Umwelt. GIT Spezial*Chromatographie **2/91**, 66, **1991.**

9. ROHMBERG K. A10 Tauern Autobahn Vollsbau ink. Um-welentlastungsmaßnahmen Projekt Bericht, **2001.**

10. DURAN A. DE LUCAS A., CARMONA M., BALL-ESTROS R. Simulation of atmospheric PAH emissions from diesel engines. Chemosphere,. **44 (5)**, 921, **2001.**

11. http://www.umweltanalytik.com/lexikon/ing8.htm, Polyzy-klisch aromatische Kohlenwasserstoffe (PAK).

12. LAI (Länderausschuß für Immissionsschutz) (Hrsg.): Kreb-srisiko durch Luftverunreinigungen, Ministerium für Um-welt, Raumordnung und Landwirtschaft-NRW, Düsseldorf, **1993**.

13. LETZEL T. Analytik partiell oxidierter polizyklischer aroma-tischer Kohlenwasserstoffe und Abbau von Benzo[a]pyren auf Russaerosolpartikeln durch Ozon. Dissertation. Tech-nische Universität München, **2001.**

14. SCHEEPERS P. T. J., BOS R. P. Combustion of diesel fuel from a toxicological perspektive. Ineternational Archives of Occupational and Enviromental Health **64**, 163, **1992.**

15. Health Effects Institute. Diesel exhaust: A critical analysis of emissions, exposure, and health effects. Health Effects Institute, Cambrige, MA, USA**, 1995.**

16. MATZ G., MÜNCHMEYER W., WALTE A. On-line Anal-yse gasformiger und partikelgebundener Aromazen in Ab-gasen mit einem mobilen Massenspektrometer, VDI, Hei-delberg, **1996.**

17. LÖHMANNSRÖBEN H-G., ROCH TH. Laserfloreszen-zspektroskopie als extraktionsfreies Nachweisverfahren für PAK und Mineralöle in Bodenproben. Analitiker Taschen-buch, Springer-Verlag Berlin Heidelberg, **1997.**

18. SCHNEIDER K., SCHUMACHER U.S., OLTMANNS J., KALBERLAH F., ROLLER M. PAK (Polyzyklische aroma-tische Kohlenwasserstoffe), in: Eikmann, T.; Heinrich, U.; Heinzow,B.; Konietzka,R. (Hrsg): Gefährdungsabschätzung von Umweltschadstoffen. Loseblattsammlung, Kennziffer D 815, Berlin**, 2000.**

19. SANGHUN K. Immissions-, Depositions-, und Dieselmo-toremissionsmessung von PAK, Nitro-PAK und 3-Nitroben-zanthron Dissertation, 28.10.2005. http://opus.kobv.de/tu-berlin/volltexte/2005/1121/.

20. SJOGREN V., LI H., BANNER J., RAFTER R., WETER-HOLM R., RANNUNG U. Influence of physical and chemi-cal charavcteristics of diesel fuels and exhaust emissions on biological effects of particle extracts: a multivariate statistical analysisi of ten diesel fuels. Chem. Res. Toxicol. **9,** 197, **1996**.

21. ARDONE M., MAZZONCINI M., MENINI S., ROCCO V., SENATORE A., SEGGIANI M., VITOLO S. *Brassica cari-nata* as an alternative oil crop for the production of biodiesel in Italy: agronomic evaluation, fuel production by trans-esterification and characterization. Biomass and Bioenergy. **25**, 623, **2003**.

22. CARRARO E., LOCATELLI L.L., FERRERO C., FEA E., GILLI G. Biological activity of particle exhaust emissions from light-duty diesel engines. Journal of Environmental pathology, Toxicology and Oncology. **16 (2-3)**, 101, **1997**.

23. KRAHL J., BAUM K., HACKBARTH U., JEREBIEN H.E., MUNACK A., SCHUTT C., SCHRODER O., WALTER N., BUNGER J., MULLER M.M., WEIGEL A. Gaseous com-pounds, ozone precursors, particle number and particle size distribution, and mutagenic effects due to biodiesel. Trans-action of the ASAE. **44 (2)**, 179, **2001**.

24. MAKAREVICIENE V., SENDZIKIENE E., JANULIS P. Usage of new raw materials for biodiesel fuel production. – New methods, Means and Technologies for Applications of Agricultural Products. Proceedings of Int. Conference. – Raudondvaris, pp 52-57, **2003.**

25. P. JANULIS, E. SENDZIKIENE, V.MAKAREVICIENE, K. KAZANCEV. Usage of Fatty Wastes for Production of Biodiesel. Environmental research, engineering and man-agement, No**. 4(34)**, 101, **2005**.

26. http://www.oehha.ca.gov/air/toxic contaminants/Asbes F.html.