Vol. 1, No. 2, 2007 Chemical technology

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QUALITY AND ECOLOGICAL SAFETY OF MOTOR FUELS

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Received: March 30, 2007

Abstract. Article considering interconnection of fuel quality for transport and ecological safety. Main directions were offered of solving ecological-energy problem system "human-environment-fuel-transport".

Key words: fuel, transport, ecological safety, ecological properties.

Energy ecological problems and aspects of its rational development are very urgent today (Fig. 1).

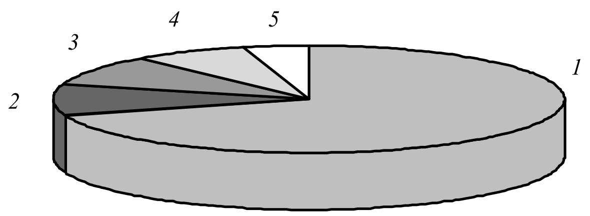

Fig. 1. Harmful substances emission balance during transport exploitation:
1 - automobile transport (70 %); 2 - agricultural (9.4 %); 3 - railway (9.2 %); 4 - air (7.3 %); 5 - water (4.1 %)

Fuel for transport engines is well-known toxically harmful substances, which can cause industrial injury, diseases or health problems of people who work in specific area. Environment pollution by oil products is caused by its evaporation or leakage and fuel combustion emissions into atmosphere during engine working.

High atmospheric air quality providing is one of the most important aspects. Ukraine with other industrialized countries signed and performs Montreal protocol (1988) about ozone depletion protection, Convention of Organization of United Nations at New-York (1992) about climate change and Kiyoto Protocol (1997), which assigned decreasing of harmful substances emissions to the whole country and separately to each branch of economy, where energy is individual part. The main goal is to prevent global consequences from carbon dioxide and other emissions, which cause ozone depletion.

Requirements for harmful substances emissions regulate by rule 49 EEC OUN and directive 88/77 EU (Tables 1-3).

Table 1

Regulations for transport ecological compatibility

Directive EU and rules EEC OUN	Harmful substances emissions, g/кw			
	CO	CH	NO_x	Particular matter
Rule 49 EEC OUN	14.0	3.5	18.0	-
Directive 88/77 EU	11.2	2.4	14.4	-
Euro-1 (from 1993)	4.5	1.1	8.0	0.36
Euro-2 (from 1996)	4.0	1.1	7.0	0.15
Euro-3 (from 1.10.2000)	2.0	0.6	5.0	0.1
Euro-4 (2003–2005 years)	1.5	0.5	3.5	0.08
Euro-5 (2006–2009 years)	1.0	0.5	2	0.05

Table 2

Regulations dynamic for automobile toxicity

Norms	Engine type	Introduction term (Europe)	Maximum-permissible emissions of harmful substances, g/km				
			CO	CH	NO_x	CH + NO_x	Particular matter
Euro-1	Petrol	1993	2.72	-	-	0.97	-
	Diesel		2.72	-	-	0.97	0.14
Euro-2	Petrol	1996	2.2	-	-	0.05	-
	Diesel		1.0	-	-	0.7	0.08
Euro-3	Petrol	2000	2.3	0.2	0.15	-	-
Euro-4	Petrol	2005	1.0	0.1	0.08	0.3	0.025
	Diesel		0.5	-	0.25	-	-

Table 3

Regulations dynamic for diesel automobile toxicity

Norms	Introduction term (Europe)	Maximum-permissible emissions of harmful substances, g/kW·h			
		CO	CH	NO_x	Particular matter
Euro-2	1996	4	1.1	7	0.15
Euro-3	2000	2.1	0.66	5	0.1-0.13
Euro-4	2005	1.5	0.25	2	0.02
Euro-5	2008	1.5	0.25	2	0.02

USA selected strategic direction in reformulated petrol producing for increasing of petrol ecological characteristics. California State developed hardwired production and application of reformulated petrol - California Air Resources Board (CARB-I, CARB-II). Comparison of USA petrol quality indexes with European indexes is in the Table 4.

Table 4

Petrol quality indexes comparison

Quality index	Regular petrol USA	European petrol	Reformulated petrol (simple model)	Reformulated petrol (composite model)	CARB-I	CARB-II
Benzene content, % v/v	2	5	0.8	0.8	1	0.8
Aromaticity, % v/v	32	-	27	25	25	22
Olefinic content, % v/v	9.5	-	8.5	8.5	6	4
Oxygen content, % v/v	-	-	2	2	2	-
Sulfur content, ppm	339	500	130	130	40	30

European countries from the year 2000 implemented new specification on automobile petrol's. Ecological requirements to European automobile petrol according to EN 228 specified benzol content decreasing from 5.0 to 1.0 rel. %, and total aromatic hydrocarbons from 42.0 to 30.0 rel. %.

Table 5

Physical-chemical petrol indexes comparison

Index	Quality category. World market classes				DSTU data 4063 for types A-76, A-80, A-92, A-95, A-98
	I	II	III	IV	
Octane number, not less: — research method	91.0 95.0 98.0	91.0 95.0 98.0	91.0 95.0 98.0	91.0 95.0 98.0	80.0; 92.0; 95.0;98.0
— motor method	82.0 85.0 88.0	82.5 85.0 88.0	82.5 85.0 88.0	82.5 85.0 88.0	76.0; 76.0; 82.5; 85.0; 88.0
Breakdown time of oxidation, min, not less	360	480	480	360	360; 360; 360; 360; 360
Sulfur content, % not more	0.10	0.02	0.003	5–10 ppm	0.05; 0.05; 0.05; 0.05; 0.05
Lead concentration, g/dm^3	0.013	absent	absent	absent	0.013; 0.013; 0.013; 0.013; 0.013
Phosphorous concentration, g/dm^3	-	absent	absent	absent	not regulates
Manganese concentration, g/dm^3	-	absent	absent	absent	not regulates
Oxygen concentration, %, not more	2.7	2.7	2.7	2.7	2.7; 2.7; 2.7; 2.7; 2.7
Fractional volume of hydrocarbon olefins, %, not more	-	20.0	10.0	10.0	not regulates
Fractional volume of aromatic hydrocarbons, %, not more	50.0	40.0	35.0	35.0	42; 42; 45; 45; 48
Fractional volume of benzene, %, not more	5.0	2.5	1.0	1.0	5.0; 5.0; 5.0; 5.0; 5.0
Soluble gum concentration, mg/100 sm^3 petrol, not more	5	5	5	5	5.0; 5.0; 5.0; 5.0; 5.0
Density at 288 K, kg/m^3	715-780	715-770	715-770	725-780	700-760; 700-760; 725-780; 725-780

Table 6

Ecological requirements for petrol (Directive of European Union 2003/17/EU)

Parameters	Unit	Limits	
		Min	Max
Octane number - research method - motor method		 95 85	 - -
Vapor pressure, summer period	kPA	-	60.0
Distillation: - % evaporation at 373 K - % evaporation at 423 K	 % v/v % v/v	 46.0 75.0	 - -
Hydrocarbon analysis: - olefins - aromatics - benzene	 % v/v % v/v % v/v	 - - -	 18.0 42.0 1.0

Oxygen content: Oxygenates - methanol (stabilizing additives) - ethanol (stabilizing additives possible) - iso-propyl alcohol - tret-butyl alcohol - iso-butyl alcohol - ethers containing five or more carbon atoms per molecules - other oxygenated	% m/m % v/v % v/v % v/v % v/v % v/v % v/v % v/v	- - - - - - -	2.7 3 5 10 7 10 15 10
Sulphur content	mg/kg	-	150
Lead content	g/l	-	0.005

Table 7

Ecological requirements for diesel fuel (Directives of European Union 2003/17/EU)

Parameters	Limits	
	Min	Max
Cetane number	51.0	-
Density at 388 K, kg/m^3	-	845
Distillation: - 95 % (v/v) evaporated at temperature, K	-	633
Content of polycyclic of aromatic hydrocarbons, % m/m	-	11
Sulphur content, mg/kg	-	350

These requirements reflected in european standards of series Euro-2, 3, 4, 5 (Tables 1-3), requirements of World Charter of fuel producers (Table 5) and Directive of European Union 2003/17/EU (instead of Directive 98/70/EU), assigned ecological requirements to fuels (Tables 6. 7).

Automobile transport development perspectives are very broad, which indicates level of anthropogenic influence increasing on atmospheric air purity, flora and fauna.

Diesel fuel producing and consumption is increasing with parallel automobile petrol large volume producing. Diesel transport is one of the main sources of environmental pollution by sulfur oxides, nitrogen, soot particles and toxic aromatic hydrocarbons.

On December'2000 directive of Management on environmental protection USA (EPA) was published, according to directive requirements from June'2006 sulphur content in diesel fuel should not be more then 0.0015 % mass.

European Union standard EN 590, which decreases sulfur content from 0.2 % to 0.005 %, is an example of ecological requirements toughen as to diesel fuels. None of technical decisions accepted without thorough ecological expertise.

Aviation transport increasing in transport complex system of developed countries economy. For example, in 1970 USA aviation transport consumed 7.5% of energy, which used by transport sector. In 1985 energy consumption by aviation increased up to 27 %, in 2000 – to 32.5%. Amount of air planes (AP) is rising up. In 1970 world AP park counted 7301 planes, but today there are more then 8000. Subsonic aircraft contains 90 %, rest 10 % – supersonic AP. During the 1990 to 1995 world park of civil AP increased from 357.5 thousands aircrafts to 369.1 thousands, on 3 %.

Forecast International published information that in 2004-2013 more then 5835 huge civil and transport airplanes will be build in the world. According to World Airfleet data there are about 2 thousands air companies, which have 50 thousand aircrafts.

Administrative aviation develops lately and aviation of business class. According to National association of administrative aviation of USA data in 1990 World Park of certain class AP had 14727 airplanes, 6728 airplanes with turbojet engine.

Aviation engine fuel production is one of the most developing branches in oil refining industry of the world (Table 8).

Table 8

Fuel quality indexes comparison of jet fuels of different countries-producers

Index	Value				
	PT (Ukraine)	TC-1 (Ukraine)	TC-1 (Russian Federation)	PT (Russian Federation)	Jet A-1 (USA)
Density at 293 K, kg/m^3, not less	775	775	810	775	775-840
Fractional composition: — boiling point, K	Not normed	Not normed	Not more 150	Not less 408, not more 428	Not normed
— 10 % distillation at *t*, K, not more	448	448	448	448	478
— 50 % distillation at *t*, K, not more	498	498	498	498	505
— 90 % distillation at *t* , K, not more	543	543	543	543	-
— 98 % distillation at *t*, K, not more	553	553	553	553	573
Kinematic viscosity, mm^2/s, — at 233 K, not more — at 293 K, not less	16 1.25	16 1.25	16 1.5	16 1.25	15 (at *t* – 307.4 K) 8 (not more)
Low heat value, kDj/kg, not less	43 100	43 120	42 900	43 120	42 800
Height of sootless flame, mm, not less	25	25	20	25	25
Acidity, mg KOH/100 g of fuel, not more	0.7	0.7	0.7	0.2-0.7	0.1
Iodine value, g/100g of fuel, not more	0.5	3.5	2.0	0.5	-
Flash point in closed crucible, K, not lower	303	301	303	301	311
Chilling point, K, not higher	218	218	213	218	226
Oxidation stability: — residue amount, mg/100 sm^3 of fuel, not more — critical temperature, K, not less	6 388	18 388	6 -	6 -	14 -
Aromatic hydrocarbons mass fraction, %, not more	22	22	20	22	20
Soluble gum concentration, mg/100 sm^3 of fuel, not more	4	5	6	4	7
Sulfur mass fraction, %, not more	0.1	0.25	0.1	0.1	0.3
Sour sulfur mass fraction, %, not more	0.001	0.003	0.001	0.001	0.003
Hydrogen sulfide content	Absent	Absent	Absent	Absent	-
Testing on copperplate at 373 K 3 hours	Holds	Holds	Holds	Holds	-
Ash value, %, not more	0.003	0.003	0.003	0.003	-
Interaction with water, number, not more	1	1	-	1	1
Conductivity, pCm/m — at 293 K, not more	600	600	-	600	450
Mechanical impurities and water content	Absent	Absent	Absent	Absent	Absent
Water soluble alkali content	Absent	Absent	Absent	Absent	-
Water soluble acids and alkaline content	Absent	Absent	Absent	Absent	-
Naphthenic acid soap content	Absent	Absent	Absent	Absent	-
Antiwear properties in conditions of sliding friction on UPS-01 unit, antiwear properties criteria, %, not less	95	95	-	-	-
Mass fraction of naphthalene hydrocarbon, % mass, not more	1.5	3	-	1.5	3
High temperature corrosion: sample mass loss, g/m^2 at 293 K, not more — for copper — for bronze type VB23NC	3.0 2.5	15 2.5	- -	- -	- -
Lumenmeter number, not less	50	50	-	50	45

Automobile emissions contain more then two hundred types of toxic elements, such as: carbon oxide, nitrogen, sulfur, heavy metals, carcinogens and mutagens, hydrocarbons, aldehyde, aerosols, sulfurous anhydride, etc. (Table 9). Every year automobile imbibe 4350 kg of oxygen from atmosphere, and emitted 3250 kg of carbon and 530 kg carbon monoxide, 90-150 kg unburnt hydrocarbon, 40 kg nitrogen oxide, up to 1 kg of lead. Also 96 % carbon oxide, 30 % nitrogen oxide, 68 % hydrocarbons are emitted into atmosphere through exhaust pipe of automobile. Wrong exploitation of transport can be the reason for toxic substances emission increasing CO, C_nH_m – up to 25–30 %, NO_x – up to 15 %.

Table 9

Specific loss of petrol and diesel engine

Harmful substance	Specific loss, Petrol engine	g/kg fuel Diesel fuel
CO	37.8	20.8
NO_x	21.0	41.0
CH	30.0	10.5
Particular matter	1.5	7.6
SO_x	1.5	5.6
Aldehyde	0.93	0.78

Intensity of harmful substances emissions by one diesel locomotive is an analog to 15-20 trucks or 40-60 automobiles. One aircraft TU-154 during take off and landings is emitting into the atmosphere 100 times more harmful substances then car. 2-4 mg/min of carcinogenic substances (benzopiren) is emitted into atmosphere during the work of turbo jet and turboprop engines. Air plane is emitting 3.7 t carbon oxide, 2 t hydrocarbons (unburned fuel) and 1.7 t nitrogen oxide per day by take offs and landings.

In 1985 world aviation emitted into atmosphere more then 1.2 (100) mln. tones of CO, 0.8 (25) mln. tones CH, 1.4 (15) mln. tones NO.

The main danger of harmful substances is its emissions at cites, streets, parking lots, airports where contain in bottom layer on the level of human respiratory organs. Fuel evaporation is dangerous and poisonous; it can cause harm for human, plants and animals. When air saturated with petrol evaporations is inhaled in amount of 5-10 mg/l, acute poisoning reaches human organism. Harmful substances formation conditions, which is contained in transport engine exhaust gas described in details in special literature.

Hydrocarbons are the most harmful substance, which pollute atmosphere and have dangerous impact on human. Hydrocarbons are indicators of carburetion and combustion process poor organization or major lack of air in engine fuel mixture. Fuel combustion products contain various hydrocarbons: methane CH_4, ethane C_2H_6, propane C_3H_8, acetylene C_2H_2, ethylene C_2H_4, benzol C_6H_6, toluol $C_6H_5CH_3$ etc. Hydrocarbons enter to photochemical reaction with nitrogen oxides under the influence of the sun, produce wide spectrum of substances (peroxide, ozone etc.), which accelerate corrosion of different materials, harmful for plants, and one of the reason of smog formation, which causes lungs diseases. Ozone is the most dangerous among photo oxides. When concentration is 200 mkg/m^3 it is causes irritation of eyes, nose mucosa and headache. Exhaust gas hydrocarbons has carcinogenic influence on human organism. Benzopiren has biological influence (БаП, 3,4-benzopiren, $C_{22}H_{14}$).

Tetraethyl lead (TEL) $(C_2H_5)_4Pb$ and tetra methyl lead (TML) $(CH_3)_4Pb$ are very toxic components, used for petrol octane number increasing contains lead. For removing of combustive products effluxes are used (lower bromide, chloride); decrease lead content in 3-5 times in combustive chamber. It means that 90-98 % of lead contained in ethyl petrol is emitted in atmosphere. Lead forms aerosols with automobile gases, which absorbed by lungs with air and stored with food and water in stomach and causes disorder central nervous system, fainting, injury of liver, kidney, decreasing of vision, genetic disfunction. Because of definite element toxicity most countries forbid its content in petrol's and require automobile exploitation on non-ethylene petrol.

Another reason of atmosphere contamination - is fuel evaporation during transportation, storage, technological discharge operations, loading, refueling and from transport fuel systems. From all types of losses this one have class "irretrievable", part of them protected and regulated by oil products losses (kg/t) according to “Norms of oil products natural loss during storage, distribution and transportation” reflects natural loss of various types of oil products in different technological operations. When consumption of oil products increasing, damage to economy and ecosystem also increasing in the result of natural losses. Small dirt part (list of them contain viewed emissions) is huge in conditions of anthropogenic atmospheric pollution and depletion of Earth “protective shield” – ozone layer. Ozone decreasing is registered today and theoretical model analysis help scientists to predict changes of ozone in the nearest years by given concentration changes of various harmful substances from anthropogenic sources. Inherent decreasing of ozone layer (up to 10 % and more) is real in the nearest 15-30 years, because of emissions increasing. According to Environmental protection International committee data ozone holes are located above every city, and above Antarctica the hole has diameter of 8 km.

To realize statements of Kiyoto protocol and used article 2 (iv and vii, IPCC method) we have done calculation of greenhouse gases into equivalent of CO_2. Initial data is daily emissions from regular refueling station in amount of 60 kg particular volatility organic compounds

(VOC); we have to consider potential of global warming defined by 100 years term. Emissions on such term are **2160000 kg**. Transferring of received amount of VOC into CO_2 (in regard to potential of global warming indexes for CH_4, that at UNFCCC evaluation is 23) we got 0.00506 Tg equivalents to CO_2.

Conclusion

Analysis mentioned above shows to solve ecologically energetic problems of energy, connected with transport exploitation and motor fuel application, optimal complex approach applied to system "human – environment – fuel – transport", granting all technological chains specifications from the moment of oil extraction to product transformation of unburnt gases and fuel.

Main directions of ecologically energetic problem solving of system "human – environment – fuel – transport" are: 1) motor fuel quality increasing with ecologically safe characteristics; 2) engine construction improvement with purpose of combustion efficiency and harmful substances emission transformation in unburnt gases increasing; 3) alternative fuels application; 4) environmental procedures on the object of oil products complexes, system of transportation, refueling stations, petroleum storage depot; 5) organizational procedures including harsh regulations (standards), which control harmful substances emissions in unburnt gases and volatile hydrocarbons, which evaporate into atmosphere.

ЯКІСТЬ І ЕКОЛОГІЧНА БЕЗПЕКА ПАЛИВ ДЛЯ ТРАНСПОРТНИХ ЗАСОБІВ

Анотація. *У статті розглянуто взаємозвязок якості палив для транспортних засобів та екологічної безпеки. Запропоновано головні напрямки вирішення эколого-енергетичних проблем системи "чоловік – навколишнє середовище – паливо – транспортний засіб".*

Ключові слова: *паливо, транспортні засоби, екологічна безпека, екологічні властивості.*