

## **Determination of the phase separation temperature and the water solubility in the mixtures of gasoline with biobutanol and bioethanol**

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**Abstract.** Original hydrocarbon composition, volatility, compatibility with materials, calorific value and stability of the mixture in the presence of water are monitored usually. This paper deals with the stability of gasoline-biobutanol and gasoline-bioethanol mixtures in the presence of water. Biobutanol is better biofuel than bioethanol using the same raw materials. Different contents of alcohol and oxygenated cosolvents are evaluated. Experimental analysis are focused on the water solubility and phase stability. Solubility in water of butanol and ethanol mixtures is very similar. Butanol-gasoline mixture provides better phase stability upon contact with water or atmospheric moisture oppose to ethanol mixtures. Butanol also does not enter to the aqueous layer and fuel properties remain in phase separation preserved. Further, it was found that crystals occur at low temperatures after exclusion of water was seen. Moreover, the temperature of phase separation can affect the content of alcohol, water, hydrocarbon composition and cosolvents added. The only difference found between more beneficial butanol and less beneficial ethanol was ABE (Aceton–Butanol–Ethanol) fermentation with *Clostridium Acetobutylicum* allowing to ferment also saccharidic cellulose to biobutanol according to standard of second generation biofuels.

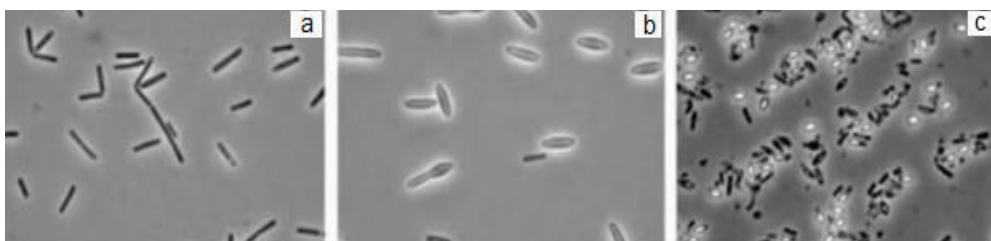
**Key words:** BioEthanol, BioButanol, Water, MTBE, ETBE.

### **INTRODUCTION**

Raw materials for bioethanol and biobutanol production are identical (Lipovský et al., 2009).

- 1) starchy (potatoes, corn, wheat, rice);
- 2) sugary (sugar beet molasses, whey);
- 3) lignocellulosic (straw, wood).

Traditional materials for the production of butanol are starchy crops (cereals, maize, potatoes) and molasses from sugar cane or sugar beet show that starch is also fermentable if proper technology is used. Other alternative materials such as whey, waste glycerol or unicellular algae accumulating starch in their cells need also advanced processing technology (Groot et al., 1992; Hönig et al., 2014; Pointner et al., 2014). Second generation biofuels (especially ethanol but also butanol) are sourced by saccharidic cellulose of different materials, e.g. straw or waste paper waste and energy crops (Tutt & Olt, 2011; Tutt et al., 2012; Raud et al., 2014). ABE (Aceton-Butanol-Ethanol) fermentation with *Clostridium Acetobutylicum* is able to ferment also saccharidic cellulose to biobutanol.



**Figure 1.** Solvent-generating bacteria of the genus *Clostridium*: acidifying (a), solvent-generating (b) and inactive (c) life cycle stages; magnification 2000x.

Smaller inner-papers in Fig. 1c spores are released from the cells of raw material. By adding alcohol to gasoline a certain physico-chemical properties of the fuel are changed, primarily:

- 1) volatility (vapor pressure and distillation curve);
- 2) octane number;
- 3) water solubility;
- 4) compatability with materials
- 5) calorific value.

Characteristics of bioethanol are significantly different oppose to hydrocarbons of gasoline. Polar nature and strong affinity to water makes ethanol completely miscible. Ethanol significantly increases the solubility of water in the hydrocarbon fuel, which can be useful (for example, for preventing freezing of the fuel system). But, this ability to retain water in some form in the gasoline-ethanol mixture is greatly affected by temperature. Miscibility of gasoline and water is in ppm low. Ethanol is part of this water layer, which decrease the fuel quality. When the temperature drops below a certain level the water layer is separated from fuel. Octane value is decreased, volatility is changed and oxygen lost. The aqueous phase can also cause corrosion of metallic materials in the tanks or the fuel system of the vehicle. Extraction of ethanol to the aqueous layer is an irreversible process usually. It is also possible, under certain conditions that it will dissolve back to the whole volume of water-ethanol layer into the hydrocarbon base (Patáková et al., 2010; Wang et al., 2011; Tutt et al., 2013).

After separation of aqueous phase the water content dissolved in the hydrocarbon layer is lower. Volume of water-ethanol phase is decreasing water content in gasoline layer continously.

Gasoline containing bioethanol can in this regard cause much more serious problems in distribution network and for consumer than gasoline without bioethanol, where the collected water does not represent a significant risk of changes in fuel quality (Beran, 2011; Küüt et al., 2011; Eisenhuber et al., 2013).

The amount of ethanol extracted into the aqueous phase is generally influenced by:

- 1) alcohol content in gasoline;
- 2) hydrocarbon composition of gasoline;
- 3) ratio of the amounts of aqueous and hydrocarbon phases;
- 4) the presence of cosolvents;
- 5) temperature (to some extent).

Polar character of ethanol and its ability to form hydrogen bonds increases solubility of water in ethanol–gasoline mixtures. Ethanol intended for fuel purposes must meet standard of maximum allowable water content of 0.39% vol. to be called waterless.

Ethanol is highly hygroscopic. If it is in free contact with the atmosphere it absorbs very readily the water from air humidity (Melzoch & Rychtera, 2014). Therefore, in storage or vehicle tanks volume of fuel is changing with temperature. This effect is called ‘breathing fuel’.

Solubility of water in gasoline-ethanol mixture depends on:

- 1) temperature;
- 2) ethanol content;
- 3) hydrocarbon composition of gasoline containing aromatics and olefins;
- 4) other oxygenates (so-called cosolvents) content.

The separation of water from fuel is caused by temperature, temperature fluctuations during the day and at night, or by changed content of ethanol when different types of gasoline are mixed. Another possible cause of water and fuel separation may occur in mixture of gasoline with waterless ethanol or in mixtures of different gasolines of different compositions (Kamimura & Sauer, 2008; Hromádko, 2011; Pirs & Gailis, 2013).

Water solubility can be influenced to a certain extent also by hydrocarbon composition of gasoline. Aromatics and olefins are due to the presence of  $\pi$ –bonds easier miscible with water than saturated hydrocarbons.

Solubility continues to increase with the addition of other oxygenates (cosolvents) which can be added to the gasoline together with alcohols up to the limit of oxygen content of 2.7% wt. according to EN 228 (Yuksel & Yuksel, 2004; Mužíkova et al., 2010; Pospíšil et al., 2014).

The ability of fuel to maintain a certain amount of water in single phase system depends on temperature. Such temperature is called phase separation. Phase separation precedes usually visible turbidity at so-called cloud point. The sample with a given amount of water is gradually cooled. Cloud and consequent exclusion of the aqueous phase (possibly ice crystals) is observed. Cloud point identifies better the two formed phases (upper and lower water filling).

### **The cosolvent effects of oxygenates**

Also other oxygenates – cosolvents (stabilizers) with respect to the maximum permitted content of oxygen in gasoline according to standard EN 228 (max. 2.7% wt.)

can be added. Cosolvents are added into ethanol–gasoline mixtures from the following reasons:

- 1) solubility of water in gasoline-ethanol mixture is improved;
- 2) the amount of ethanol extracted into the aqueous phase is reduced;
- 3) the increase of vapor pressure is reduced;
- 4) the temperature of phase separation is decreased.

As cosolvents are used following matters:

- 1) branched higher alcohols (TBA tertbutylalcohol, IBA isobutylalcohol, IPA isopropylalcohol) in usual ratio of 1:1 volume with ethanol;
- 2) higher aliphatic alcohols (1–hexanol, decanol);
- 3) ethers (DIPE diisopropylether, TAME tert–amyl–methylether, MTBE methyl tert–butylether, ETBE (ethyl tert–butyl ether).

To 5% vol. of ethanol in gasoline is possible to add maximally permitted oxygen content about 5% vol. of MTBE or ETBE or about 4% vol. of TBA or 3% vol. of IPA. The cosolvent effects have also aromatic hydrocarbons.

Added cosolvents must meet the following requirements:

- 1) oxygen cosolvents should primarily meet EN 228 standard;
- 2) good miscibility with all components of fuel;
- 3) very low water solubility and minimal tendency to pass into the aqueous layer;
- 4) minimum of azeotrope in hydrocarbons minimizing boiling point and increasing the vapor pressure.

The experiments deals with possibilities of application of biobutanol as an alternative to bioethanol and its low temperature properties. Gasoline–ethanol and gasoline–butanol mixtures at low temperatures behave differently with respect to hygroscopicity of ethanol.

## MATERIALS AND METHODS

The experimental part of the paper focuses on phase equilibria of butanol-gasoline mixtures in presence of water. Performed procedure according to ASTM D 6422 standard has identified cloud point, which represents a temperature when emulsion in fuel mixture of homogeneous sample appears. Separation into two phases – upper hydrocarbon and lower water occurs if the sample is cooled further.

A sample of pure gasoline that meets the requirements of the standard EN 228 for the winter season (class F1) was analyzed. It contained 32.21% vol. aromatic hydrocarbons, 10.29% vol. olefins, and 0.52% vol. benzene. The water content was 48.00 mg kg<sup>-1</sup> and oxidation stability exceeded 360.0 minutes.

Further, the MTBE (methyl tert–butyl ether) and ETBE (ethyl tert–butyl ether) produced by Czech refinery joint stock company, n–butanol p.a. (Lachner, Ltd) and distilled water were used. The tested bioethanol has fully met requirements of prEN15376:2013 standard.

The tested samples were labeled with working names

1. ETH for bioethanol;
2. BUT for n–butanol.

## RESULTS AND DISCUSSION

The solubility of water in pure hydrocarbon gasoline varies depending on the content of aromatics between 60 and 100 mg kg<sup>-1</sup>. With increasing ethanol content in gasoline the solubility of water increases nonlinearly.

Tested mixtures with concentration of 2, 4, 5, 6, 8 and 10% vol. of butanol (Figs 2, 3, 4 and 5) were further enriched by ethers in quantities of 5 and 10% vol. to study influence phase stability of mixtures.

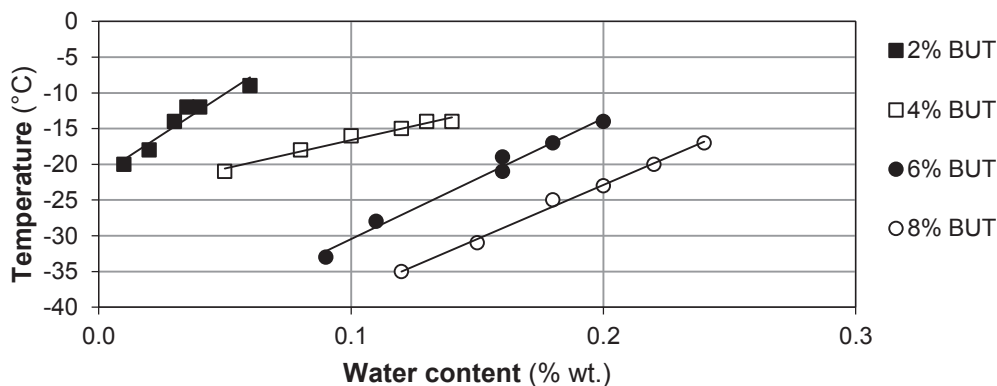


Figure 2. Water solubility according to temperature in gasoline-butanol mixture.

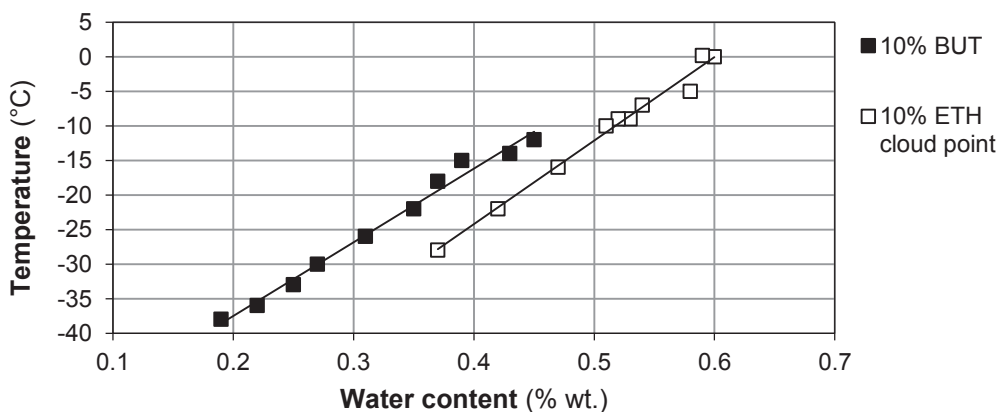
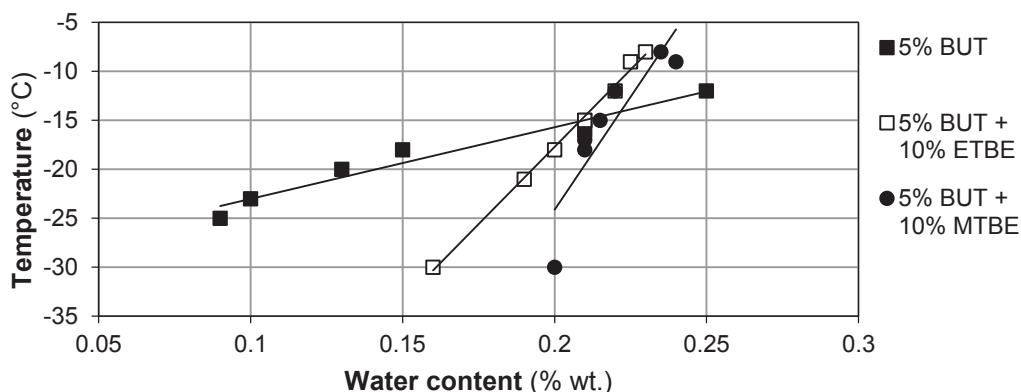


Figure 3. Water solubility expressed as the temperature of crystallization of gasoline-butanol mixtures and cloud point of gasoline-ethanol mixtures.

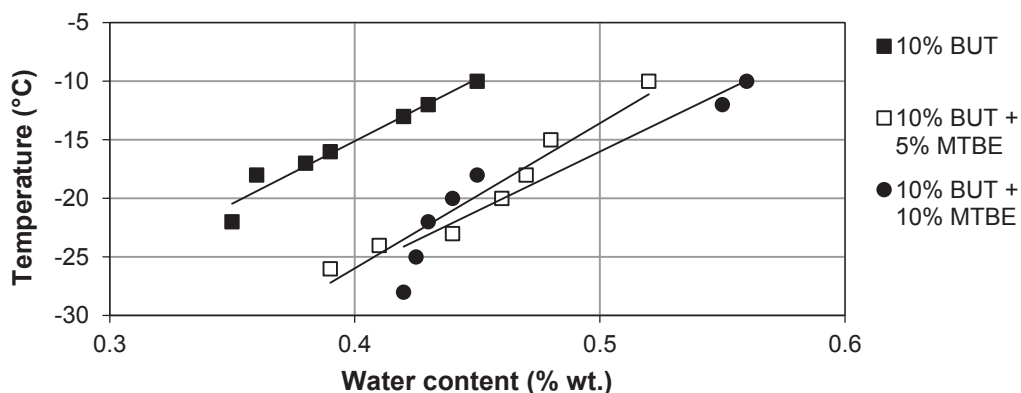
Freezing point of water below 0 °C is proving alcohol in aqueous phase.

Gasoline comprising 10% vol. of ethanol is very sensitive to temperature changes. Therefore, the safe content of water in gasoline containing up to 10% vol. of ethanol should have up to 0.02% wt. or (2,000 ppm) for both summer and winter conditions.

The cloud point of butanol fuel mixture during cooling couldn't be reliably determined as separation of liquid water phase was not clearly visible oppose to ethanol-gasoline mixtures. Crystals of water in the fuel mixture have emerged as soon as temperature has decreased below freezing point. This makes butanol-gasoline mixture more favorable oppose to ethanol-gasoline mixture (Fig. 3). The fuel distribution system and engines are less damaged by crystals of ice in the fuel than by ethanol-water. Properties of butanol fuel mixtures are not changed because water layer doesn't appear at all under low temperatures oppose to ethanol-gasoline mixtures. Such mixtures of butanol and gasoline needn't cosolvents.



**Figure 4.** Water solubility expressed as the temperature of crystallization of gasoline-butanol, MTBE and ETBE mixtures.



**Figure 5.** Water solubility expressed as the temperature of crystallization of gasoline-butanol and MTBE mixtures.

Added MTBE and ETBE affect only a little the solubility of water in fuel mixture. Gasoline containing both ether and butanol mixture (Figs 4 and 5) acts in terms of phase stability similarly as butanol-gasoline mixture. There is no visible cloud, followed by phase separation. Water is eliminated directly as ice crystals. Butanol, MTBE or ETBE

in gasoline was found temperature of crystallization, which corresponds qualitatively to temperature of separation of aqueous phase. Butanol remains dissolved in the hydrocarbon phase also at very low temperatures without being transferred to aqueous phase opposed to ethanol. This feature butanol is ultimately far more acceptable than the transition of ethanol to the aqueous phase as fuel properties doesn't endanger engines.

We may deduce from butanol properties that if both butanol and ethanol are present in gasoline mixtures the phase stability is significantly influenced. Water doesn't appear only in shape of ice crystals, but cloud and phase separation occurs. From this we can conclude that such a phenomenon always occurs in the presence of both alcohols if their presence in the fuel volume will be comparable. Gasoline mixture containing 5% vol. ethanol and 5% vol. butanol shows in terms of phase behavior very similar properties to characteristics of pure gasoline-ethanol mixture with 10% vol. ethanol.

The measured values of water solubility show that the mixture with 10% vol. of butanol at 0 °C is about 5,400 mg kg<sup>-1</sup>. In the case of a mixture with 10% vol. of ethanol it is about 5,900 mg kg<sup>-1</sup>.

## CONCLUSIONS

Solubility of water in butanol and an ethanol mixtures is very similar. Ethanol is completely miscible with water, butanol is watermiscible only to limited extent. Water in MTBE and ETBE is poorly soluble in tens of units of mg.kg<sup>-1</sup> being similarly soluble as hydrocarbons. Butanol in gasoline fuel mixture in contact with water or atmospheric moisture improves its phase stability at low temperatures oppose to ethanol. Low temperatures exclude water crystals from fuel mixture. Butanol does not transit to aqueous phase as ethanol does. Parameters of gasoline-butanol mixture remain preserved during separation phases. Such mixtures of butanol and gasoline needn't cosolvents neither special treatment in storage. Mixtures of both ethanol and butanol with gasoline require cosolvents and special treatment in storage due to above described reactions with water.

More beneficial butanol fuel mixtures, opposed to ethanol, opens also possibility for second generation biofuels if ABE (Aceton-Butanol-Ethanol) fermentation with *Clostridium Acetobutylicum* is used for fermentation of saccharidic cellulose.

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