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The analysis of the influence of biobutanol and bioethanol mixture with ethers on the vapour pressure of gasoline

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Abstract. In addition to widely known species automotive fuels that are currently on the market, there are many other chemicals which are used or can be used as fuels or fuel components for current automotive internal combustion engines. Implementation of such ingredients car brings a number of technical problems. The vapour pressure is the pressure in the system in which they are at a certain temperature gaseous and liquid phases in equilibrium. The addition of alcohols such as gasoline constituents significantly affects the volatility of the resulting mixture. The article is focused on assessing the addition of biobutanol as n–butanol or isobutanol vapour pressure compared to the already commonly used in bioethanol. Also included is the possibility to use ethers for influencing the vapour pressure of the resulting mixture. Part of the experiment is to assess the influence of the quantity and type of oxygenates and composition of gasoline. Based on the measured data it is clear that addition of alcohol to gasoline create complications. Effect biobutanol as possible alternatives is different than bioethanol. It is therefore necessary to take into account the influence of alcohol, even at low concentrations corresponding to the limit according to standard EN 228. Biobutanol compared bioethanol can be used as 100% fuel. For the low vapour pressure of the fuel experiment also aims to increase its value using pentane.

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

INTRODUCTION

Process of liquefying gases is opposite to evaporating liquids. When the liquid is in a closed container only partly filled it evaporates. Evaporation represents the transition from the liquid to gaseous phase. It progress at any temperature but only from the free surface.

The evaporation speed depends on:

1. surface of area;
2. temperature;
3. removal of vapour from surface.

The pressure above the liquid is increasing, some molecules are passing again into liquid phase. Bidirectional transition is still in progress between liquid and gas (evaporation and condensation). The same rate of evaporation and condensation leads to the equilibrium state in which the vapour pressure of the solvent doesn't change (Pirs & Gailis, 2013).

Vapour pressure (equilibrium vapour pressure or the pressure of saturated or saturated vapour pressure) is pressure of single component system, when a given temperature gaseous phase is in equilibrium of liquid and solid phase. Vapour pressure is the highest pressure at which the substance can exist in equilibrium gaseous state at a given temperature. It is also the lowest pressure at which the substance can exist in liquid or solid state at a given temperature (Dukulis et al., 2009; Hromádko et al., 2011; Küüt et al., 2011).

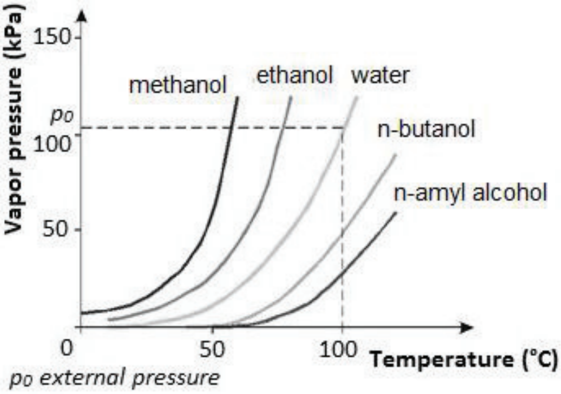

Figure 1. The dependence of vapour pressure on temperature.

Equilibrium of vapour pressure at constant temperature stabilizes without being dependent on quantity of liquid. As soon as pressure of saturated vapour reaches gas pressure in surroundings a liquid is boiling (Campos et al., 2002; Ezeji et al., 2007; De Wit & Faai, 2010).

The corresponding temperature is called the boiling point. Both boiling and also boiling point depends on the external pressure being described by vapour pressure curve (Fig. 1).

The socalled normal boiling point means temperature by which the pressure is equal to saturated vapour pressure of 101.325 kPa. Liquid can be warmed up to temperature by which pressure of saturated steam is equal to outside pressure if it is maintained at a constant value. This pair of values of the temperature–pressure is called the boiling point of liquid (Patáková et al., 2010).

The normal boiling point (T_N) is temperature of liquid with given composition in phase equilibrium with its vapour at normal atmospheric pressure (101.325 kPa). We may say, that the vapour pressure at the normal boiling point of all substances is equal to 101.325 kPa.

Liquid–vapour system receives heat from outside to maintain isothermal conditions during evapouration (Hendrich et al., 2005). A molar heat of vaporization is heat consumed during vaporization of amount of liquid substance. This is equal to molar vaporization enthalpy (ΔH_M). The dependence of vapour pressure on temperature may be expressed by the following equations.

Augustus equation

$$\log p = A - \frac{B}{T} \tag{1}$$

where: p – saturated vapour tension of the liquid; T – temperature; A,B – empirical constants.

Antoine equation

$$\log p = A - \frac{B}{C + t} \tag{2}$$

where: p – saturated vapour tension of the liquid; t – temperature; A,B,C – empirical constants

Result of Antoine equation is based on pressure unit [torr]. Therefore, it must be converted to pressure in units (Pa) after calculation.

$$torr = 133.3kPa \tag{3}$$

This calculation method has only limited accuracy. Therefore, it is suitable for lower pressures not being applicable for all substances. This is only a mathematical approximation of equilibrium of real situation.

Clausius – Clapeyron equation

$$\frac{d \ln p^o}{dT} = \frac{\Delta H_M}{RT^2} \tag{4}$$

where: p^0 – saturated vapour tension of the liquid; T – temperature; ΔH_M – molar vaporization enthalpy; R – universal gas constant (8.314 J $K^{-1}mol^{-1}$).

Assuming that the molar vaporization enthalpy of measured temperature range is constant the relationship is obtained by integration of equation (1):

$$\ln p^o = A - \frac{\Delta H_M}{R} \cdot \frac{1}{T} \tag{5}$$

which can be rewritten as:

$$\ln p^o = A + \frac{B}{T} \tag{6}$$

where A,B – are equation constants, which are usually assessed on basis of experimental data.

Vapour pressure above liquid

The release of particles from the liquid surface (evaporation) is process, which more or less intensively occurs at each temperature. Vapour pressure (vapour pressure) above the liquid is function of temperature. The higher temperature the higher pressure tendency occurs (Fig. 1). The temperature at which the saturated vapour tension reaches the external pressure is called the temperature of boiling point. The boiling point is important physical parameter of substance. It depends on relative molecular weight, polarity of substance and possibility of formation of hydrogen bridges. The socalled volatility of substance is related to boiling point (Groot et al., 1992; Moiser et al., 2005; Melzoch et al., 2010).

Vapour pressure is equilibrium of vapour and liquid phases at given temperature. Interval of vapour pressure is set by standard EN 228 according to climatic conditions during the year. Summer gasoline has lower vapour pressure (45–60 kPa) to prevent loss of fuel by increased evaporation and also to decrease emergence of vapour cushions. Vapour pressure of winter gasoline ranges from 60 to 90 kPa. Higher vapour pressure are necessary for sufficient fuel evaporation and reliable start at low temperatures (Hromádko et al., 2009; Hromádko et al., 2010).

The vapour pressure of fuel is closely related to boiling point. In purely hydrocarbon gasoline the highest vapour pressure have low boiling butanes (350–390 kPa) and pentanes (i–pentan 115 kPa). Its content can reliably regulate the resulting vapour pressure of gasoline directly during manufacturing. Biofuels, especially bioethanol, is becoming more important in recent years. Adding ethanol and other oxygenates in gasoline is causing change of vapour pressure (Mužíková et al., 2010; Hönig et al., 2014; Pointner et al., 2014).

An objective of this paper is to test if biobutanol can compete with bioethanol. Bioethanol is currently commercially produced and used as a component of gasoline or as E85. Selection of raw material for production of alcohols depends on the enzymatic equipment of microorganisms. Cultures of *Clostridium acetobutylicum* are used to produce biobutanol in shape of n–butanol (butan–1–ol). Researchers focus their attention also on blue–green algae strain of *cyanobacteria* that produce biobutanol as isobutanol (Mosier et al., 2005; Patáková et al., 2010; Pointner et al., 2014).

Effect of commonly used MTBE and ETBE on vapour pressure of mixture is also analysed. MTBE and ETBE are current cosolvents added to gasoline. Therefore, its influence on gasoline–butanol mixtures is necessary to know (Mužíková et al., 2012).

MATERIALS AND METHODS

Standard procedure determines the vapour pressure according to method of Reid (RVP). The measurement is performed at temperature of 37.8 °C in a sealed vessel with a volume about 500 ml, which is equipped with manometer. The ratio of the volume of air chamber to volume of fuel chamber is exactly 4:1. The sample in fuel chamber is saturated with air at 0–1 °C.

The vapour pressure of mixtures of pure gasoline without added oxygen and additives are used according to standard EN 228 for winter (labelled with W) and summer period (labelled with S).

Further, MTBE (methyl tert–butyl ether) and ETBE (ethyl tert–butyl ether) produced by Czech refinery joint stock company, n–butanol p.a. (Lachner, Ltd), isobutanol p.a. (Lachner, Ltd), n–pentante p.a. (Lachner, Ltd) and anhydrous ethanol were used.

Standard of Reid according to ASTM D323 the vapour pressure of gasoline mixtures and influence of alcohols and ethers was used.

The test samples are labelled as follows:

1. ETH for bioethanol;
2. nBUT for n–butanol;
3. isoBUT for isobutanol.

RESULTS AND DISCUSSION

Fig. 2 shows that the vapor pressure of gasoline containing 10% vol. of ethanol corresponds to vapour pressure without presence of ethanol. Surprisingly, emerged mixture of 5% vol. has higher vapour pressure than original gasolines. This phenomena is seen at peak of W – gasoline curve in interval 0–10% vol. of alcohol volume (Fig. 2). This negative commingling (mixing) effect is called by vapour pressure of ethanol in gasoline.

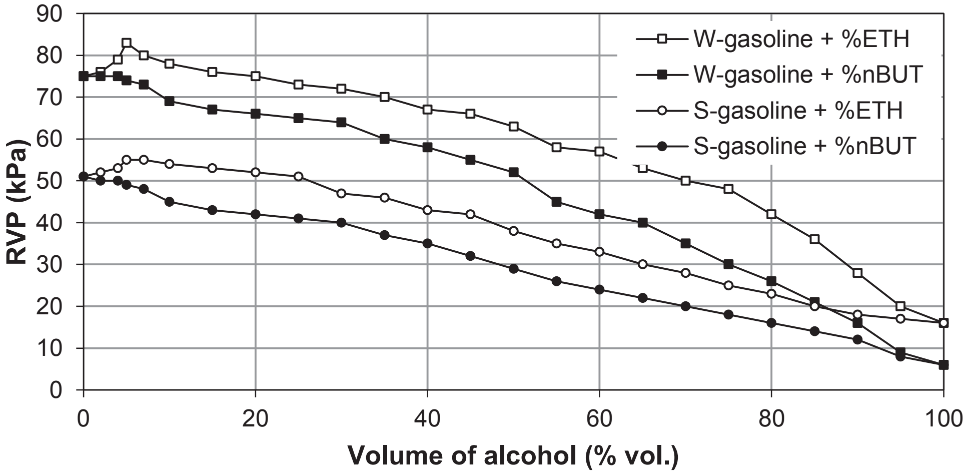

Figure 2. Vapour pressure of winter (W) and summer (S) gasoline mixtures depending on amount of added alcohol.

Ethanol actually creates new azeotrope with minimum boiling point, while the pressure of the newly formed mixture is increased. The amount of change of the vapour pressure depends on proportion of both gasolines and ethanol in the resulting mixture (Fig. 2).

Added ethanol to gasoline up to 8% vol. has maximum increase of vapour pressure. Further increasing of ethanol content in mixture decreases vapour pressure. The mixture comprising about 20% vol. of ethanol has the same vapour pressure as without ethanol being present.

The vapour pressure of E85 (85% vol. of ethanol) mixture is moving below the lower limit (45 kPa) for summer automotive gasoline. When preparing a 5% vol. mixture of ethanol in summer gasoline is necessary to have sufficient vapour pressure up to 8 kPa, and simultaneously reduce C_4 fraction. Vapour pressure of gasoline mixed with biobutanol can be attributed to sum of both components and its points of vapour pressure.

The courses of influence of n–butanol and isobutanol on vapour pressures of gasoline are very similar. Therefore, the influence of isobutanol is shown separately in Fig. 3. Vapour pressure of mixtures containing up to 5% vol. n–butanol and isobutanol is insignificant opposed to ethanol. Higher concentrations of alcohols in gasoline lead to lower vapour pressure of resulting mixtures (Figs 2 and 3).

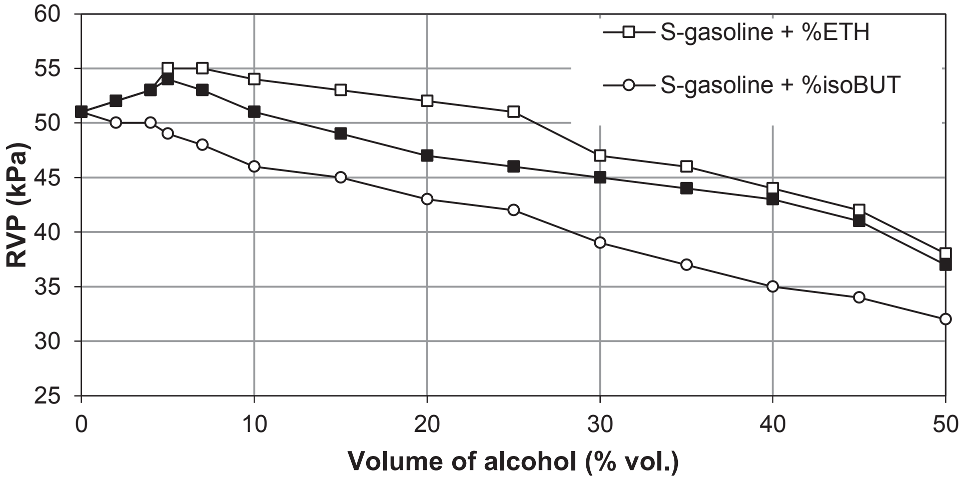

Figure 3. Vapour pressure of summer (S) mixtures of gasoline depending on added isobutanol.

With increasing boiling point of hydrocarbon the boiling point of the azeotrope increases. Alkanes n–C_4 n–C_5 have lower boiling point than ethanol. Decreased boiling point of the azeotrope of ethanol is lower opposed to e.g. n–octane. Formed azeotrope with ethanol alkanes increases vapour pressure of azeotrope more than ethanol with aromatics.

Vapour pressure of mixture of gasoline with ethanol may be positively influenced by presence of n–butanol and isobutanol (Figs 3 and 4). The growth of vapour pressure with added 5% vol. of ethanol in the mixture, which already contains 2% vol. butanol, causes a pressure increase up to 6 kPa (Fig. 4). Increasing pressure may be observed at other compositions of both alcohols.

Fig. 4 shows that in case of 5/10% vol. (ethanol/n–butanol) and 10/5% vol. is vapour pressure theoretically the same. The vapour pressure of gasoline containing 5% vol. of ethanol is characterized by formation of a new azeotrope with higher vapour pressure. The presence of n–butanol (also isobutanol Fig. 3) reduces vapour pressure of this gasoline–ethanol mixture. Vapour pressure of mixture containing 10% vol. ethanol is less than mixture containing 5% vol. of ethanol. To reduce the vapour pressure according to mixture 5/10% vol. is required smaller amount of n-butanol 10/5% vol. Differences of vapour pressures of mixtures containing 5 and 10% vol. of ethanol is also seen in mixtures 5/2% vol. and 10/2% vol.

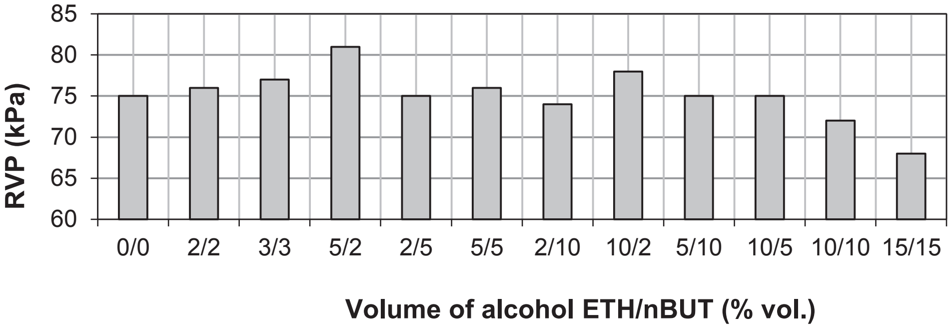

Figure 4. Vapour pressure at 37.8 °C for winter mixture of ethanol/n–butanol with gasoline.

Ethers (MTBE, ETBE) may significantly reduce increase of vapour pressure ethanol is added while azeotrope is emerging. Fig. 5 shows how a smaller amount of ether added to mixture could decrease vapour pressure of low mixtures of ethanol.

ETBE has more favourable effects opposed to both ethanol and butanol as vapour pressure of mixtures is less affected. ETBE is decreasing vapour pressure in interval of 45–90 kPa. Effect of MTBE depends on initial vapour pressure of hydrocarbon base. Vapour pressure of mixture of gasoline, n–butanol and MTBE below 55 kPa increases but, above this limit decreases. Therefore, this lower vapour pressure of summer gasoline was sample selection criteria.

The bottom axis on Fig. 5 shows the amount of n–butanol/MTBE and n–butanol/ETBE.

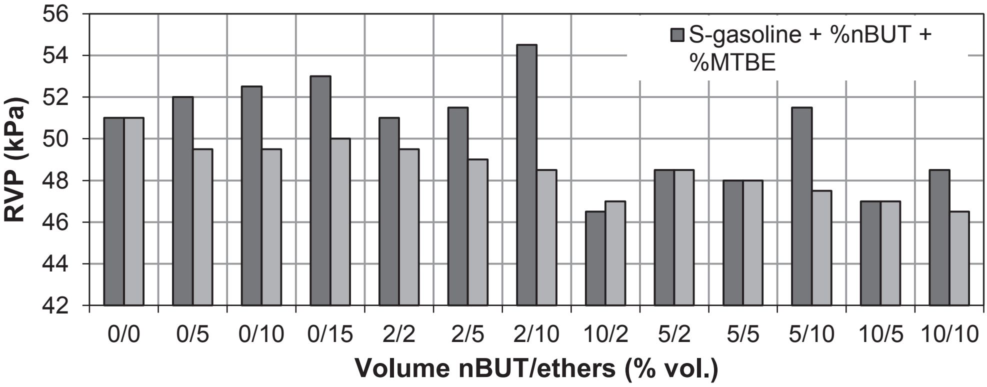

Figure 5. The vapour pressure at 37.8 °C of summer mixtures of gasoline with n–butanol, MTBE and ETBE.

The very low vapour pressure of pure biobutanol requires to know temperature of gasoline mixtures with butanol. Otherwise, cold start of engine a minimum volatility of gasoline with a minimum vapour pressure of 5 kPa is needed. This is the lowest limit allowing start of engine.

The vapour pressure of gasoline containing high percentages of ethanol, n–butanol and isobutanol must be increased by hydrocarbon component with sufficiently high volatility. Requirement of minimum fuel volatility for starting of engine at low temperatures is fulfilled in this case. Low boiling components (hydrocarbons C_3–C_5) of gasoline allow starting of engine well, for example. Use of these hydrocarbons in commercial gasoline is due to its high vapour pressure limited. Resulting balance of refinery without watching C_3–C_5 gasoline components is also suitable enhancement.

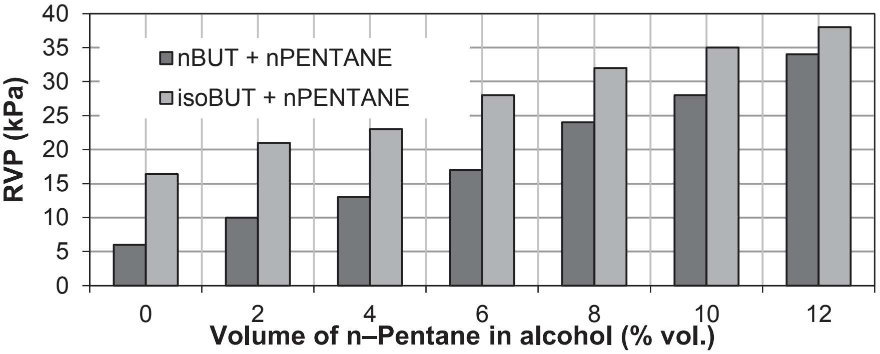

Figure 6. Vapour pressure at 37.8 °C of n–butanol and isobutanol depending on the added pentane.

The vapour pressure of biobutanol can be increased if n–pentane is added. This method may be applied for 100% biobutanol (n–butanol or isobutanol) biofuel (Fig. 6). If applied pure n–butanol or isobutanol without added volatile component (or special equipment) it would be very difficult to start engine even at temperature 37.8 °C according to method of Reid.

CONCLUSIONS

Application of renewable biofuels brings a number of technical problems. Alcohol fuel and ether mixtures affect the volatility both up and down significantly. Bioethanol and biobutanol in gasoline need adjustments of either engine or fuel according to vehicle specifications. Vapour pressure and distillation curve affect driveability of engine and fuel leaks into air during distribution.

Gasoline mixture with ethanol up to 10% vol. creates a new azeotrope with minimum boiling point, which increases vapour pressure. Gasoline mixture with butanol (n–butanol and isobutanol) a reserve of vapour pressure of gasoline needn't be created as emerging azeotrope has no impact.

Vapour pressure of gasoline containing high percentages of ethanol (for example E85), n–butanol and isobutanol needs to be increased by low–boiling gasoline components C_3–C_5. Butanol can also be administered as a pure fuel in comparison with bioethanol if n–pentan is added, for example.

Ethers (MTBE, ETBE) in gasoline with alcohols may cause unpredictable phenomena as vapour pressure of winter and summer gasoline differ and its effect is not easily predictable. The vapour pressure of the resulting mixtures must be monitored to prevent negative impact on engine starting and for fuel distribution and storage. Mixtures with a higher content of bioethanol or biobutanol require optimizing of fuel/air ratio, which is influenced by oxygen content in gasoline.

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