TOXICITY OF EXHAUST EMISSIONS FROM COMBUSTION OF LIQUID BIOFUELS AND FUELS WITH BIOCOMPONENTS

TOKSYCZNOŚĆ SPALIN Z CIEKŁYCH BIOPALIW I PALIW Z DODATKIEM BIOKOMPONENTÓW

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Abstract

The consumption of liquid biofuels as a transport fuels shows growing tendency so positive environmental aspects of using biomass is mainly used. Biofuel combustion prevents many of the toxic chemical compounds associated with conventional fuels to be emitted. The paper focused on health aspects of using liquid biofuels as a transport fuels in comparison with conventional fuels. There are provided characterization of exhaust emissions formed during combustion of liquid biofuels as well as toxicity tests of its exhaust components.

Keywords: liquid biofuels, toxicity, exhaust emissions

Streszczenie

Zastosowanie ciekłych biopaliw jako paliw transportowych wykazuje tendencję wzrostową przy czym wskazuje się głównie na pozytywny aspekt wykorzystania biomasy. Jednakże spalanie biomasy podobnie jak w przypadku konwencjonalnych paliw powoduje emisję wielu toksycznych związków chemicznych. W pracy skoncentrowano się na zdrowotnych aspektach użycia biopaliw jako paliw transportowych w odniesieniu do paliwa konwencjonalnego. Przedstawiono charakterystykę emisji powstającą podczas spalania ciekłych biopaliw jak również badania toksyczności składników spalin.

Słowa kluczowe: ciekłe biopaliwa, toksyczność, emisja spalin

Abbreviations:

B20	fuel blend consist of 20% biodiesel and 80% diesel
B100	fuel consist of 100% biodiesel
CO	carbon monoxide
E50	fuel blend consist of 50% ethanol nad 50% reforming gasoline
E85	fuel blend consist of 85% ethanol nad 15% reforming gasoline
EPA	Environmental Protection Agency
HbCO	carboxyhaemoglobin
HC	hydrocarbons
IARC	International Agency for Research on Cancer
l.d.	lack of data
NMHC	non methane hydrocarbons
NO_x	nitrogen oxides
PAH	polycyclic aromatic hydrocarbons
PM	particulate matter
RFG	reformed gasoline
RME	rapeseed methyl ester

Nadesłano: 03.08.2010
Zatwierdzono do druku: 01.09.2010

Introduction

Currently unconventionally power industry plays very important role in energy supplies. Biomass is one of the biggest renewable source of energy and has 11% share in global energy consumption [1]. Biomass is use in heat, electricity and fuel production.

In the European Union the highest amount of biomass has been using in heating production (92%) while only 1% in fuel production [2]. This direction in biomass conversion shows growing tendency, so an increase in biofuel consumption has been observed. Leader in this are Sweden (3%), the Czech Republic (2.84%) and Austria (2.5%) [3]. In 2005, the rate of use of biofuels for transport in Poland amounted to 0.4% but in 2006 exceeded 1% [4]. Biofuel combustion emits chemical compounds, which aren't neutral for human health. Growing participation of biofuel in conventional fuel consumption cause necessity of researches about their influence on human health and on the environment.

This paper presents information about exhaust gases toxicity from the combustion of biofuels and fuels with biocomponents and comparing them with conventional fuel exhaust gas toxicity. Exhaust gas toxicity has been characterized in terms of emission of harmful substances and their toxicity using in vitro assays for mutagenicity and cytotoxicity studies.

Terms connected with biofuels

Issues related with biomass have created the need to define new terms and, in the case of biocomponents and biofuels, precisely which final products from biomass conversion have been included to this group.

The field of biocomponents and biofuels in Poland has been regulated by an Act from 25th August 2006 [5]. According to this Act biofuels are:

a) engine gasolines containing over 5.0% by volume biocomponents and over 15.0% by volume ethers,
b) diesel fuel containing over 5.0% by volume biocomponents,
c) ester, bioethanol, biomethanol, dimethylester and fine vegetable oil which are self-contained fuels,
d) synthetic biofuels – synthetic hydrocarbons or blends of synthetic hydrocarbons produced from biomass, which are self-contained fuels.

Others terms used in connection with biofuels and fuels with biocomponents:

Biocomponents – bioethanol, biomethanol, ester, dimethylester, fine vegetable oil and synthetic hydrocarbons.

Bioethanol – ethyl alcohol produced from biomass also bioethanol in ethyl-tert-butyl ether and ethyl-tert-amyl ether.

Biometanol – methyl alcohol produced from biomass, also biomethanol in methyl-tert-butyl ether and ethyl-tert-amyl ether.

Biodiesel – diesel which is, or contain biological component like methyl or ethyl rapeseed esters [6].

Ester – methyl or ethyl ester of fatty acids produced from biomass.

Fine vegetable oil – vegetable oil produced from oil plants during pressing, extraction and others similar processes; fine or refined.

Synthetic hydrocarbons – synthetic hydrocarbons or blends produced from biomass.

Basic properties of conventional fuels and biofuels

Some properties of fuels and biofuels have been shown in Table 1. Biodiesel properties are quite different from gasoline properties and they are similar to diesel properties. Fuel blend consist of 20% biodiesel and 80% diesel (B20) only in heat of combustion is similar to gasoline. Other properties contained in Table I shows its similarity to diesel and biodiesel (B100).

Table I. Properties liquid fuels and biofuels [7–9]
Tabela I. Właściwości paliw ciekłych i biopaliw [7–9]

Property Fuel	Density, ρ, g/cm^3	Cetane rating, LC	Heat of combustion, Qs, MJ/kg	Kinematic viscosity in 40° C, mm^2/s
Gasoline	0.72–0.76	14	45	0.6
Diesel	0.81–0.89	40–55	43	2.0–3.5
B100	0.87–0.89	45–65	37	3.5–5.0
B20	0.84	53	42	3.1

Toxic products from the combustion of liquid biofuels and fuels with biocomponents

The composition of exhaust gases formed during combustion of biofuels and fuels with biocomponents is varied according to fuel or fuel blend.

The number of publications about this subject is very large, so the data presented in tables below are only sample values. The reason for this is the fact that researchers have used for:

- fuels with biocomponents from various stocks,
- fuels or fuel blend with various quantitative composition,
- vehicules with different engine types and at different rotational speed,
- vehicules with different age.

Table II shows substances emitted during the combustion of diesel, B100 and B20 fuels on dynamometric test stand using heavy-duty high-pressure engine.

Table III shows substances emitted during combustion of reformed gasoline, E50 and E85 fuel.

Table II. Compounds emitted during combustion of diesel oil, B100 and B20 fuel according to Ref. [7, 10]
Tabela II. Składniki emitowane podczas spalania oleju napędowego, paliw B20 oraz B100 [7, 10]

Fuel Emitted compound	Diesel [g/kWh]	B20* [%]	B100* [%]
CO	2.1	−12	−48
PM	0.26	−12	−47
NO_x	5.3	+2	+10
PAH	$9.66 \cdot 10^{-3}$	−13	−80
HC	0.6	−20	−67
Formaldehyde	$42.7 \cdot 10^{-3}$	+19	l.d.
Acetaldehyde	$15.8 \cdot 10^{-3}$	+6	l.d.
Benzene	$4.2 \cdot 10^{-3}$	+62	l.d.
Toluene	$14 \cdot 10^{-3}$	−77	l.d.
Xylenes	$9.3 \cdot 10^{-3}$	−63	l.d.

* – percent change in relation to diesel

Table III. Compounds emitted during combustion of reformed gasoline, E50 and E85 fuel according to Ref. [11]
Tabela III. Składniki emitowane podczas spalania benzyny reformowanej, E50 oraz E85 [11]

Fuel Emitted compound	RFG [g/mile]	E50* [%]	E85* [%]
CO	3	−13	−23
PM	l.d.	l.d.	l.d.
NO_x	0,2	−25	−25
PAH	l.d.	l.d.	l.d.
NMHC	0,2	−25	−25
Formaldehyde	$2{,}8 \cdot 10^{-3}$	+29	+29
Acetaldehyde	$0{,}8 \cdot 10^{-3}$	+1300	+2050
Benzene	$9 \cdot 10^{-3}$	−44	−79
1,3-butadiene	$0{,}8 \cdot 10^{-3}$	−50	−75

* – percent change in relation to RFG

Toxicology of compounds emitted during the combustion of conventional fuels and biofuels

Carbon monoxide is the main toxic compound from combustion of conventional fuels, biofuels and fuels with biocomponents. Exhaust gases emitted during uncomplete combustion of liquid fuels contain from 5 to 9% CO. The amount of CO is dependent on the state of the engine, fuel type, driving speed, outdoor condition (mainly temperature), ignition setting, etc.

Severe exhaust gas poisoning is strongly connected with toxicity of CO. Carbon monoxide forms strong coordination bonds with haemoglobin. This connection is far more stable than oxyhaemoglobin, so during poisoning tissue oxygenation is low.

Symptoms of carbon monoxide poisoning are dependent on the concentration level of HbCO in blood. HbCO concentration in the blood at 20–30% mainly manifests in headache and cutaneous vasodilation.

Strong headache, weakness, dizziness, nausea, cardiac arrhythmia and collapse can occur at concentration of 30–50%. HbCO concentration above 50% manifests in dysfunction of the heart, breathing trouble, convulsion and coma. At a concentration of 60% or higher may be death.

Another group of compounds emitted during combustion of fuels are NO_x: nitrogen monoxides and nitrogen dioxide. Source of NOx are mainly high temperature combustion processes. 40–50% of the total amount of nitrogen oxides emitted into the atmosphere comes from engine fuels combustion.

Nitric oxides activity shows a sharp negative impact of the functioning of the lungs. Nitrogen dioxide affects the lung in the similar way, but his influence is stronger.

Chronic poisoning characterize: respiratory system mucosal inflammation, bronchiolitis, conjunctival irritation, inflammation and ulceration of the mouth, damaging the enamel, drop in blood pressure and slow pulse.

Indirectly toxicity of NOx relies on the fact that nitrogen oxides are ozone precursors. High concentration of ozone in the air is the cause of the so-called "Ozone smog" [12].

Important role in exhaust gases toxicity play particulate matter-particles with various shapes and sizes suspended in the air. Particulate matter consists mainly of products uncompleted combustion of fuels. Figure 1 shows the main components of PM.

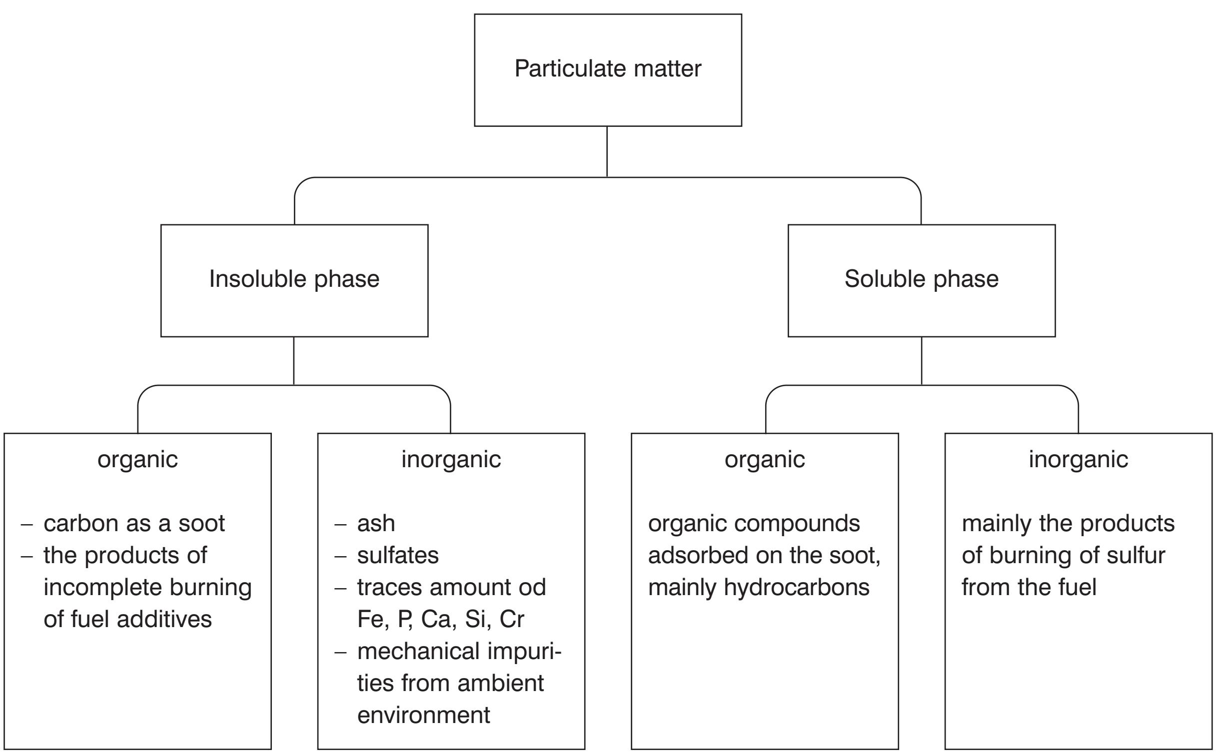

Figure 1. The main components of particulate matter according to Ref. [11]
Rycina 1. Zasadnicze części składowe cząstek stałych

The most dangerous to health are particles size below 50 nm. They can penetrate the alveoli, where are recognized like a foreign bodies. It cause defensive reaction in body which leads to inflammation and cells damage. Particulate matter emitted from Diesel engine shows cardiotoxic effects in animals. In human it causes acute coronary syndrome and other thrombotic syndromes.

Toxicity of particles is dependent on the nature of the substance adsorbed on their surface. Soot particles show high ability to adsorb products from uncompleted combustion of fuel and diesel. The soot, after adsorption of carcinogenic and mutagenic components, is very dangerous for health [13].

Polycyclic aromatic hydrocarbons (PAH) are one of the most toxic group of compound in the exhausted gases. PAH are chemical compounds with a ring structure and similar chemical properties. It is known more than 100 different compounds which are assigned to this group. In the environment most often occur 17 PAHs: acenaphthalene, acenaphthene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, genzo(g, h, i)perylene, chrysene, dibenzo(a, h)antracen, fluoranthene, fluorene, indeno(1, 2, 3-cd)pyrene, phenanthrene, pyrene, benzo(e)pyrene, benzo(j)fluoranthene. The most of the PAHs are present in air as vapours or aerosols. PAHs doesn't exist in the environment like a single compounds but always they are multicomponent mixtures.

PAHs can get into the body through the respiratory system, digestive system and through the skin.

To respiratory system PAHs get in the vapour form or adsorbed on particles of dust. Polycyclic aromatic hydrocarbons get into the digestive system with food and water. Exposure to PAHs through the skin occur mainly in terms of occupational exposure by direct contact.

Mechanism of toxicity is based on the fact that PAHs are mainly metabolized through the specyfic enzymic system to epoxides, which are active carcinogenic substances. Enzymes such as epoxide hydrolase and glutathione transferase deactivate epoxides and probability of carcinogenic changes after exposure to procarcinogen is dependent on the speed of enzymic systems: activating and inactivating.

Nitro-PAHs are classified as high toxic compounds. According to the IARC: 2-nitrofluorene, 1-nitropyrene, 4-nitropyrene, 6-nitrochrysene, 1, 6-dinitropyrene, 1, 8-dinitropyrene are carcinogenic (2B group-substances possibly carcinogenic to human) [14, 15].

Formaldehyde and acetaldehyde are low molecular weight organic compounds present in exhaust gases. Concentration of formaldehyde in industrialized and urbanized regions may be high (up to 197 mg/m^3). Industrial production, the combustion of energy fuels in power plants, thermal power stations and boiler rooms and the combustion of fuels in car engines are very important sources of formaldehyde. In addition, formaldehyde is formed as a result of natural photooxidation of aromatic hydrocarbons from car exhaust gases.

Epidemiological and health studies confirm that formaldehyde has negative influence on human health. It is related to strong irritation of eyes and upper and lower respiratory tract. In 2006 formaldehyde has been classified by IARC as 1-group carcinogen, with proven carcinogenicity to human. Acetaldehyde also has been classified as a very toxic and extremely flammable substance with possible carcinogenicity to human. Symptoms acetaldehyde activity on human body are: headache, dizziness, conjunctivitis, nusea, burning sensation in the throat, cough, shortness of breath. In high concentration ethanal shows narcotic action on central nervous system.

Important, in terms of exhaust gases toxicity are low molecular, aromatic organic compounds: benzene, toluene and xylene. The main sources of benzene in the environment are tobacco smoke, industry, exhaust fumes. The last two sources accout for 20% of exposure to benzene.

Benzene is a substance that can get into the body through the respiratory system, digestive system and through the skin. It also shows narcotic action on central nervous system and high affinity for the bone marrow, where benzene and its metabolites damage young erythrocytes and leukocytes. Benzene is very dangerous for human health during long-term exposure. Chronic poisoning is manifested in a loss of appetite, headache, somnolence or excitability and paleness. Leukaemia is described as a complication of benzene poisoning. Benzene is classified as a carcinogen to human [16, 17].

Toluene is added to fuels as a substance increasing the octane number. It is harmful through the respiratory system. Vapours may cause somnolence and dizziness. Toluene has a similar toxicity to benzene, but it works stronger on the nervous system and shows a stronger irritation. Tolune has lower than benzene influence on hematological processes.

Xylenes are a group of compounds consisting of three isomers of 1, 2-Dimethylbenzene (o-Xylene); 1, 3-Dimethylbenzene (m-Xylene); 1, 4-Dimethylbenzene (p-Xylene). The mixture of these isomers is a colorless, flammable and sweet-smelling liquid. Xylene is absorbed from the respiratory tract, gastrointestinal and through the skin.

Xylene toxicity is closely linked to their affinity for nerve tissue, bone marrow and adipose tissue.

In the exhaust fumes is also 1, 3-Butadiene (C_4H_6) – unsaturated hydrocarbon which belongs to the dienes group. 1, 3-butadiene is classified as carcinogen to humans [16, 18].

The regulation of emissions of harmful compounds in the exhaust fumes

Emissions of nitrogen oxides, carbon monoxide, hydrocarbons and particulate matter are regulated for the most vehicles in the European Union. The standards limit emissions from new cars sold in the EU set out a European standard for exhaust emissions. Another, more restrictive standards are placed at intervals of several years. Since 1992 the Euro 1 standard applied, since 1996 Euro 2, since 2000 the Euro 3, since 2005 the Euro 4. Since October 2009 the Euro 5 standards has been adopted together with Euro 6, which will enter into force five years later [19].

In Polish legislation the content of gas pollutants and particulate matter in the exhaust fumes is regulated by the Decree of the Minister of Economy and Labor of August 19, 2005 on detailed requirements for internal combustion engines to reduce emission of gas pollutants and particulate matter for these engines [20].

The impact of liquid biofuel on exhaust composition

The results of comparative studies of the emission of substances formed during combustion of diesel oil, pure biodiesel and biodiesel blends indicate that composition of exhaust gases is depended on quality of fuel and vehicle used to research. Generally, in comparison to emission from combustion of diesel oil, the biodiesel exhaust may contain up to 60% less of toxic CO and 20% less content of hydrocarbons [7, 9, 10]. Additionally the combustion of pure biodiesel fuel is not connected with emission of sulfur oxides. However, usually higher emission of nitric oxides is observed, which potentially may cause adverse health effects and are precursors of ozone in the troposphere. Ozone, which is present in the ambient air, has a very negative impact on human body, it may cause breathing problems and probably increases the incidences of asthma [23].

Particulate emission is usually decreased in combustion of biodiesel and biodiesel blends comparing to particulate content in diesel exhaust. However, with the reduced of total content of particulate there is a higher proportion of their soluble organic fraction in compare to particulate, which is emitted from combustion of diesel oil [24]. Lower emission of particulate together with higher soluble organic content may influence the toxicity and biological effects. However, the biodiesel particulates contain lower content of PAHs and their nitrated derivatives, which are mainly responsible for carcinogenic effects of diesel exhaust [32, 33]. In addition, the dust emitted in the exhaust of biodiesel is usually characterized by a smaller average particle size, but it is attributed to significant reduction in the formation of large particles rather than to the higher emissions of smaller particles size [7].

The greatest uncertainties are still associated with the emission of carbonyl compounds such as formaldehyde, acetaldehyde and other aldehydes and ketones. In some studies there is observed significant reduction in emission of this compounds [21, 29] while in others their emission increases when compare to diesel oil exhaust [9, 30, 31].

The EPA analyzed impacts of on 11 unregulated hazardous air pollutants referred to as gaseous toxics. These included acetaldehyde, acrolein, benzene, 1, 3-butadiene, ethylbenzene, formaldehyde, n-hexane, naphthalene, styrene, toluene and xylene. The conclusion from the analysis is that the total toxics are reduced when biodiesel is added to conventional diesel fuel. However, the reduction is not so intensive as reduction of total hydrocarbons with the addition of biodiesel, giving actually increase in the mass ratio of total toxics to total hydrocarbons. The analyzes for individual toxics suggest a statistically significant reduction only in acetaldehyde, ethylbenzene, formaldehyde, naphthalene and xylene emissions with increasing biodiesel concentration. The results for the others are not conclusive or suggest very small effect [21]. The analysis showed, that there was a shift in the composition of total hydrocarbon towards more unregulated pollutants, however the shift is not large enough to cause total toxic emissions to increase with biodiesel use compare to diesel oil [25].

The combustion of gasoline with addition of ethanol and pure ethanol in spark-ignition engine usually results in significant reduction of carbon monoxide emission and increase in emission of acetaldehyde [12]. Acetaldehyde is a toxic and potentially carcinogenic compound for human. In the atmosphere acetaldehyde is a precursor of peroxyacetylic nitrate (PAN), which is irritating compound while inhalation and toxic for plants. It takes part in transfer of nitric dioxide for long distances contributing to ozone forming. The review by Niven [27] indicates that testing of addition of ethanol and emission of nitric oxides does not give clear results. Other toxic compounds such as 1, 3–butadiene, formaldehyde are emitted in compare or some lower quantity after addition of ethanol to gasoline. Significant reduction is observed for benzene (increase in a few studies), toluene and xylenes. While there is increase in emission of acroleine.

Addition of methanol to gasoline results in lower emission of CO and organic compounds. Among toxic compounds there is observed reduction of forming of benzene, 1, 3-butdiene and acetaldehyde [12]. However, emission of formaldehyde increases several times as a very negative phenomenon. Formaldehyde is irritating and carcinogenic compounds and its potential to form ground-level ozone is the highest of all carbonyl compounds [28].

Liquid biofuel exhaust emission and toxicity tests

Due to reduction in CO emission the less acute toxicity of exhaust gases was shown from combustion of ethanol as a fuel compare to exhaust gases emitted from combustion of gasoline [34]. The reduction in CO emission is also significant in case of using biodiesel fuel, so less acute toxicity is expected compare to conventional diesel fuel.

Subchronic inhalation exposure to soybean oil-derived biodiesel exhaust emission was tested in rats. Biological significant exposure-related effects were limited to the lung. The dose-related increase in the numbers of alveolar macrophages was observed and only minor changes in a few female rats at the highest exposure level. At the intermediate level none other than expected physiological macrophages response to repeated particle exposure was shown. There were no significant exposure-related impact on the other health parameters [35].

There are rather limited data regarding mutagenic potential of biodiesel exhaust. In bacterial in vitro assays most of the mutagenic property is related to small part of compounds contained in a soluble fraction of emitted particulate, primarily PAH and their derivatives. The mutagenic potential of particulate formed during combustion of rapeseed oil-derived biodiesel was compared with the particulate from diesel oil in the Ames test using TA97a, TA98, TA100, TA102 (Salmonella test). Significant increase in the number of mutation among TA98 and TA100 was observed after adding the extracts of particulate matter from both types of fuel. However the amount of revertants was significantly higher for conventional diesel fuel than for biodiesel. The most amount of revertants was observed during combustion of fuel in cold engine. It was demonstrated that particulate matter from biodiesel significantly reduced mutagenic potential compare with that from diesel fuel. This effect is probably due to lower emission of PAH, however masses of particulate matter were reproducibly higher for RME than for conventional diesel fuel [36].

Very high mutagenic effect was observed for particulate mater and condensate of gases emitted during combustion of pure rape oil fuel while regulated pollutants were in acceptable range. In the same study comparable mutagenic potential was found for extract of particulate matter and condensate of gases for RME and diesel oil [37]. Similar to mutagenic effect of dust extracts from diesel exhaust was observed also for 20% RME biodiesel blend [9].

Generaly, the plant oil-derived biodiesel fuel demonstrates similar or even lower mutagenic potential of particulate matter emitted during combustion, most likely due to lower content of PAH and their derivatives in the soluble fraction of dust [9, 36, 37, 38, 39].

Cytotoxic property of biodiesel exhaust was compared with that from conventional diesel fuel. The study demonstrates higher cytotoxic effect of biodiesel (RME) exhaust than that of diesel oil. The results show even 4 times higher toxicity of culture cells for biodiesel than diesel oil exhaust (as effective dose 50%, ED50) and the most cytotoxicity occurred during idle. The authors attributed the increase in cytotoxic effects to higher emission of carbonyl compounds and unburned fuel [39]. Other studies showed, however that increasing concentration of RME in diesel oil caused decrease of cytotoxic effects of particulate matter extracts emitted during combustion in Diesel engine or analysis suggested a statistically no significant effects [36, 40].

Based on analyzed data it can be stated that using of liquid biofuels may reduce the emission of many toxic compounds. However, in many cases the particulate matter from plant oil-derived biodiesel fuel exhaust. By contrast, studies of cytotoxicity does not give clear results which is probably related to variability in the composition of exhaust emissions. There is still need for futher research. The carcinogenicity of liquid biofuel exhaust emissions is one of the priority task in IARC for the years 2008–2014 [22].

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