Fuel 88 (2009) 1351–1356

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Volatility and phase stability of petrol blends with ethanol

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ARTICLE INFO

Article history:
Received 9 June 2008
Received in revised form 28 January 2009
Accepted 5 February 2009
Available online 27 February 2009

Keywords:
Ethanol
ETBE
Vapour pressure
Phase separation
Water extraction

ABSTRACT

Blending ethanol in to petrol can be associated with problems related to volatility and phase stability of the blends. Ethanol up to 20 vol% in petrol forms an azeotropic mixture with hydrocarbons. Ethanol has affinity to water and air humidity and it increases the water solubility in ethanol–petrol blends. In this work, the influence of ethanol up to 10 vol%, ETBE up to 10 vol% and hydrocarbon composition over volatility, distillation characteristics and miscibility of ethanol–petrol blends with water was studied. It was found that higher content of saturated hydrocarbons in petrol increased the vapour pressure of azeotropic ethanol blend. Aromatics and alkenes influenced the azeotrope vapour pressure, phase separation temperature and ethanol extraction in a positive way. The results showed that the ETBE can soften effects of the ethanol blending to petrol. ETBE decreased the vapour pressure and the phase separation temperature of the ethanol–petrol blends.

1. Introduction

Bioethanol is one of the most frequently used biofuels in the European Union. Some ethanol properties differ significantly from those of petrol hydrocarbons [1]. Namely, it is a polar character of ethanol and its high affinity to water. Unlike hydrocarbons, ethanol is perfectly miscible with water and it forms azeotrope with them. Bio-ETBE (ethyl tert.-butyl ether) that is made from bioethanol can be used as biofuel in the same way as bioethanol. Properties of ETBE are similar to hydrocarbons properties [1].

Ethanol content in automotive petrol is limited to 5 vol% according to the current European quality standard EN 228. However, an increase up to 10 vol% in near future is intensively discussed [2]. The maximum content of ETBE in automotive petrol is limited to 15 vol% according to EN 228. It can be added with ethanol to petrol currently providing that the oxygen limit 2.7 wt% is not exceeded. For example 5 vol% of ethanol can be combined with 5 vol% of ETBE, the oxygen content in this blend is 2.53 wt% and the total content of biofuels is 10 vol%.

The drawback of ethanol utilization is a formation of an azeotrope with lower boiling point [3–6]. The azeotrope is formed between ethanol and hydrocarbons boiling in the range 30 °C to about 120 °C and it is consecutively reflected in a higher volatility of the ethanol–petrol blends and in their higher vapour pressure [7,8]. Whereas the vapour pressure of ethanol is low the 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 the pure alcohol and therefore basically affect the volatility of the fuels [3,4,9]. Another problem arises from mixing two petrols with different content of ethanol. Such an effect is called the commingling effect [10]. For example, mixing two petrols with the same vapour pressure (62 kPa), 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 (68 kPa) can be higher than that for the initial petrols [11]. The increase in vapour pressure value is given by a ratio of the two petrols blended [11].

The basic standardised parameter dealing with volatility of automotive fuels is the vapour pressure according to Reid (RVP). 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 petrol distributed now in Czech Republic have to meet the requirements of the European standard EN 228, i.e. RVP in the range of 45–60 kPa in summer and 60–90 kPa in winter.

A second issue is that ethanol improves significantly the solubility of water in hydrocarbon fuel [1,6,11]. High solubility of water in ethanol–petrol fuel blends is affected by polar character of ethanol and its ability to form hydrogen bridges. Ethanol should be practically water free 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 alkenes) and content of other oxygenates

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0016-2361/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2009.02.003

(cosolvents) [12–17]. Due to existence of π-bonds in molecule, aromatics and alkenes would be easily miscible with water compared with saturated hydrocarbons.

Higher water solubility in ethanol–petrol blends may be very useful and desirable (e.g. prevention of fuel system freezing), however an ability to keep water in the soluble state is strongly affected by temperature. A decrease of the fuel temperature under specific level brings about separation of the 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 [8,6,18-20]. Extraction of ethanol into water layer represents usually an irreversible process. A backward dissolution of ethanol and water into hydrocarbons phase should occur theoretically under entirely exceptional conditions [20,21].

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 cosolvents contents, temperature). The technological discipline has to be respected and storage tank breathing should be minimised to decrease humidity access into storage tanks and distribution systems.

The purpose of this study is to characterize mainly the vapour pressure and the water phase stability of ethanol–petrol blends with ethanol in the amount up to 10 vol%. The influence of hydrocarbon composition of petrol and the influence of ETBE was studied over properties of ethanol–petrol blends.

2. Experimental

2.1. Materials

Analytical grade ethanol (absolute) and hexane were purchased from Merck Chemicals for blending to petrol. ETBE (ethyl terc.butyl ether) of a purity 98%, commercially available automotive petrol without oxygenates and petrol fractions (alkylate, isomerate, reformate, FCC petrol) were obtained from refinery Ceska rafinerska, a.s., Czech Republic. Petrol fractions were used to prepare petrols with different hydrocarbon composition.

2.2. Methods

Reid Vapour Pressure (RVP) was determined according to ASTM D6378, the repeatability for this method is 0.5 kPa. The phase separation was determined according to ASTM D6422 with the repeatability of 2 °C. Karl Fischer titration according to ASTM D6304 was used to determine the water content. Distillation curves were determined according to ASTM D86 with the semiautomatic equipment. Ethanol content in petrol was determined with Hewlett-Packard 6890 gas chromatograph (GC) equipped with an HP-PONA column and flame ionisation detector (FID), quantitative results were obtained with *n*-propanol internal standard. The repeatability of the ethanol content determination was determined to 0.5 wt% in our laboratory. Petrol composition (hydrocarbon groups) was determined with the same equipment.

Extractions were done in the 150 ml funnel with 100 ml of the fuel. The agitation was done with the automatic agitator for 30 min with 180 rpm. The ethanol content was determined in the hydrocarbon phase by GC–FID after intensive agitation and 15 min of emulsion breaking. The standard deviation was determined from ten measurements to 3.7 for the loss of the ethanol content in petrol in rel% after extraction.

3. Results and discussion

3.1. Volatility of automotive ethanol–petrol blends

3.1.1. Vapour pressure measurements

The RVPs of ethanol and ETBE were determined to 16.6 kPa and to 31.3 kPa. Blends of petrol with different hydrocarbon composition and 5 vol% of ethanol were prepared to study the influence of hydrocarbon composition on the azeotropic vapour pressure increase.

At first the blends with variable ratio of unsaturated hydrocarbons (alkenes + aromatics) to saturated hydrocarbons were prepared so that the isomerate fraction was added to the base petrol (composition: 15 vol% of alkenes, 36 vol% of aromatics) in the concentrations 10–70 vol% by 10 vol%. Isomerate is a saturated fraction with hydrocarbons with 5 and 6 carbon atoms (73% of isoalkanes and 27% of *n*-alkanes and cycloalkanes), the RVP was determined to 86.4 kPa. The ratio of alkenes to aromatics was kept constant. Mixtures with 5 vol% of ethanol were prepared from these hydrocarbon blends. The vapour pressure results are presented on the Fig. 1. The RVP growth after addition of ethanol is increased with the increase of the saturated hydrocarbons content. The lowest RVP growth of about 0.85 kPa was determined for the ratio of unsaturated to saturated hydrocarbons of 0.8 and the growth of about 5 kPa was measured for the highest content of saturated hydrocarbons (ratio 0.18). The RVP of the fully saturated isomerate fraction was increased by 8 kPa after addition of 5 vol% ethanol.

The second experiment was focused on variable content of *n*-alkanes and isoalkanes while keeping ratio of saturated to unsaturated hydrocarbons constant. Isomerate fraction (as isoalkanes) and *n*-hexane (as *n*-alkane) in various mutual ratios were added in the constant volume to the same base petrol used in the first experiment. Blends with 5 vol% of ethanol were prepared. The vapour pressure results are presented on the Fig. 2. It is clear from the Fig. 2 that the differences in the RVP between petrol–ethanol free and ethanol–petrol blends remained practically constant (6–8 kPa) independent on the content of isoalkanes or *n*-alkanes.

These two experiments showed that the larger increase in the vapour pressure of about 6–8 kPa can be expected from addition of 5 vol% of ethanol to automotive petrols with higher content of saturated hydrocarbons. The global tendency is to decrease the content of alkenes and aromatic hydrocarbons in automotive petrol which is 18 and 35 vol% according to EN 228. In the future, trend of an increasing utilization of alkylates and isomerates

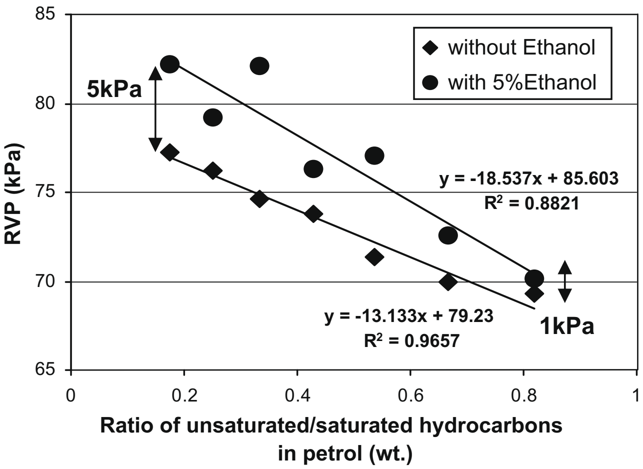

Fig. 1. The influence of petrol hydrocarbon composition on the rise in the RVP of blends with 5 vol% of ethanol.