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# VOLATILITY AND DISTILLATION PROPERTIES OF ETHANOL-PETROL BLENDS

*Abstract*

*This experimental study deals with the influence of oxy-compound content (ethanol, MTBE, ETBE) on the Reid vapour pressure (RVP) and on the distillation characteristic (ASTM D86) of petrol blends.*

*Effect of hydrocarbon composition of petrol blends on their volatility and distillation properties was also investigated.*

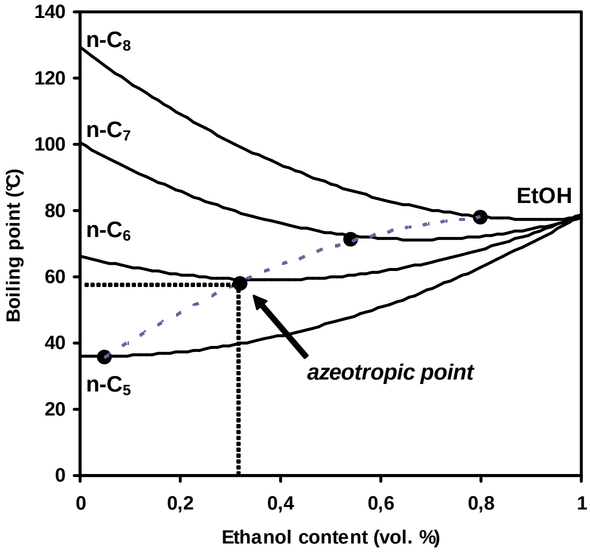
*Production, storage, distribution and utilisation of automotive fuels are associated with many technical problems especially in cases when the fuels contain some biocomponents. Biofuels blended into petrol and/or diesel fuels can affect their quality and as a consequence that can result in inferior acceptance of these fuels by consumers. In case of petrol blends with bioethanol there are some serious problems that could be resolved, such as stability of the blends, their susceptibility to aerial humidity as well as their high volatility.*

## 1. Vapour pressure of automotive ethanol-petrol blends

The basic standardised parameter dealing with volatility of automotive fuels is the vapour pressure according to Reid (RVP). This parameter defines the vapour pressure over the liquid level at a temperature of 100°F (37.8 °C) while the volume ratio of the vapour and liquid phase of the sample is 4:1 (ASTM D 323). RVP value should be high enough to allow good starts of cold engines. Simultaneously, it should be low enough to guarantee minimum evaporation loses during fuel distribution and in service of vehicles. Automotive petrols distributed now in Czech Republic have to meet the requirements of the standard EN 228, i.e. RVP in the range of 45–60 kPa in summer and 60–90 kPa in winter. RVP value corresponds with the contents of petrol components with the highest volatility [1], i.e. n-butane (350 kPa), isobutane (390 kPa), isopentane (115 kPa), and MTBE (55 kPa). During production the RPV value can be well regulated by the amount of $C_4$ fraction added to the petrol blend.

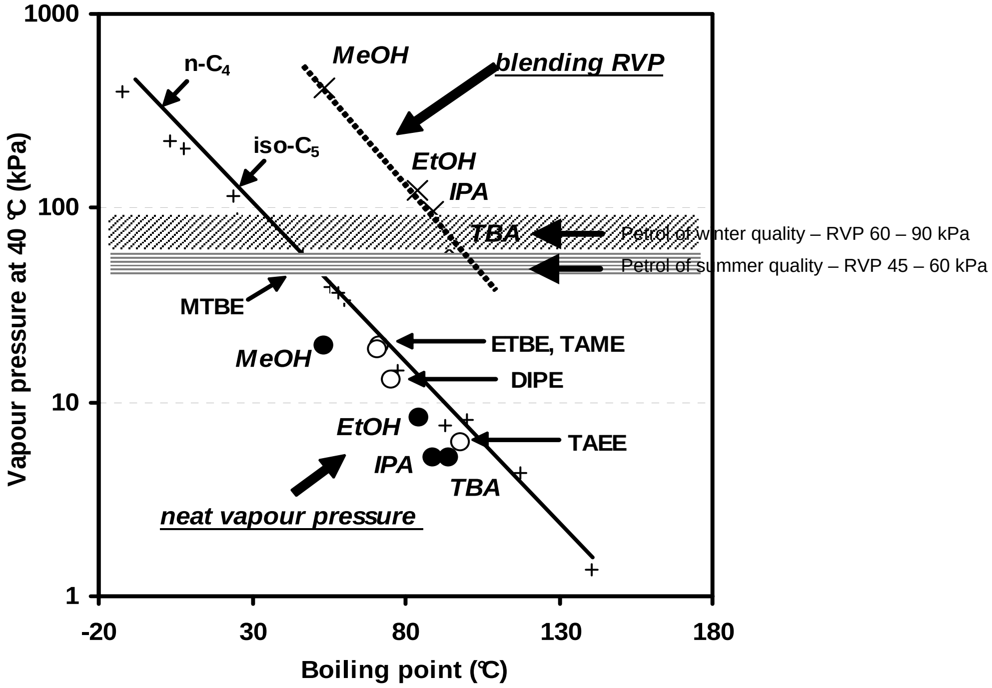
Vapour pressure of automotive petrol is highly influenced by the addition of alcohols [2]. Liquid blends of hydrocarbons and polar compounds (such as alcohols $C_1$ – $C_3$) with similar volatility can form azeotropes with very low boiling points. Vapour pressure in these cases is higher than follow from the Raoult law. Ethanol can form azeotrope with hydrocarbons boiling in the range from 30 ℃ to about 120 ℃, i.e. about 42–47 ℃ bellow and/or above the boiling point of ethanol. This range corresponds to boiling points of hydrocarbons about $C_5$ – $C_8$ with a large variety of isomers and character (alkanes, olefines, aromatics). Example of azeotrope formation is shown in Figure 1. The higher boiling point of the hydrocarbon, the higher is the boiling point of azeotrope, and the lower is content of hydrocarbon in the azeotrope. Alkanes have stronger effect on lowering of the azeotrope boiling point than aromatics of similar volatility. Boiling points of cyclanoalkanic azeotropes lies between the alkanic and aromatic azeotropes. Formation of azeotropes can be influenced by a pressure in both directions. Ethers as one of the petrol components are relatively non-polar in comparison with alcohols and, therefore, they did not form azeotropes [2].

Figure 1: Effect of ethanol content in a mixture with alkanes on the formation of azeotrope [2]



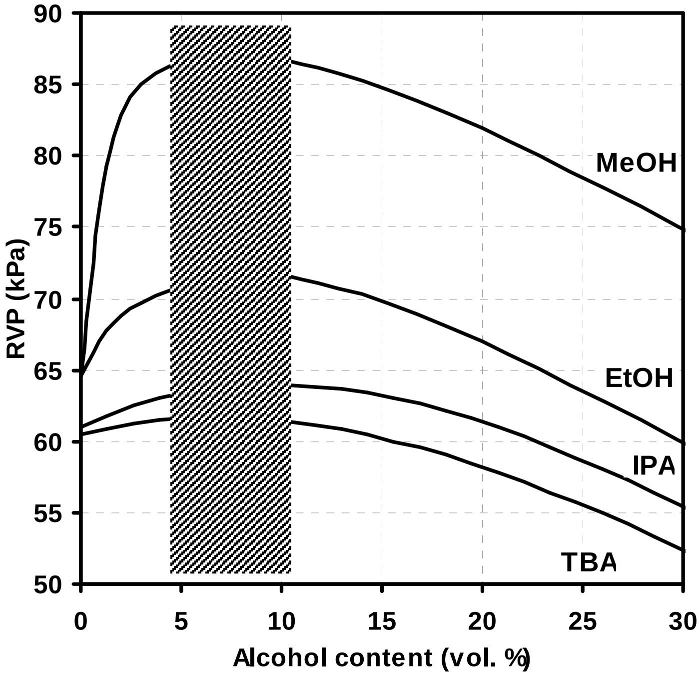
Formation of azeotrope and its lower boiling point are consecutively reflected in a higher volatility of the ethanol-petrol blends and in their higher vapour pressure. Whereas vapour pressure of individual alcohols is low formation of azeotropes has crucial impact on the final volatility of ethanol-petrol blends. Blending vapour pressures could thus be about 15–20 times higher than that of pure alcohols [3] and therefore basically affect the volatility of the fuels (see Figure 2). Blending of $C_4$ fraction into ethanol-petrol blends should thus be largely avoided, especially for a summer quality of fuels with more stringent requirements on the vapour pressure.

Figure 2: Relationship between boiling point of hydrocarbons, ethers, and alcohols and their vapour pressure [1,3]



Maximum increase in the vapour pressure can for the ethanol-petrol blends be noticed for the 5–10 vol % content of alcohol (see Figure3) [4]. Higher alcohol content in the blends leads to lowering the RVP values. Vapour pressure of 20–25 vol % ethanol blends are nearly the same as that of initial hydrocarbon petrol. So, automotive fuels with high alcohol content (E85, M85) are less dangerous with respect to emissions of volatile compounds than commercial ethanol-petrol blends according to the EN 228 standard with alcohol content restricted to 5 vol % (EtOH) or 3 vol % (MeOH). For such blends, an increase in RVP value of 5 kPa (5 vol % of EtOH) or of about 20 kPa (3 vol % of MeOH) should be taken into account.

Figure 3: Effect of some alcohols on the vapour pressure of their blends with petrol [4] (*MeOH = methanol, EtOH = ethanol, IPA = 2-propanol, TBA = t- butanol*)



Another problem arises from mixing two petrols with different content of ethanol. Such an effect is called the commingling effect. For example, mixing two petrols, one with 0 % and the other with 10 vol % of ethanol, can lead to a mixture with 5 vol % of ethanol, however, resulting vapour pressure can be higher than that for the initial petrols. Increase or other change in the RVP value is given by a ratio of the two petrols blended. The commingling effect is shown in Figure 4. This situation can be typical for mixing different petrols at petrol stations.

It is very important from the view of production of petrol fuels that addition of co-solvents, such as MTBE and/or ETBE, did not increase the vapour pressure of the ethanol-petrol blends. On the contrary, their presence can lower the RPV value by 2–3 kPa for addition of 5 vol % of ETBE into petrol with 5 vol % of ethanol. Experimental data are presented in Figure 5.

Figures 6 and 7 present effect of petrol composition on vapour pressure in the presence of 5 vol % of ethanol in the petrol blends. It is clear from the figures that RVP values trends are nearly the same independently on the content of ethanol.

However, the RVP values of ethanol-petrol blends are noticeably higher due to the formation of azeotrope. In the region of commercial petrols and their composition, difference in the vapour pressure between ethanolic and non-ethanolic petrol blends are almost independent on the hydrocarbon composition of the petrol. Attention was paid to changes in the ratio of n- and iso-alkanes (Figure 6), as well as in the ratio of unsaturated (incl. aromatic) vs. saturated hydrocarbons (Figure 7). In the future, a trend of increasing utilisation of alkylates should be taken into account for the petrol blending. That probably will lead to a partial increase in the vapour pressure of petrol blends and this effect will further be pronounced by the utilisation of ethanol in automotive fuels.

Figure 4: Commingling effect and its influence on RVP values [5]

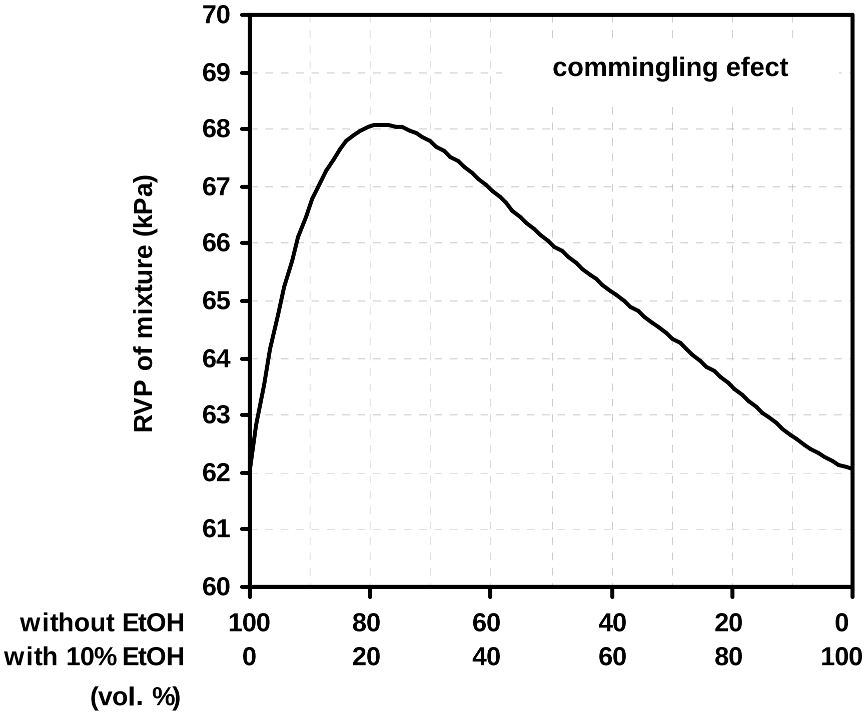


Figure 5: Effect of ETBE on the vapour pressure of ethanol-petrol blends

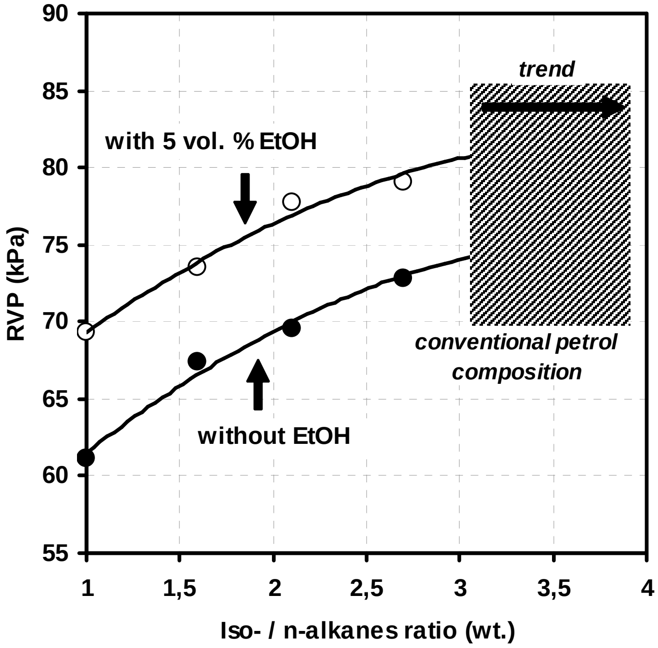


Figure 6: Influence of hydrocarbon composition on vapour pressure; n- and isoalkanes

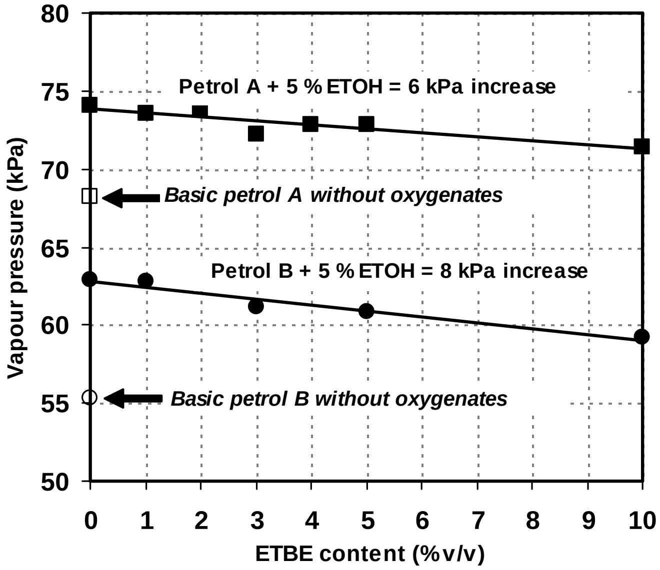
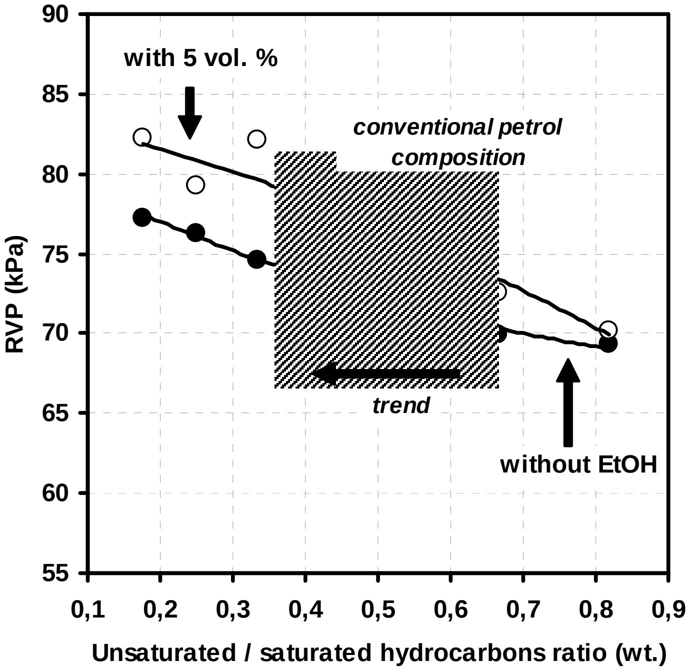


Figure 7: Influence of hydrocarbon composition on vapour pressure; saturated and unsaturated hydrocarbons



## 2. Distillation characteristics of ethanol-petrol blends

Distillation test according to ASTM D 86 standard represents another significant characteristic of automotive fuels in relation to their volatility. From the view of the standard EN 228, important parameters are represented by the start and end point of distillation, and, in addition, by the point E70, E100 and E150 that correspond to amount of fuel distilled off at temperatures of 70 ℃, 100 ℃, and 150 ℃. In Figure 8 there is clearly shown that ethanol significantly affects the beginning part of the distillation curve. In the region of 50–70 ℃ there is clearly seen the formation of flat azeotropic plateau. This fact should be kept in mind in production of automotive fuels. About 5–10 vol % increase of the fraction distilled at 70 C should be considered due to the effect of ethanol in the fuel. This effect is smaller, up to 5 vol %, at higher distillation temperatures and ethanol content in the fuel up to 10 vol % (Fig.8).

When ETBE is blended into the fuel as the only oxygenate, its effect on the distillation characteristics can only be seen in the middle part of the distillation curve on Figure 9. In the presence of both ETBE and ethanol (5+5 vol %) effects on the distillation characteristics of the fuel are summed. Figure 9 shows that the distillation curve is changed in a broad region of the distilled-off fuel (10–70 vol %) and broad region of distillation temperatures (50 –150 ℃). Figure 10 presents changes in the distillation characteristics of petrol with ethanol and ETBE compared with common hydrocarbon petrol.

It should be noticed that significant decrease of boiling points (about by 5 ℃ and more) in a broad distillation range should be considered when ethanol and other oxygenates are blended into petrol fuel.

Figure 8: Distillation properties of ethanol-petrol blends

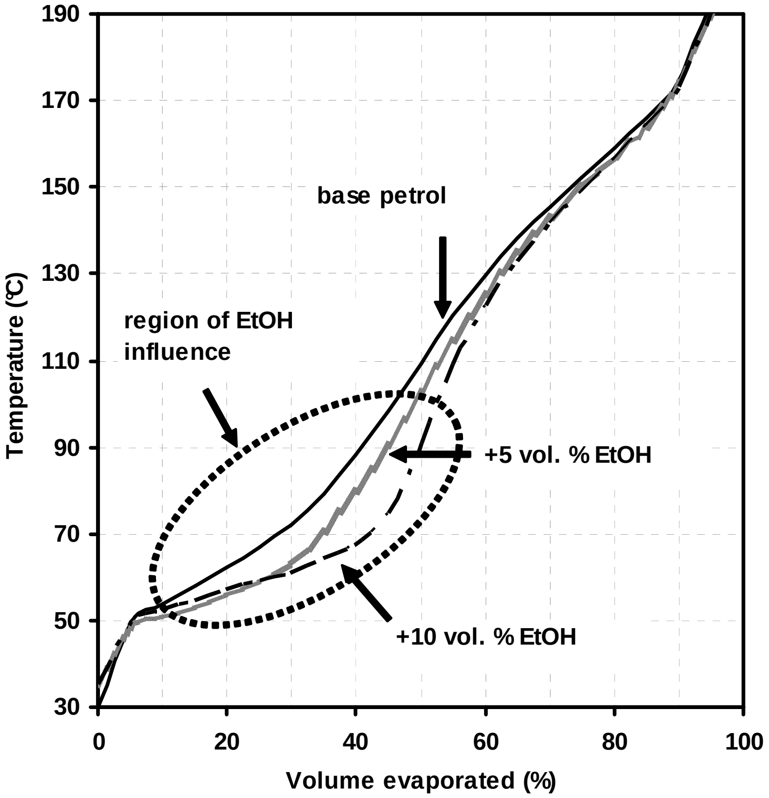


Figure 9: Distillation properties of petrol blends with ethanol and ETBE

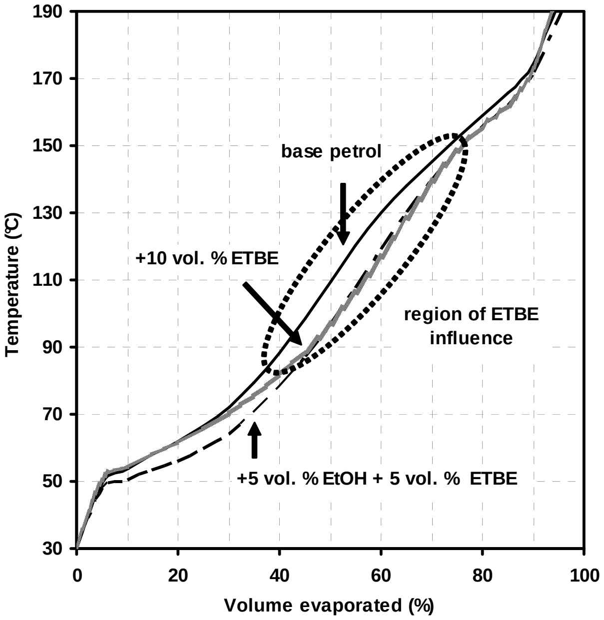
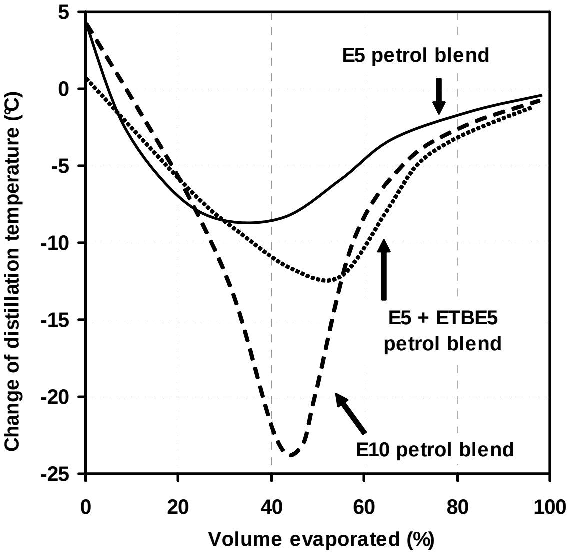


Figure 10: Influence of ethanol and ETBE on distillation temperature of petrol



# 3. Conclusion

Blending of bioethanol into automotive petrol will soon be obligatory and it will significantly affect the volatility and distillation characteristics of motor fuels. Fuel producers should accept this situation and should make some technological rearrangements influencing the volatility of automotive fuels with the aim to keep the fuel vapour pressure within limits given by the EN 228 standard. Some loosening of the current stringent limits cannot be expected in the EU, in the contrary to US market where the so called “1 psi waiver” was accepted. Utilisation of the $C_4$ fraction for the petrol production will most likely be limited, and this situation can also affect the products balance of fuel refineries.

Many problems can occur in the fuel distribution network and at the petrol stations due to the commingling effect. Typically, mixing ethanol-petrol blends with “pure” hydrocarbons fuels is most likely at these sites.

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| UDK | ključne riječi | key words |
|---|---|---|
| 621.434-632.5 | specifikacija benzinsko/etanolnih mješanih goriva | specification for gasoline/ethanol blended fuels |
| 665.733.5.038.3 | etil-tert-butil-eter | ethyl-tertiary-butil-ether |
| 536.423.16 | Reid, tlak para | Reid vapour pressure |
| 536.423.1 | destilacijska krivulja | distillation curve |

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