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THE MIXTURE OF BIOBUTANOL AND PETROL FOR OTTO ENGINES

Saugirdas Pukalskas[1], Zenonas Bogdanovičius[2], Eglė Sendžikienė[3], Violeta Makarevičienė[4], Prutenis Janulis[5]

[1,2]Dept of Automobile Transport, Vilnius Gediminas Technical University, J. Basanavičiaus g. 28, 03224 Vilnius, Lithuania
[3, 4, 5]Institute of Environment, Lithuanian University of Agriculture, Studentų g. 11, Akademija, Kaunas Region, Lithuania
E-mails: [1]saugirdas.pukalskas@vgtu.lt; [2]zenonas.bogdanovicius@vgtu.lt; [3, 4, 5]agrotech@lzuu.lt

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Abstract. The expansion of production and the use of biofuels are determined by the legal acts of the European Commission and National legal acts encouraging such production and usage. It would be meaningful to use the mixtures of butanol and petrol in Otto engines. It was determined the possibility of producing biobutanol as a biofuel of the second generation from lignocellulose hydrolyzed to C_5/C_6 carbohydrates. If the 20–30% potential of lignocellulose biomass in Lithuania is used, it would be possible to produce 200–300 thousand t of biobutanol per year. The amount of carbon monoxide CO decreases by more than 80% when the engine works using the mixtures of petrol and butanol if compared to the CO amount of the engine working with petrol. When the engine works using the mixture of 30% butanol and petrol, the amount of carbon dioxide CO_2 decreases by 4% on average, and in case it works with the mixture of 50% butanol and petrol – by 14% if compared to the CO_2 amount of the engine working using petrol. When the engine works using the mixture of 30% butanol and petrol, the amount of hydrocarbons HC decreases by 26% on average, and if it works with the mixture of 50% butanol and petrol, the amount increases by some 4% if compared to the HC amount of the engine working using petrol. To generalize the results of the performed experiment, it is possible to state that the optimal mixture would consist of 70% petrol and 30% biobutanol.

Keywords: petrol, biobutanol, emissions, Otto engines, biofuel, engine speed.

1. Introduction

The expansion of production and the use of biofuels are determined by the legal acts of the European Commission and National legal acts encouraging such production and usage (Directive 2003/30/EC; Council Directive 2003/96/EC; Lietuvos Respublikos biokuro... 2000; Lietuvos Respublikos akcizų... 2004). Producing and using biofuels has opened a new area in Lithuania as well as researches in this area (Matijošius and Sokolovskij 2009; Raslavičius and Bazaras 2009; Raslavičius 2009; Bazaras and Raslavičius 2008; Lebedevas and Lebedeva 2009; Lingaitis and Pukalskas 2008a and 2008b; Lebedevas *et al*. 2007a and 2007b; Raslavičius and Markšaitis 2007; Labeckas 2005; Makarevičienė 2005).

Yet in 1936, the additives of anhydrous ethanol were used in petrol in Lithuania, however, the wide industrial use of those started only in 2000 when a spirit factory in Šilutė was reconstructed to the plant of water-free bioethanol containing at least 99.6% of organic substances. The company *Biofuture Ltd.* is the Lithuanian flagman of producing alcoholic biofuels. In 2008, the company produced 25 thousand tons of bioethanol a major part of which was purchased by the refinery *Mažeikių nafta* (Mažeikiai oil) and used as a 5% bioethanol additive in petrol. Bioethanol can be also used as raw material for producing bioethyltretbutylether that can be added to petrol as an octane additive making up to 15%. Bioethanol does not allow expanding its usage volumes, except for biofuel E85 containing up to 85% of bioethanol (Bureika 1996; Bureika and Pukalskas 1998; Pikūnas *et al*. 2003; Butkus and Pukalskas 2004; Butkus *et al*. 2005; Pikūnas *et al*. 2006). However, such biofuel with high bioethanol content can be used only in special 'flexible' Otto engines. Nevertheless, there are only several cars in Lithuania having a similar engine. It is possible to use a very wide range of raw materials for producing bioethanol (on the contrary to producing biodiesel fuel) including cereal and corn grains, sugar

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beets, molasses, potatoes as well as raw materials containing lignocellulose – wood and wood waste, rapidly growing ligneous plants, cereal and rape straws etc. (Festel 2006; Ramey and Yang 2004; Alasfour 1997; Maddox and Murray 1983). An enormous potential of raw materials makes searching for the substitutes of bioethanol that could be made from the same raw materials without increasing material and energetic expenditure and cost price. The higher alcohols, especially butanol, could fall into the category of such products.

As millions of people worldwide are suffering from a lack of food products, our country as well as other EU Member States should get oriented to producing biofuels from raw materials unsuitable for food (Butkus *et al.* 2007). Until now, bioethanol has been mainly made from food products in Lithuania, particularly from triticales. Thus, it is important to assess technological differences between the production of bioethanol and biobutanol using sugars and starch or non-food raw materials containing lignocellulose.

The potential of raw materials containing lignocellulose suitable for producing biobutanol has not been examined in our country yet, neither have been evaluated its production technologies that could be used in the present companies of bioethanol production (in the ideal case) after they are reconstructed and modernized accordingly. However, it has to be noted that producing biobutanol from lignocellulose has not been sufficiently examined and there is not a single company in the world making such a product. Therefore, in order to show the perspectives of biobutanol and its production possibilities in our country, it is necessary to carry out such evaluation. Besides, it would be meaningful to analyze the properties of biobutanol as a kind of fuel or a biofuel component when comparing it to bioethanol and other fuels.

The methods of producing biobutanol from relatively dry biomass could be divided into several groups:

1. Applying fermentation methods biobutanol is made from substrates containing sugars (directly derived or made from starch). Fermentation methods could be divided as follows:
   - to decompose sugars, classical ABE (acetone, butanol, ethanol) including microorganisms *Clostridium beijerinckii* modified by MBI and Du Pont-BP-British Sugar plant are used (Madihah *et al.* 2001; Website of SysMO 2009);
   - producing biobutanol in the fibrous load bioreactors at two stages during the continuous process (DIRCRTM) using two separate Clostridium stems (Ezeji *et al.* 2005 and 2007);
   - 'Achievement technology' of Green Biology developed in the United Kingdom using thermophillic stems.
2. Technology of cellulose hydrolysis that uses mineral acids, enzymes and other modes followed by the fermentation of C5/C6 sugars to biobutanol.
3. Dehydration technology of bioethanol to butanol using Sangi hydroxyapatite (HAP) catalysis.
4. Gasification of biomass to synthetic gases to produce biobutanol. The possibilities of producing biobutanol (together with methanol) from synthetic gases have been analyzed by the *Achema Ltd*.

The purpose of this paper is to evaluate the potential of raw materials for biobutanol, its production technologies and suitability of the product to be used as a fuel as well as to conduct exploitation tests on the mixtures of petrol and butanol in the Otto engine determining the emissions of oxides.

2. Methodology

The *density* of fuel is determined according to the standard LST EN ISO 12185:1999. The vibratory method of U-tube is applied. Viscosity according to the standard LST EN ISO 3104+AC:2000 is established. Kinematic viscosity is determined by Stabinger viscometer – SVM 300. The octane number is determined according to the standard LST EN 228:2004-11. Calorific capacity is determined by calorimeter IKA C2000 V1 according to the standard ISO 1928:2009.

Tests on the Otto engine having a carburetor with a device were carried out at the Laboratory of Internal-combustion engines. The characteristics of the used engine are presented in Table 1.

Exhaust emissions were measured by AVL DiCom 4000 gas analyzer. Fuel consumption was measured using electronic scales while the time was measured using a secondometer. The selected testing modes are listed in Table 2.

Table 1. Technical characteristics of the tested Otto engine

Characteristics	Description
Type of engine	Otto
Volume V_h, cm^3	1392
Compression ratio ε	9.5
Power P_e, kW (min^{-1})	55 (6000)
Torque M_s, Nm (min^{-1})	112 (4000)
Cylinder diameter D, mm	73.5
Piston stroke S, mm	82.0
Idle speed, rpm	850

Table 2. Testing modes of the Otto engine

Engine speed, rpm	Engine torque, Nm
2500	7
2500	14
2500	21
3000	14
3000	28
3000	42
4000	21
4000	42
4000	64

The tests were carried out after the lambda probe (oxygen sensor) was switched off. This was done in attempt to eliminate the influence of the control unit on the process of regulating the composition of the fuel mixture.

3. Results and Discussions

3.1. Potential for Producing Biobutanol

Due to the high fertility of root-crops (potatoes, sugar beets, Jerusalem artichokes), they may be used for producing biobutanol. However, using them has several serious disadvantages such as harvesting requires high labour expenditures, difficult storage (cannot be stored for the whole period necessary to secure stable work of a company), trifling by-products (due to a small amount of proteins in the draff, the company looses an important additional income resource). Thus, it is possible to state that root-crops may be used only in such areas where they can grow well as an 'additional' raw material for the company producing biobutanol.

An analysis of suitability for cereal plants**:**

- triticale, wheat, rye – the amount of starch they contain may markedly differ; big viscosity due to the presence of pentozanes; demand for additional ferments; the use of anti-foamers may be necessary;
- barley is very abrasive, fertility is lower than that of other corns. Demand for special ferments (beta-glucanase); the use of anti-foamers is necessary;
- corn is the most popular source of starch in the world, its bigger amounts could be grown in our country due to its high fertility (up to 8 t/ha); an ideal raw material for biobutanol in the areas where it can easily grow; supply in the market is high.

Nevertheless, the main attention should be paid to producing biobutanol (and bioethanol) from raw materials containing lignocellulose. The production mode of biobutanol from raw materials containing lignocellulose has not been completely analyzed. However, as the production technologies of biobutanol and bioethanol are similar and the output of biobutanol from the same amount of raw materials is a little higher, the output ratio from materials containing lignocellulose should be also similar.

It was determined that the yield of bioethanol along with biobutanol from raw materials containing lignocellulose is not lower than the yield from the similar amount of raw materials containing starch or sugars. The output of ethanol from cereal cultures is 365–405 l/t and butanol makes 388–415 l/t. It is the highest yield with regard to grain while the output of alcohol from straws and stems is about 10% higher. However, the remaking process of those is still more expensive; nevertheless, it is possible to expect that cheaper ferments and other materials necessary for the process will be made in the near future that would allow equating the cost price of products received from both groups of raw materials.

The potential of raw materials containing lignocellulose is quite high in our country. The main resources of these materials are as follows:

1. Wood cutting volumes in Lithuania make 6.3 mln. m^3 (Website of Department of Statistics... 2009*)*:
   - cutting waste – 0.8 – 1,1 mln. m^3/year;
   - firewood makes about 15% of the cut of the total volume size that would be 0.9–1.0 mln. m^3/ year.
   - not marketable wood (dead wood) – 23 m^3/ha, would make up to 3 mln. m^3/year;
   - industrial waste of wood 1.5 mln. m^3/year;
   - energetic plantations – 7 th. t /year.
2. Agricultural products and waste:
   - straw – about 3 mln. t/year;
   - rape straw – about 6 mln. t/year;
   - energetic plants – 1.8 mln.t/year.

It is forecasted that in 2010, the amount of 3.3 mln. m^3 wood for fuel will be needed. The Directorate General of State Forests forecasts that in 2010, up to 2.0 mln. m^3 firewood would be available and up to 0.7–0.8 mln. m^3 cutting waste could be used. In order to fill a lack of wood for fuel production, willow plantations may be used. Up to 11.5 thousand ha of willow energetic plantations should be introduced in 2009–2013. In order to guarantee a continuous supply of biomass, similar planting rates of energetic plantations should be maintained in the period until the year 2030.

If 20–30% of the potential of biomass containing lignocellulose is used, it would be possible to make 200–300 thousand tons of biobutanol a year.

3.2. Comparison of Physical-Chemical Characteristics of Biobutanol Important for Biofuels, with Bioethanol and Other Types of Fuels

Butanol tolerates humidity better and is less corrosive than ethanol, thus it is more suitable for supply through present petrol piping. Low pressure of biobutanol vapor (lower than of petrol) means it is not necessary to reduce vapor pressure. In case of the mixtures with diesel or petrol, butanol tends to separate from fuels less than ethanol if some water gets inside. The synergetic effect of vapor pressure is important if mixtures with petrol containing ethanol are made. This makes the storage and distribution of mixtures with fuels containing butanol easier. The general characteristics of fuels are presented in Table 3.

Except for kinematic viscosity, the indexes of butanol and petrol are very similar. However, when the mixtures are prepared, this difference gets reduced. Although the calorific capacity of various mixtures of butanol and petrol can be calculated, the tests showed that the economy effect of fuels was not proportional to the calculated calorific capacity of the mixtures. The octane number of butanol is similar to petrol but is lower than that of ethanol and methanol. The Research Octane Number (RON) of butanol is 96, whereas that of Motor Octane Number (MON) is 78.

Table 3. General characteristics of fuels

Fuel	Calorific value MJ/l	Stechiometric ratio (kg of air/kg of fuel)	Density at 15 °C kg, m^3	Latent vaporific heat MJ/kg	Viscosity, 20 °C, cSt	Octane number	
						searching	engine
Petrol	32	14.6	720	0.36	0.60	97	86
Butanol	29	11.2	810	0.43	3.60	96	78
Petrol 50 – Butanol 50	30	13.0	764	0.40	2.00	96	82
Petrol 70 – Butanol 30	31	13.6	748	0.38	1.50	97	83
Ethanol	19.6	9.0	789	0.92	1.52	129	102
Methanol	16	6.5	792	1.20	0.70	136	104

The fuels having a high octane number tend to detonate less (sudden combustibility happens due to pressure) and any control system of a modern car engine may use this advantage because it can regulate the ignition moment.

The elemental composition of the analyzed fuels was determined (Table 4). Alcohol fuels, including butanol and ethanol are partly oxidized, thus they need a 'richer' mixture with oil. Standard petrol engines may regulate the ratio of air-fuel depending on fuel composition only within certain limits and depending on a model. If the limit is exceeded when the engine is in the working order and uses pure butanol or a big amount of butanol in the mixture with petrol, the engine works worse and may stop performing. If butanol is compared to ethanol, butanol may be mixed with petrol in a higher ratio and used in the present cars without their modification due to the air-fuel ratio and the amount of energy is closer to petrol.

Table 4. Elemental composition of multi-component fuels and their components

Fuel composition, %		C, %	H, %	O, %
Petrol	Butanol			
100	–	85.0	14.9	0.1
–	100	64.9	13.5	21.6
70	30	79.0	14.5	6.5
50	50	75.0	14.0	11.0

The viscosity of alcohols grows along with the length of their carbon chain. With this regard, butanol may be used as an alternative to short chain alcohols when more viscous solvents are desirable. The kinematic viscosity of butanol is several times higher than that of petrol and is almost as high as that of high quality diesel.

Fuel must be evaporated in the engine before combustion. Evaporation is an important problem when alcohol fuels are used and when the engine is ignited with cold air. The latent evaporation heat of butanol is twice smaller than that of ethanol, thus the start of the engine using butanol should be easier than that using ethanol or methanol.

The standards of the mixture of ethanol and methanol with petrol exist in many countries, including the EU, USA and Brazil. The estimated equivalent butanol mixtures may be calculated according to the stoichiometric ratio of fuel–air for butanol, ethanol and petrol. The amount of ethanol in the most widely sellable mixture of ethanol and petrol varies from 5 to 10%. In case of butanol, this amount may be higher by 60% than in the case of ethanol and may vary from 8 to 32%. However, due to solubility, latent evaporation temperature and octane number as well as the amount of butanol in the mixtures with petrol may reach 25%.

Figs 1–6 show the results of experimental tests on the engine.

Fig. 1 indicates the dependency of the hourly consumption of fuel on the engine torque. The figure clearly shows that the consumption of fuel grows proportionally with an increase of torques and the revolutions of the engine. Besides, the influence of the sort of fuels is also evident as the more butanol the mixture contains the higher consumption of fuel is.

The influence of the sort of fuel on specific fuel consumption is similar to the hourly consumption of the fuel as specific fuel consumption is higher when the amount of butanol in the mixture is larger (Fig. 2). This is understandable because the calorific capacity of butanol is 35.8 MJ/kg while that of petrol is even 44 MJ/kg. Thus, in order to generate the same amount of energy, a larger amount of fuel is needed.

The revolutions of the engine almost do not have any influence on specific fuel consumption while the torque has quite a big influence as when the torque of the engine (load) increases, specific fuel consumption decreases.

Fig. 3 shows that when the amount of butanol in the mixture increases, the air-fuel ratio also increases because butanol contains oxygen which increases the amount of oxygen in the mixture. The oxygen sensor analyzing exhaust gases was switched off during the conducted tests, i.e. the composition of the fuel mixture was not corrected, and therefore the influence of the additional factors on the tested results was eliminated.

Changes in the amount of carbon monoxide were the same as in all carburetor engines, i.e. when the load is small, the mixture is richer, thus the amount of CO is also larger (Fig. 4) and when the load increases, the mixture becomes leaner and the amount of CO decreases while under the big load, the mixture again gets richer and the amount of CO increases. Such effect is evident when the engine runs on petrol. When the engine works using the mixture of petrol and butanol, the fuel mixture gets leaner due to oxygen present in butanol and the combustion process becomes better, thus the amount of CO gets reduced to vanishingly small amounts.

The amount of CO characterizes the combustion process because the larger is the amount of CO, the better the fuel burns and vice versa. Thus, the amount of CO would be larger when the air-fuel ratio comes closer to 1. When the air-fuel ratio is smaller than 1, the mixture is rich and the fuel does not burn completely while the amount of CO in the exhaust gases increases along with a decrease in CO_2. When the air-fuel ratio is higher than 1, the mixture is lean and then the fuel burns better but the amount of O_2 increases in the exhaust gases on the contrary to decreasing CO_2.

Thus, this tendency can be seen in the carried out tests (Fig. 5). When the amount of butanol in the mixture increases, the fuel mixture gets leaner and the amount of CO_2 gets smaller.

The amount of hydrocarbons (HC) in the exhaust gases decreases when 30% butanol is added to petrol (Fig. 6), however, when the amount of butanol in the mixture reaches 50%, then the amount of hydrocarbons becomes even larger than when pure petrol is used.

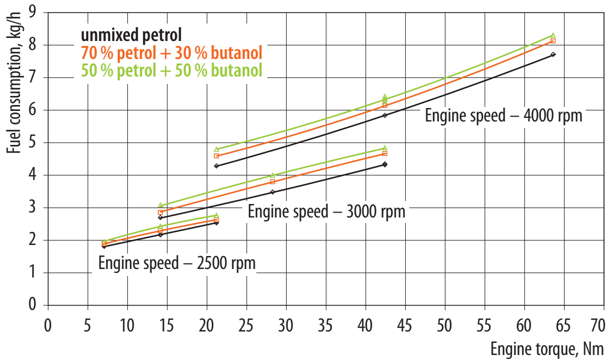

Fig. 1. The relationship between fuel consumption and the engine torque for the engine using various fuel mixtures

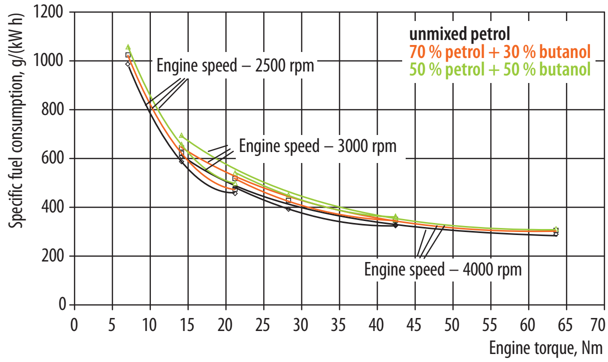

Fig. 2. The relationship between specific fuel consumption and the engine torque for the engine using various fuel mixtures

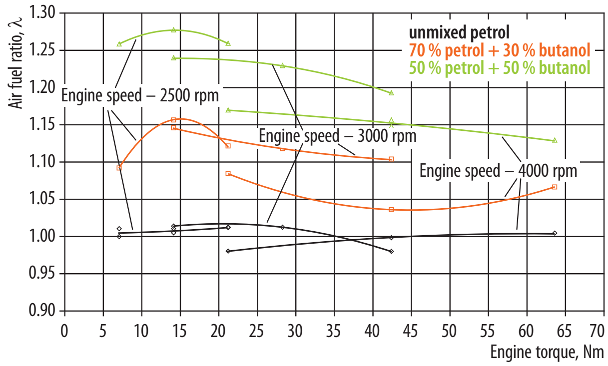

Fig. 3. The relationship between the air fuel ratio and the engine torque for the engine using various fuel mixtures

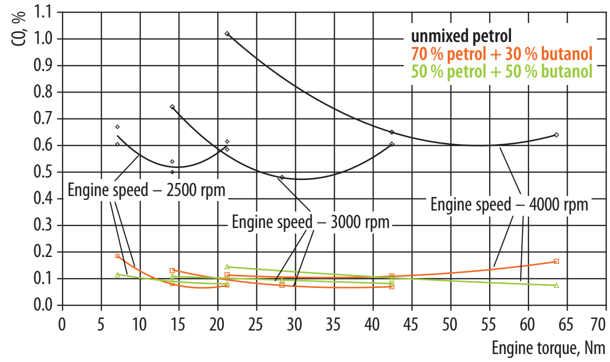

Fig. 4. The relationship between CO and the engine torque for the engine using various fuel mixtures

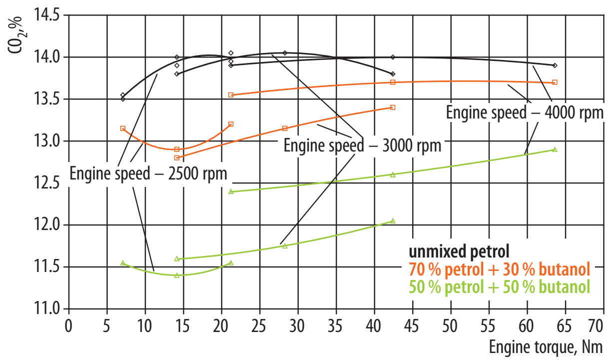

Fig. 5. The relationship between CO_2 and the engine torque for the engine using various fuel mixtures

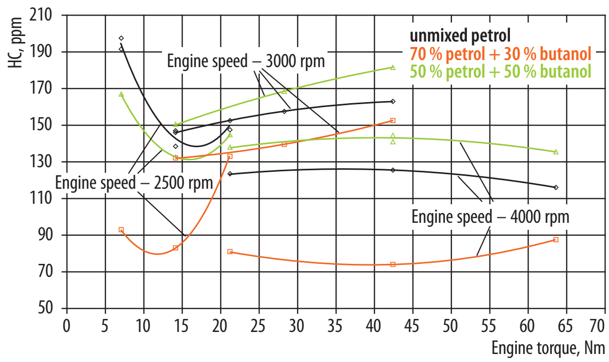

Fig. 6. The relationship between HC and the engine torque for the engine using various fuel mixtures

An increase in the amount of HC may be affected by a leaner fuel mixture (Fig. 3) that becomes difficult to be ignited by spark plug.

To generalize the results of the performed tests, it is possible to state that if the engine works under such conditions, the optimal mixture would consist of 70% petrol and 30% butanol.

4. Acknowledgment

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5. Conclusions

1. It is meaningful to make biobutanol using biotechnological methods when the company producing bioethanol is modernized and uses substrates containing sugars such as grains, sugar beets, potatoes, etc. now used to make bioethanol. The national resources of raw materials are enormous and even a small part of those could satisfy the required demand.
2. It is possible to make biobutanol as biofuel of the second generation from lignocellulose hydrolyzed to C_5/C_6 sugars. If 20–30% of the biomass potential containing lignocellulose is used, it would be possible to make 200–300 thousand tons of biobutanol a year.
3. The expansion of producing biobutanol is also motivated due to a lower cost price. Different authors have differently calculated the price and profit, however, it is possible to state that when biobutanol and bioethanol are made from the same raw materials (corn grains) and in the plant of the same capacity, the cost price of biobutanol will be 5-6% lower than that of ethanol.
4. The consumption of fuel grows proportionally to the amount of butanol in the mixture. When the engine works using the mixture of 30% butanol and petrol, fuel consumption increases by 6% on average, and in case it uses the mixture of 50% butanol and petrol, fuel consumption increases by 11% on average if compared to the consumption of petrol.
5. Having completed the testing procedure for the switched-off lambda probe, i.e. when the composition of the fuel mixture is not regulated, the air-fuel ratio increases proportionally to the amount of butanol in the mixture. When the engine works on the mixture of 30% butanol and petrol, the air-fuel ratio increases by 10% on average, and in case it operates using the mixture of 50% butanol and petrol – by 21% if compared to the air-fuel ratio of the engine working on petrol.
6. The amount of carbon monoxide CO decreases by more than 80% when the engine works using the mixtures of petrol and butanol if compared to the amount of CO used by the engine working on petrol.
7. When the engine works using the mixture of 30% butanol and petrol, the amount of carbon dioxide CO_2 decreases by 4% on average, and in case it uses the mixture of 50% butanol and petrol – by 14% if compared to the amount of CO_2 used by the engine running on petrol.
8. When the engine works using the mixture of 30% butanol and petrol, the amount of hydrocarbons HC decreases by 26% on average, and if it works on the mixture of 50% butanol and petrol, the amount increases by some 4% if compared to the HC amount of the working engine using petrol.
9. To generalize the results of the performed tests, it is possible to state that if the engine works under above discussed conditions, the optimal mixture would consist of 70% petrol and 30% butanol.

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