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WATER TOLERANCE OF PETROL-ETHANOL BLENDS

Abstract

Water tolerance of ethanol-petrol blends of various compositions (ethanol, ethers, aromatics, olefins) was investigated. Tempe-ratures of haze formation as well as separation of petrol into two phases were measured experimentally. Simulation of long term storage stability of ethanol-petrol blends was also performed.

1. Introduction

From 2007, January 1st, an addition of biocomponents (ethanol, ETBE, FAME) to commercial petrol and/or diesel fuel becomes mandatory for all producers and importers of motor fuels in the Czech Republic. The measure reflects the Directive 2003/30/EC of the European Parliament and of the Council on the promotion of the use of biofuels or other renewable fuels for transport. According to the current quality standard EN 228 ethanol content in petrol is limited to 5 vol %, however, an increase up to 10 vol % in near future is intensively discussed. The addition of ethanol to petrol can affect the following physical-chemical properties of motor fuel:

- volatility (vapour pressure and distillation properties),
- octane number,
- water solubility,
- compatibility with construction materials,
- heating value

Some ethanol properties differ significantly from those of petrol hydrocarbons. Namely, it is polar character of ethanol and its high affinity to water (unlike hydrocarbons ethanol is perfectly miscible with water) [1]. Ethanol therefore improves significantly the solubility of water in hydrocarbon fuel. It is very useful and desirable (e.g. prevention of fuel system freezing), however an ability to keep water in the soluble state in petrol-ethanol blend is strongly affected by temperature. A decrease of fuel temperature under specific level brings about separation of water phase, to which main portion of ethanol from fuel blend is transferred. This results in significant petrol quality degradation – part of oxygen content is disappeared, octane value goes down and volatility is changed [2]. Thus the use of petrol-ethanol blends can cause much more problems at regular consumers than ethanol free motor fuel, for which separated water does not pose a significant risk of petrol quality change.

Problems concerning low stability of petrol-ethanol blends have promptly to solve all motor fuel producers and distributors to prevent a possible negative public acceptance of biocompounds as a standard part of motor fuels.

2. Solubility of water in petrol-ethanol blends

High solubility of water in petrol-ethanol fuel blends is affected by polar character of ethanol and its ability to form hydrogen bridges. Ethanol should practically be water free (max. 0,3 vol % water according to Czech standard CSN 66 0810) to be blended into petrol. However, ethanol is strongly hydroscopic and therefore absorbs easily water in form of air humidity, e.g. during diurnal breathing of storage tanks. Solubility of water in petrol-ethanol blend is influenced by:

- temperature,
- ethanol content,
- hydrocarbon composition of petrol base (content of aromatics or olefins),
- content of other oxygenates (co-solvents)

The main effect on water solubility in petrol-ethanol fuel blends show ethanol content and temperature change [1]. Rising content of ethanol in petrol influences the increase of the water solubility in fuel blend by nonlinear way (see Figure 1). The solubility of water in petrol containing 10 vol % of ethanol (E10) is approximately 2.5 times higher compared with fuel containing 5 vol % of ethanol (E5) only. The water solubility decreases linearly with decreasing temperature and is more noticeable for E10 than E5 fuel blend.

A decrease of temperature from 10 ℃ to -10 ℃ results in decrease of water solubility by approx. 30 % rel for E10 fuel blend and/or approx. 14% rel for E5 fuel blend (see Figure 2). Thus a change of temperature (e.g. day – night temperature deviation) or change of ethanol content (e.g. in case of mixing various kinds of petrol) can cause the phase separation effect. In summer and/or winter period a “safety” water content in E5 fuel blend should be lower than 2000 ppm w/w. The content of water dissolved in petrol containing hydrocarbons or MTBE only does not pass over a limit value of 60 ppm w/w.

Solubility of water in petrol-ethanol fuel blends can also be affected by hydrocarbon composition of petrol base [1,3-5]. Due to existence of π-bonds in molecule, aromatics and olefins would easily be miscible with water compared with saturated hydrocarbons. However, experimental measurements performed didn’t show a significant effect of hydrocarbon composition on water solubility. Possible differences in experimental values didn’t pass over standard error of analytical water determination. Water solubility in fuel blend increases in consequence of the presence of other oxygen containing compounds (so called co-solvents), which can be added into petrol together with ethanol up to maximum oxygen content 2.7 wt %. For example, the addition of 5 vol % of ETBE to E5 fuel blend increases the solubility of water at 10 ℃ by approx. 600 ppm w/w (see Figure 2).

Based on facts mentioned above, it is necessary to prevent petrol-ethanol blends from air moisture intake during their storage and distribution and also to respect possible “free” capacity of fuel blend in regard to water solubility at given conditions (ethanol and other co-solvents contents, temperature).

Figure 1: Effect of ethanol in petrol blend on water solubility in petrol-ethanol blends

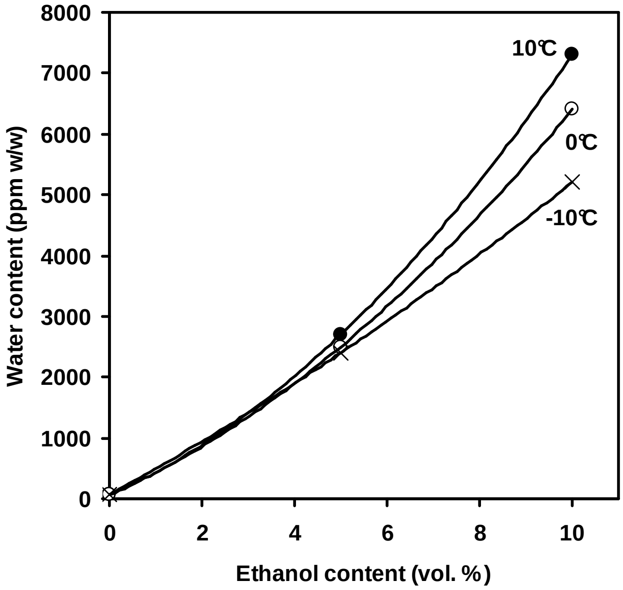
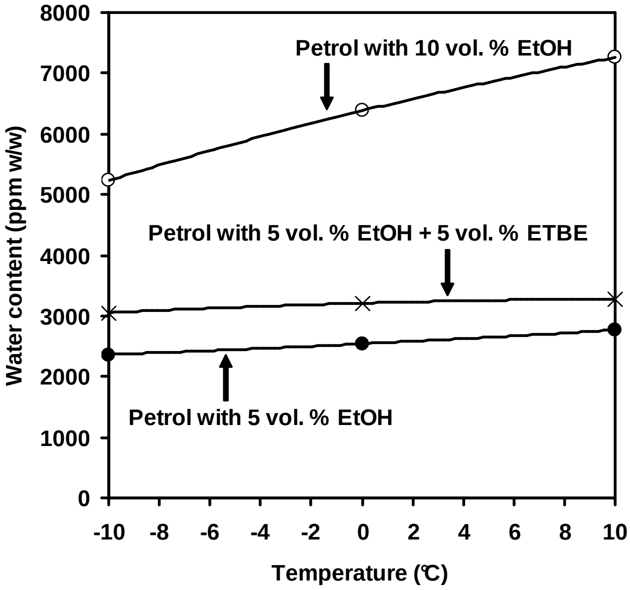


Figure 2: Effect of temperature on solubility of water in petrol-ethanol blends



3. Phase separation of petrol-ethanol blends

In common praxis the ability of petrol-ethanol blends to retain certain amount of water is often determined as the temperature of phase separation according to the ASTM D6422 standard. Before the point of the phase separation there is always clearly visible another point at which a haze of the blend appears [2]. Sample with given amount of water is gradually cooled and formation of haze is monitored at the particular temperature. This temperature is then followed by a point of phase separation and/or by a formation of ice crystals [6]. There are some cases where the phase separation cannot be clearly visible and the determination of the phase separation point can be difficult. On the other hand, formation of the haze in the sample is always very indicative and there are no problems with determination of the haze point. The most common reasons for the phase separation are the differences between the day and night temp. Another possibility can be seen in blending of petrol with azeotropic ethanol and/or mixing of petrol-ethanol blends with different composition.

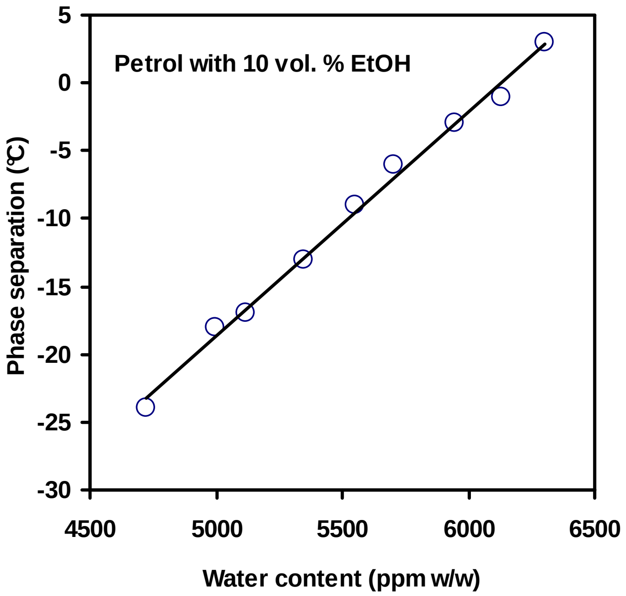
The phase separation temperature can thus depend on content of ethanol and water in the blend, additional factors are e.g. a hydrocarbon composition or content of co-solvents in the blends [2,7,8]. Keeping the water content constant the haze points as well as the phase separation temperatures are lowered with increasing content of aromatic and olefinic hydrocarbons in the petrol (Table 1). Difference of 20 vol % in the content of aromatic+olefinic compounds can have an effect of about 10 °C in the temperature of the phase separation. Increased amount of ethanol in the blends clearly lowered the phase separation temperature while keeping the water content constant. So, when it is necessary to mix hydrocarbon petrol with petrol-ethanol blend then the resulted mixture will have lower content of ethanol and, therefore, the phase separation can occurs at higher temperature than for the original petrol-ethanol blend. At constant ethanol content the phase separation temperature is lowered by a lowering the water content. When the phase separation temp. is –27°C for the fuel E10 with 5600 ppm of water, for the same fuel with 2200 ppm of water the phase separation temperature is lowered below –30 °C. For the fuel E5 with the same 2200 ppm of water is the phase separation temp. again about –27 °C (Tab. 1).

Table 1: Effect of petrol-ethanol fuel composition on the phase separation

EtOH (vol %)	Olefines (vol %)	Aromatics (vol %)	Haze point (°C)	Phase separation (°C)	Water content (ppm w/w)
5	5	26	-2	-19	2300
5	5	36	-13	-27	2200
5	15	26	-14	-25	2200
5	15	36	-15	-27	2200
10	5	26	-10	-18	5600
10	5	36	-14	-21	5600
10	15	26	-19	-27	5500
10	15	36	-19	-27	5500

Temperature of the haze appearance is linearly increasing with increase in the water content. Plot of this relation is shown in Figure 3. For example, when cooling blend E10 with water content of 6200 ppm (saturation equilibrium at 0 °C) by 10 °C, then haze appeared due to lesser water solubility by 600 ppm (Figure 3). If effect of fuel composition can be neglected then an equation for phase separation temperature assessment can be derived from the linear regression in Figure 3 for the petrol-ethanol blends with 10 % of ethanol.

Figure 3: Effect of water on the phase separation temperature for petrol

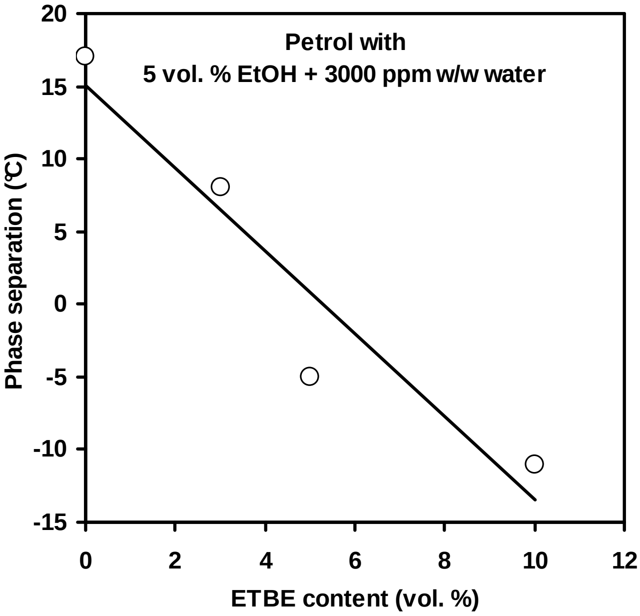


Co-solvents can lower the phase separation temperature [9,10], e.g. 5 vol % of ETBE in petrol blend with 5 vol % of ethanol can lower the phase separation temperature even by 20 °C, see Figure 4.

Based on experimental data it can be concluded that lowering the phase separation temperature can technically be accomplished:

- by increasing the aromatic and/or olefinic hydrocarbon content in petrol; however that is not in accordance with the most recent trends of increasing the non-aromatic hydrocarbons content in automotive fuels,
- by addition of oxygenates (MTBE, ETBE, higher alcohols) in amount within oxygen limits for automotive petrols of 2.7 wt %,
- by minimisation of humidity access into storage tanks and distribution systems; technological discipline have to be respected, and storage tank breathing should be minimised.

Figure 4: Effect of ETBE in the fuel E5 on the haze point



4. Extraction of ethanol from petrol blends by water

Phase separation of petrol blends is accompanied by an undesirable effect – extraction of ethanol into water layer. Due to the loss of ethanol a significant deterioration of petrol quality should be expected – decrease of octane number mainly and also a corrosive action of water phase separated on inner metal surfaces of storage tanks and/or car fuel system lines. After separation of water layer, content of water dissolved in hydrocarbon phase is generally lower than value that corresponds to the state of fuel saturation, and content of water in organic phase further decreases in dependence on volume of water layer separated [11,12]. Extraction of ethanol into water layer represents usually an irreversible process. A backward dissolution of ethanol and water into hydrocarbons phase should theoretically be occurred under fully exceptional conditions [13]. The quantity of ethanol extracted into water layer is generally affected by:

- ratio of water and hydrocarbons layers,
- content of ethanol in petrol,
- hydrocarbon composition of petrol,
- temperature (in minor measure),
- content of co-solvents

Amount of ethanol which can be extracted into water layer generally depends on content of ethanol in fuel blend and also on amount of free water, which is in direct contact with fuel blend. In table 2, there are compared relative losses of ethanol from fuel blends under situation, when the fuel is in direct contact with 0.5 or 1 vol % of free water.

Table 2: Effect of ethanol concentration and free water amount in petrol blend on losses of ethanol

Initial EtOH content (vol %)	Losses of EtOH from petrol blend (rel %)	
	0.5 vol % water	1 vol % water
5	11	20
10	16	28

High contents of aromatics and olefins in petrol show soft co-solvent effect and minimise amount of ethanol extracted (see Table 3).

Table 3: Effect of hydrocarbons composition on amount of ethanol extracted from E10 fuel blend by 1 vol % of free water

Olefins+aromatics (vol %)	EtOH losses after 1st extraction (rel %)	EtOH losses after 2nd extraction (rel %)	EtOH losses after 3rd extraction (rel %)
5+25=30	31	63	77
5+35=40	27	57	72
15+25=40	28	55	71
15+35=50	24	51	71

More noticeable effect on minimisation of ethanol amount extracted from petrol blends gives oxygen containing co-solvents. For example, combination of 5 vol % of ETBE and 5 vol % of ethanol affects in positive way the minimisation of losses of ethanol extracted into water layer by approx. 10 rel % compared with petrol-ethanol blend free of ETBE (see Table 4).

Table 4: Effect of ETBE content on amount of ethanol extracted from E5 petrol blends by 1 vol % of water

Content of EtOH/ETBE (vol %)	EtOH losses after 1st extraction (rel %)	EtOH losses after 2nd extraction (rel %)	EtOH losses after 3rd extraction (rel %)
5/0	37	60	74
5/3	32	55	70
5/5	27	50	64
5/10	23	42	57

Ethanol extraction rate depends on the way of manipulation with petrol-ethanol blend. During an intensive agitation of liquid, very fast transition of ethanol into water layer becomes already within first 10 minutes. If the mixture stays calm, phase equilibrium is established within approx. 1 week. If the fuel blend is not repeatedly exposed to contact with free water layer, losses of ethanol from primary petrol blend don't pass over 30 rel %. However, a triple extraction results in lose of 70 rel % of ethanol, i.e. 1.5 vol % of ethanol remains only in the fuel blends compared with primary 5 vol %. This petrol doesn't meet standardised value of octane number.

5. Other oxygenates as co-solvents

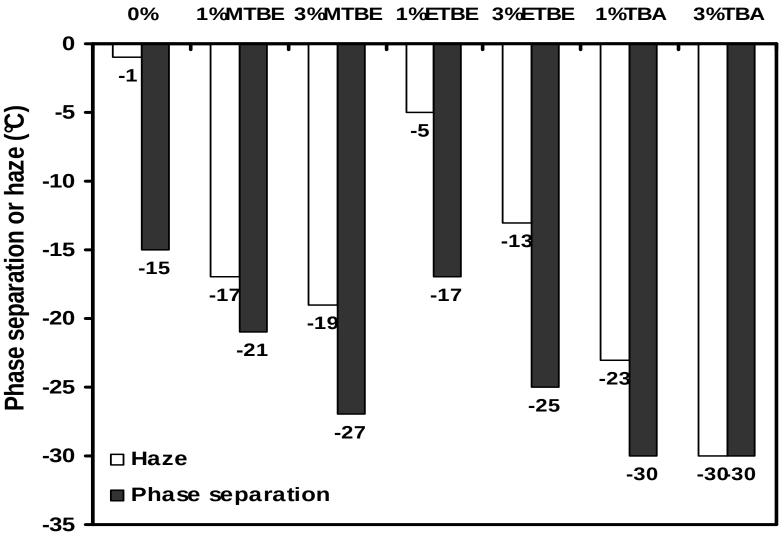
Except ethanol, there are some other oxygenates that can be blended into petrol as co-solvents. However, content of oxygen in blend has to be kept below the limit of 2.7 wt %. Co-solvents can be blended into petrol with the aim of [14]:

- better solubility of water in petrol-ethanol blend
- lowering the phase separation temperature
- lowering the amount of ethanol which can overcome into the water phase
- better vapour pressure behaviour of petrols

Often mentioned and recommended in the literature are especially the following co-solvents:

- branched higher alcohols (TBA, IBA, IPA) usually in 1:1 ratio with ethanol [2]
- higher aliphatic alcohols (1-hexanol, decanol) [15]
- ethers (DIPE, TAME, MTBE) [9,14]
- certain co-solving effect also have some aromatic hydrocarbons

Figure 5: Effect of co-solvents on the phase separation in the E5 fuel



Effects of some co-solvents on the phase separation were experimentally examined and results are presented in Figure 5. So, with the respect to oxygen limits in automotive fuels, about 5 vol % of MTBE or ETBE, or about 4 vol % of TBA, or about 3 vol % IPA can additionally be blended into petrol with 5 vol % of ethanol. For the 10 vol % ethanol blends the co-solvent TBA can be very effective. Some results obtained with that co-solvent are also shown in Figure 5. TBA already at the low concentration of 3 vol % lowered the haze point below -30℃ from initial -1 ℃. Water concentration in that experiment was as high as 6000 ppm. Ethers as co-solvents (MTBE, ETBE) are less effective. Under the same experimental conditions their effect was much lesser, see Figure 5. Effect of ETBE on extraction of ethanol into water phase can be seen in Table 4 for the petrol blends with 5 vol % of ethanol and different content of ETBE.

Oxygenates utilised as co-solvents in petrol ethanol blends should meet the requirements of the EN 228 standard. Except that they should also meet some other demands dealing with:

- good miscibility with all components of petrols,
- solubility in water, which should be as low as possible,
- minimum azeotrope formation with hydrocarbons; low boiling point of the azeotrope can have impact on increased vapour pressure of the petrol-ethanol blends.

All these demand on oxygenates are not compatible with methanol [1], on the other hand very perspective oxygenates could be some ethers.

6. Conclusion

Due to high polarity of ethanol and its affinity to water it is necessary to minimise contact of petrol blends with water and air moisture during their storage and distribution. So, by change of temperature, the phase separation of petrol-ethanol blend becomes real and water-ethanol layer occurs in a storage tank. This results in a significant decrease of ethanol content in fuel blend and loses of petrol quality (decrease of octane number value).

Use of some oxygen containing compounds is also recommended to improve phase stability of petrol-ethanol blends (i.e. reduction of phase separation temperature). The best effect brings the application of t–butanol (TBA) as the co-solvent. However, ETBE, which can be produced from bioethanol and therefore is regarded as biocompounds, is also preferred. A very low affinity of ETBE to water can also be regarded as an advantage for the use of this ether in petrol blends.

At present, problems concerning an improvement of storage and distribution stability of petrol-ethanol blends should be treated with the first priority.

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UDK	ključne riječi	key words
621.434-631.4	benzinsko/etanolno mješano motorno gorivo	gasoline/ethanol mixed engine fuel
66.061.14	otopina tekućina	solution of liquids
536.76	separacija vodene faze	water phase separation
543.81	kontaminacija vodom	contamination by water
66.022.362	stabilnost otopine	solution stability

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