The distillation characteristics of automotive gasoline containing biobutanol, bioethanol and the influence of the oxygenates

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Abstract. Bioethanol and fatty acid methyl esters are a regular part of the production of gasoline and diesel fuels, although in limited quantities. Introduction of bioethanol as part of automobile gasoline was associated with high production costs, technical and logistical problems. This article analyses changes of distillation curve of biobutanol and isobutanol as an alternative to bioethanol. Added alcohol to gasoline causes reduction of boiling point due to the formation of azeotrope. This phenomena of distillation curve are called Plato effect. Therefore, ethers (MTBE and ETBE) are added to fuel to affect the most central part of distillation curve. Especially, to decrease the distillation temperature oppose to gasoline without oxygenates of wide range of distilled volume. This article replaces simple universal models predicting properties of alcohol-gasoline mixtures. It was found that mixture of ETBE with bioethanol in gasoline the distillation curve summarise its effects. Butanol and MTBE influence distillation curve of gasoline only in values of its boiling points. Therefore, butanol is mixable with all listed fuel components without any additional addaptations.

Key words: BioEthanol, n-Butanol, IsoButanol, MTBE, ETBE.

INTRODUCTION

EU cooperates internationally in fight against climate change according to Kyoto Protocol reducing greenhouse gas emissions (GHG). Rationalisation of energy consumption and use of renewable energy sources are main sources of GHG reduction. The transport sector may reduce GHG emissions if share of biofuels is increased (Hromádko et al., 2011).

Commercialised biofuels are bioethanol and methyl ester of rapeseed oil already. Bioethanol is used for gasoline engines and rapeseed oil methyl ester for diesel engines. Methyl esters of various oils (often referred as biodiesel) represent 85% of all produced biofuels on European scale (Hönig & Hromádko, 2014). Bioethanol was introduced to diversify biofuels and increase its share in fossil fuels. Biofuels with a higher proportion of bioethanol decrease emissions (CO, HC, NOx or PM) more than methyl esters of

vegetable oils. Methyl esters are decreasing in CO_2 emissions more than bioethanol produced from sugars or starch (Pirs & Gailis, 2013; Ilves at al., 2014).

Biofuels may be divided according to method of obtaining biofuels to first and second generations. Ethanol, methyl esters of fatty acids of vegetable oils belong to first generation biofuels (Kotus et al., 2013). Ethanol is produced from wheat or sugar beet and methyl esters are obtained mainly from oilseed rape in European conditions (Sun & Cheng, 2002; Sims et al., 2010).

Second generation biofuels are produced differently. Second generation ethanol (or other alcohols) is obtained from lignocellulose of plants which are not intended for processing into food, or from lignocellulose which constitute waste substances (Groot et al., 1992; Tutt & Olt, 2011).

Table 1. Parameters of biobutanol, bioethanol and gasoline fuel

Parameter	Gasoline C_4-C_{12}	Butanol	Ethanol
Chemical formula	$CH_{1,87}$	C_4H_9OH	C_2H_5OH
Density at 15 °C$(kg\ dm^{-3})$	~ 0.73	0.81	0.79
Kinematic viscosity at 20 °C$(mm^2\ s^{-1})$	0.4–0.8	3.64	1.52
Calorific value $(MJ\ kg^{-1})$	42.9	32.5	26.8
Heat of vaporization $(MJ\ kg^{-1})$	0.36	0.43	0.92
Mixed octane number	95	94	106–130
RON			
MON	85	80–81	89–103
Oxygen content (% wt.)	< 2.7	21.6	34.7

The technology of second generation biofuels has significantly improved sustainability due to reduction of carbon dioxide emissions if bioethanol is produced from lignocellulosic materials (Yang et al., 2009; Raud et al., 2014).

Biobutanol (n-butanol, butan-1-ol) is an alternative to currently widely manufactured and used bioethanol as component of gasoline. The basic raw materials for biotechnological production of butanol are the same as for the production of ethanol (Tutt et al., 2012).

Butanol can be produced by fermentation from all lignocellulosic materials, starch and simple sugars using microorganisms, e.g. *Clostridium acetobutylicum*. Currently, researchers focus their attention on blue-green algae strain of *cyanobacteria* that produce biobutanol as isobutanol (Dien et al., 2006; Patáková et al., 2010; Pointner et al., 2014).

Table 1 lists parameters of suitability of butanol, ethanol and gasoline for engines with internal combustion. An important parameter is the oxygen content, which is limited according to the standard EN 228 up to 2.7% wt. (Hönig et al., 2014). Oxygen content is kept in accordance with this norm if 12.5% vol. of butanol is mixed with fuel.

The higher percentage of alcohols in fuel mixtures the more adaptations of engine are needed. The so–called FFV = Flexible Fuel Vehicles are vehicles adapted to fuel with an ethanol content of various content. They are equipped with a sensor recording the ethanol content in gasoline and consequently regulates combustion (Wakker et al., 2005; Küüt et al., 2012; Mařík et al., 2014).

The transition from liquid to gas is called boiling. It takes place only at boiling point in entire volume of boiled liquid. Boiling occurs when the saturated vapour pressure equals the ambient pressure. Boiling point is dependent on the atmospheric pressure, this means that the normal boiling points shows the boiling points at normal pressure (Mužíková et al., 2010).

It is relatively simple to divide components of liquid mixture by distillation. The principle of distillation is based on the different boiling points of distilled components. The degree with which component start to evaporate is called volatility. The distillation curve characterizes the volatility of gasoline along the entire boiling range (Melzoch & Rychtera, 2012).

The easiest evaporating component is the most volatile one - the lightest. Component evaporating after reaching the highest temperature is reached is the least volatile one – the hardest.

If the mixture reaches boiling point of the lightest component and it begins evaporating the heaviest component remains still in liquid phase. Vapours of volatile components are leaving the distillation column leaving its heat in condenser, where subsequently condense back to liquid phase. These are then further processed as distillation product (Dwivedi et al., 2009; Talebnia et al., 2010; Pschorn, 2012).

The distillation process is highly energy-intensive. Almost all supplied heat of distillation is removed in condenser. Distillation curve obtained as a result of distillation tests that we carry out in order to assess fractional composition of gasoline. The percentage or volume of fuel, which distils at one temperature is expressed.

Gasoline must contain light vaporizable fraction securing good start ability of cold engine without contain fractions whose boiling points are above 200°C, which would vaporize and could dilute oil in engine (Yuksel & Yuksel, 2004; Dukulis et al., 2009; Küüt et al., 2011).

For quality of gasoline according to European standard EN 228 the value of E70, E100 and E150 (evaporated at temperatures of 70, 100 and 150°C) are determining the standard range. Following values determining the fuel quality were measured and evaluated:

1. Beginning temperature of distillation varies in the range of 30–35 °C to minimise losses during fuel handling and improve work safety simultaneously.

2. T10 is temperature of 10% of distilled volume. It affects the ability to cool the engine. The tendency is to reduce T10 below 65 °C. At 37.8 °C a saturated vapour pressure is measured, which also characterizes the evaporating ability of fuel. For summer such pressure is 40–70 kPa, in winter the saturated vapour pressure of gasoline is adjusted to 60–90 kPa).

3. T50 is temperature of 50% of distilled volume. This point determines the speed of warming the engine up after a cold start, operating temperature and acceleration characteristics. Modern gasolines have this temperature close to 80 °C.

4. T95 is temperature of 95% of distilled volume. This point affects the combustion efficiency of fuel in cylinder. The hydrocarbons boiling point above 200 °C if sparks appears the engine starts, but burns incompletely. T95 is therefore is about 180 °C. Refineries try to move T95 for gasoline at temperatures 160–170 °C in future.

MATERIALS AND METHODS

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

MTBE (methyl tert–butyl ether) and ETBE (ethyl tert–butyl ether) produced by Czech refinery joint stock company, n–butanol pa (Lachner, Ltd) and isobutanol pa (Lachner, Ltd) were used. The tested bioethanol has fully met requirements of prEN15376:2013 standard. Distillation curve of mixtures was determined in accordance with ASTM D86.

The test samples were labeled by working names:
1. ETH for bioethanol;
2. nBUT for n–butanol;
3. iBUT for isobutanol.

RESULTS AND DISCUSSION

The indicated amounts at distillation curves in Figs 1, 3 and 5 correspond to volume of alcohols in mixture. Curve of pure gasoline without oxygenates is marked 'G'. Figs 2, 4 and 6 show changes in distillation curves compared to pure gasoline. Gasoline is represented as the horizontal axis.

Adding alcohol to gasoline causes reduction of boiling point due to formation of azeotrope. It appears at distillation curve as Plato effect. Bioethanol affects mainly the first half of the distillation curve (Figs 1 and 2) and in particular the temperature T50.

The course of distillation curve may records folowing changes – distillation curve decreases in a wide interval of distilled content (10–70% vol.), respectively in a wide interval of temperatures (50–150 °Cvol.) in comparison to gasoline base without oxygenates.
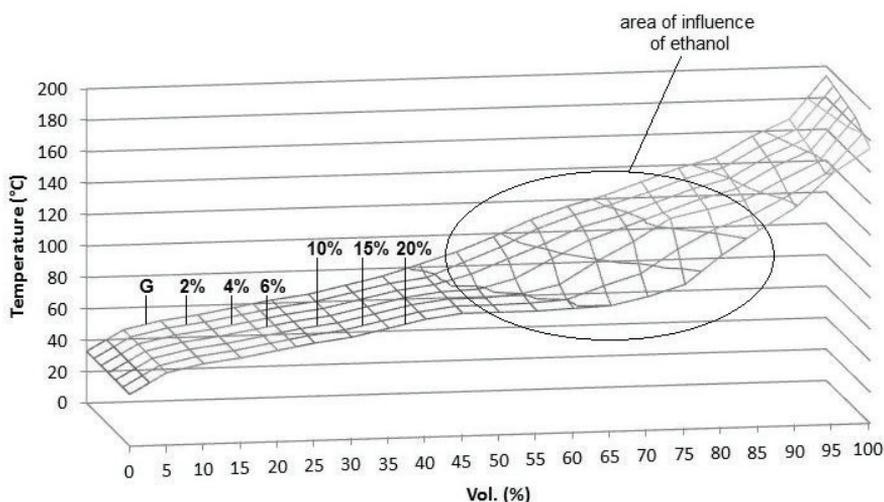
Figure 1. The distillation curve of gasoline containing bioethanol.
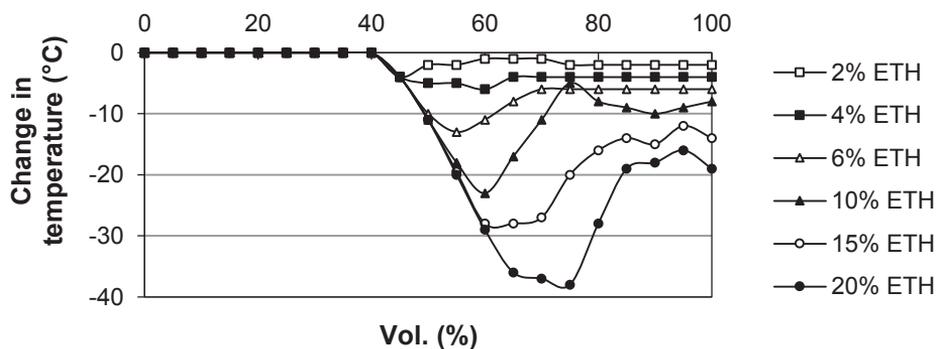
Figure 2. Changes in temperature distillation of gasoline containing bioethanol compared to gasoline base without oxygenate content.
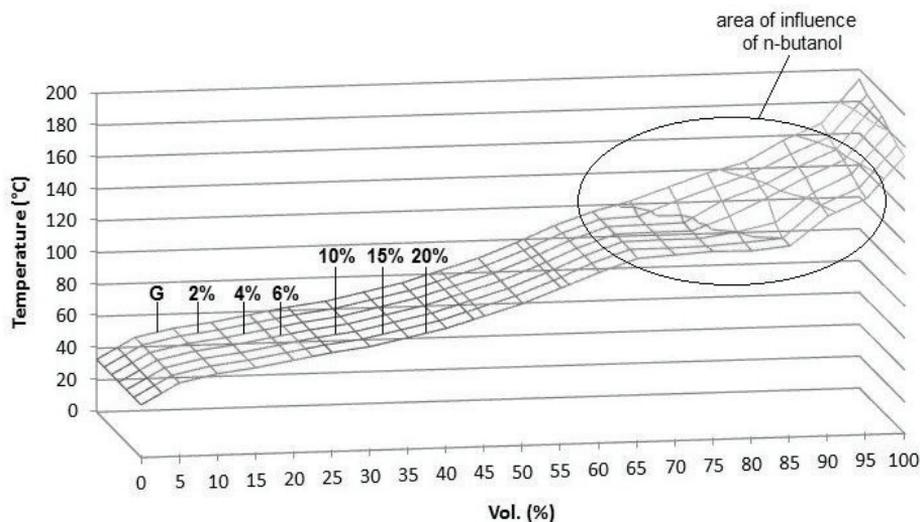
Figure 3. The distillation curve of gasoline containing n–butanol.
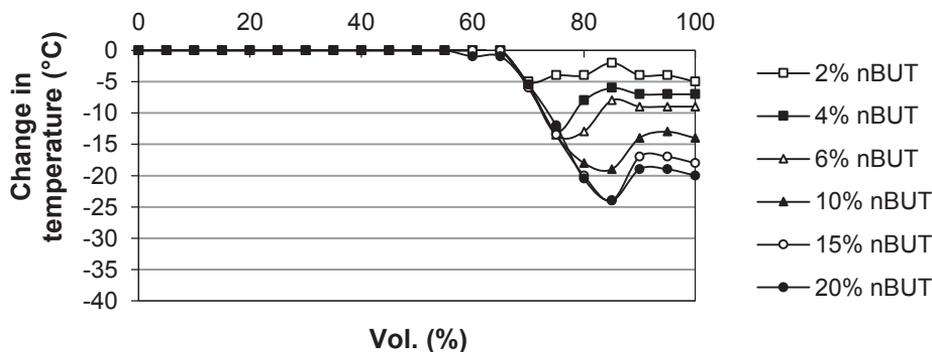
Figure 4. Changes in temperature distillation of gasoline containing n–butanol compared to gasoline base without oxygenate content.

Butanol fuels affect only the second half of distillation curve, which is considered positively. The difference in boiling points of n–butanol and isobutanol is distinctly seen on shape of distillation curves of Figs 3 and 5.
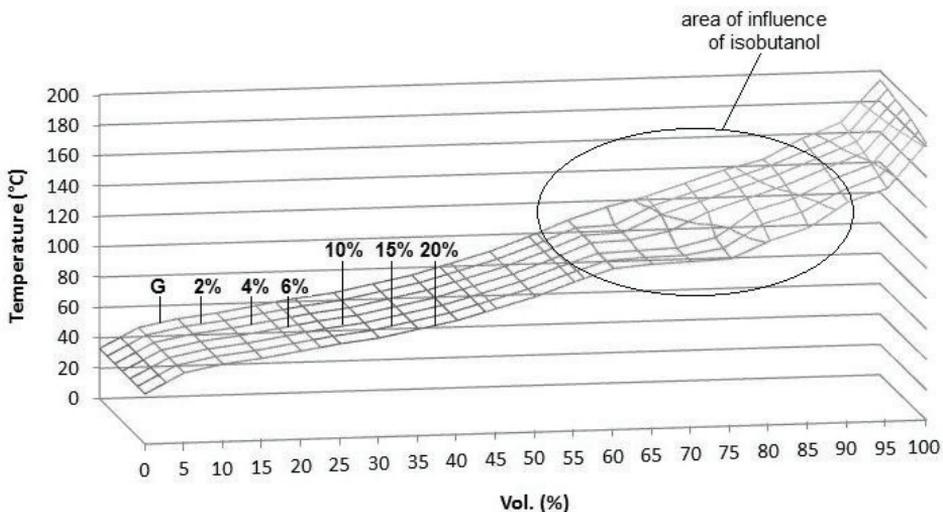
Figure 5. The distillation curve of gasoline containing isobutanol.

Decrease of temperatures of gasoline containing butanol is seen at Figs 4 and 6. Insignificant differences in boiling points of n-butanol and isobutanol are shown in different tendencies of distillation curves.
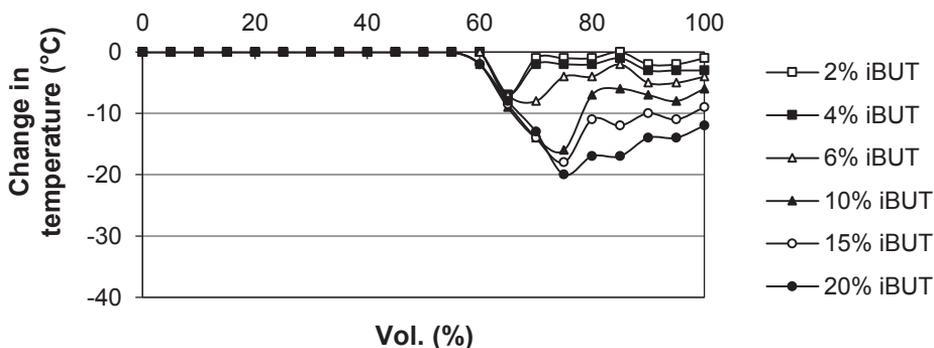
Figure 6. Changes in temperature distillation of gasoline containing isobutanol compared to gasoline base without oxygenate content.

Figs 7 and 8 are showing effect of ETBE and MTBE on analyzed mixtures. These ethers influence the course of distillation curve being well recognizable. Ethers MTBE and ETBE affect the most central part of distillation curve.
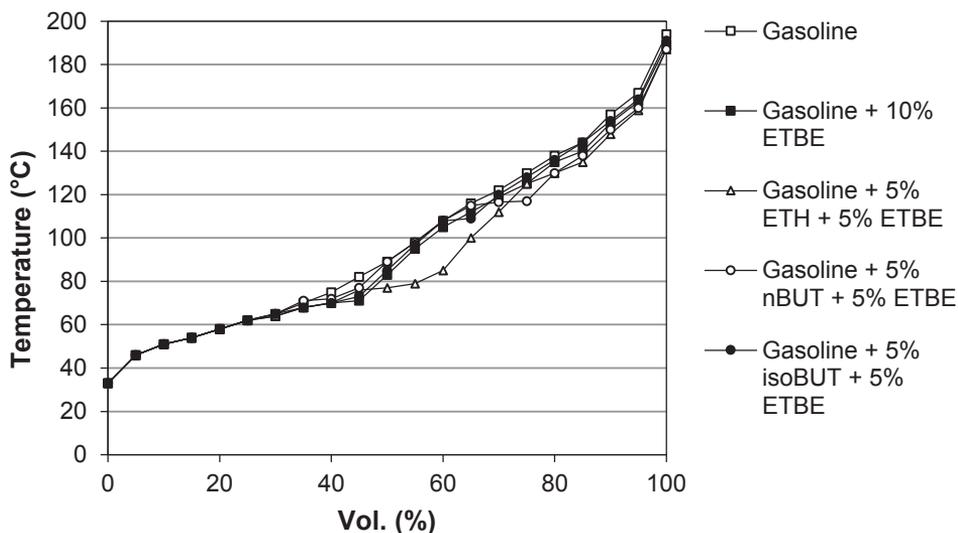
Figure 7. The distillation curves of automobile gasoline containing bioethanol, n–butanol, isobutanol and ETBE.

In case of equal representation of 5% vol. for both ethanol and ETBE the effects of these oxygenates are summarised while changing the profile of distillation curve (Fig. 7). Effect of equal representation of both ethanol and ETBE is identical as if 10% vol. of bioethanol is added to gasoline (Fig. 1).
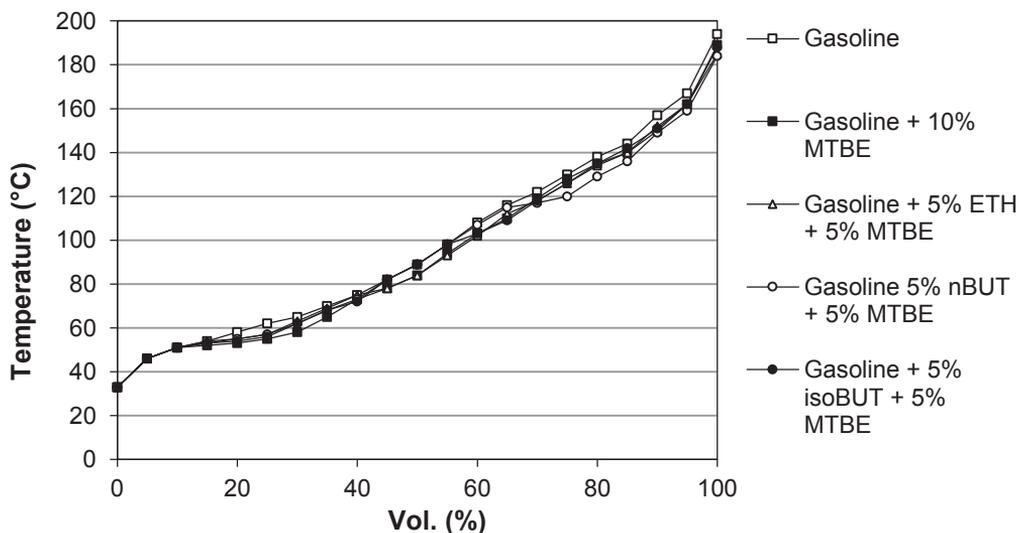
Figure 8. The distillation curves of automobile gasoline containing bioethanol, n–butanol, isobutanol and MTBE.

Figs 9 and 10 are showing change of quantity of evaporated volume at 100 °C and 150 °C (E100 and E150 according to standard EN 228) depending on addition of alcohol. These values have important implications in terms of quality parameters and also in terms of engine operation.
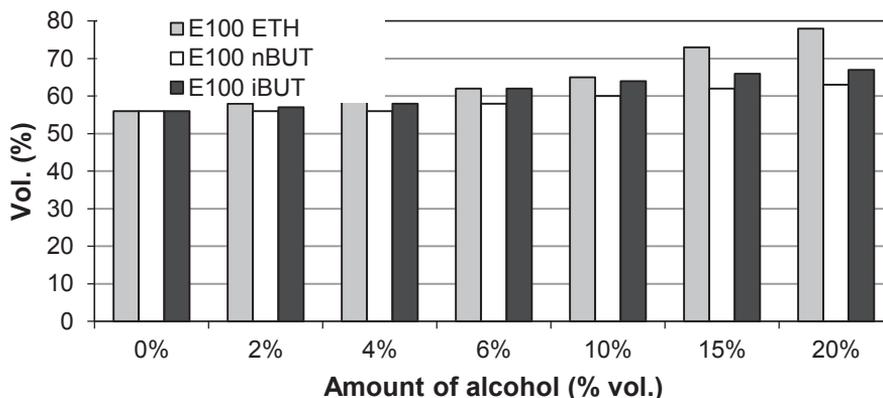
Figure 9. Effect of alcohol to E100 of gasoline.

From Fig. 9 it is seen that n–butanol value affects E100 much less than isobutanol. The boiling point of n–butanol is significantly effected by value of E150 (Fig. 10).
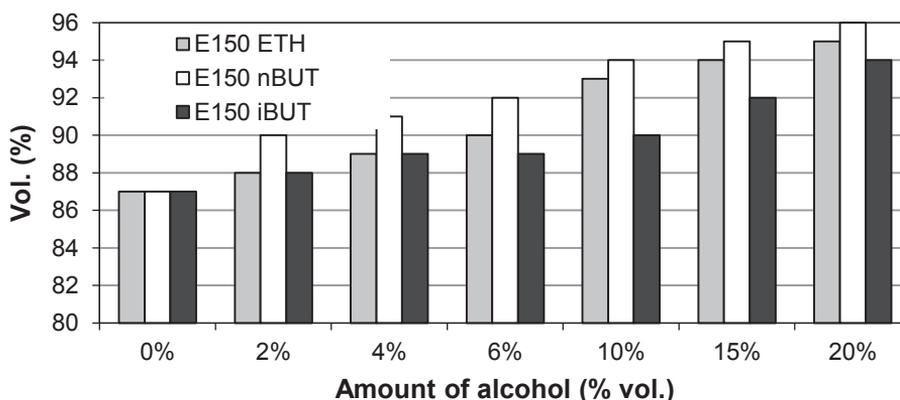
Figure 10. Effect of alcohol to E150 of gasoline.

For present oxygenates significant decrease of gasoline boiling point temperatures to min. 5 °C in wide range of distillation is necessary to expect.

Higher concentrations of alcohols and ethers (more than 10% vol. of each) cause significant changes in second half of distillation curve. If bioethanol is added to gasoline the increase of distilled volume at temperatures around 70 °C should be expected during production. Application of n–butanol and isobutanol increases distilled volume above 100 °C. This effect is seen at Fig. 9 and 10 and on values E100 and E150.

CONCLUSIONS

Changes of distillation curve of gasolines with alcohols are associated with changes of other parameters. The first part of distillation curve and temperature T50 is influenced by bioethanol if mixed with gasoline. The rest of this distillation curve follows shape of pure gasoline. Biobutanol may alternate bioethanol mixtures with gasoline but, parameters differ again. Gasoline mixtures with biobutanol either in form of n-butanol or in form of isobutanol affect only second part of distillation curve with values of E100 and E150 according to EN 228. Shape of distillation affects also performance of engine. Up to 20% of alcohols (bioethanol, n-butanol or isobutanol) in gasoline mixture shouldn't have any significant impact on combustion. But selection of gasoline, ETBE and MTBE cosolvents matters. Combination of gasoline with ETBE and ethanol summarizes its impacts on distillation curve of gasoline. Shape of distillation curve of gasoline with n-butanol or isobutanol and ethers MTBE and ETBE is according to boiling points of these components.

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