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The Effect of Bioalcohol on the Water Solubility in Reformulated Gasoline

Mihaela Neagu (Petre)*, Paul Rosca, Raluca Elena Dragomir, Oana Mihai
Petroleum-Gas University of Ploiesti, Faculty of Petroleum Refining and Petrochemistry, Bucharest Bd. 39, Ploiesti, Romania
mpetre@upg-ploiesti.ro

The present work illustrates the influence of bioalcohols in terms of water tolerance in various reformulated gasoline. Several proportions and different type of bioalcohols (methanol, ethanol, isopropanol and tert-butanol) have been used. Two gasoline samples with different hydrocarbons content were analyzed for this study. The effect of temperature, the influence of content and type of alcohol on the water tolerance has been determined. The experimental study was carried out at different temperatures between 268 K and 303 K. Several key factors have been taken into account regarding water tolerance: the chemical structure and alcohol content, the temperature, the characteristics of base gasoline. The reformulated gasoline with higher alcohols lead to lower aqueous phase separation in the storage or distribution fuel system compared with ethanol in case of temperature changes due to summer/winter or day/night period.

1. Introduction

The concept of ”reformulated gasoline (RFG)” has been adopted by the US Clean Air Act in 1990. RFG refers to the partial substitution of conventional gasoline with oxygenates by means of biofuels. Some differences from the conventional gasoline have been considered. RFG have lower level of certain compounds that contribute to air pollution (Cannon and Azimi, 1995; Sedon, 1992).

In the past decades the crisis has been triggered by reductions in oil resources and increasing in air pollution. By using renewable feedstocks the biofuels combine sustainable development and protection of fossil resources that leads to reductions in greenhouse gas emissions. European Union is focused by the legislation on promotion of the energy utilization from renewable sources. The European Council of March 2007 has proposed that 20% target for the overall share of energy from renewable resources and a 10% target for energy from renewable sources in transport through 2020.

As promising fuel blending components, the primary alcohols have been the objective of many research studies (Agarwal, 2007; Niven, 2005; Neagu, 2009; He, 2003) due to their potential to improve some properties of fuels, including the reduction of gas emissions.

Recent studies (Mužíková, 2009; Rosca, 2009; Da Silva et al. 2005) has revealed that the addition of ethanol to the gasoline compositions led to increasing of vapor pressure

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of reformulated gasoline which depends on the hydrocarbons content, vapor pressure of base gasoline and ethanol content.

Few studies (Peng et al., 1996; Gramajo de Doz et al. 2004; French and Malone, 2005; Mužíková et al. 2008) point out other major difficulties of ethanol-gasoline blends, namely their tendency to phase-separate in the presence of small amounts of water. In organic phase, a large amount of ethanol exists. As consequence, a greater volume of soluble water appears in the same time. By passing of a certain part of ethanol in the aqueous phase, the oxygen content is changed and octane values decrease. In addition, the corrosion caused by the presence of ethanol in the aqueous phase and the environmental contamination potential are another negative effects.

The water tolerance in blends is defined as the amount of water (volume percent) that a blend can retain in a solution (tolerate) at a given temperature without phase separation. In addition, this value depends on the temperature, type and volume of added alcohols and on the aromatic content.

2. Experimental

In this paper an experimental study concerning the water tolerance effect on different gasoline types is presented. Two base gasoline types without additives, designated as gasoline A and B obtained by mixing of C_8-based components have been prepared. The catalytic cracking gasoline, the catalytic reforming gasoline and an isomerization fraction have been used for experiments, as follows: 1) gasoline A: 40 vol% catalytic cracking gasoline, 40 vol% catalytic reforming gasoline and 20 vol% isomerization fraction; 2) gasoline B: 45 vol% catalytic cracking gasoline, 30 vol% catalytic reforming gasoline and 25 vol% isomerization fraction.

The composition of hydrocarbon fuels has been analyzed by Irox 2000 Fuel Analyzer Portable Gasoline Analysis with MID-FTIR from Grabner Instruments. The characteristics of gasoline A and B are given in Table 1. The water content in both base gasoline is different and is directly influenced by the aromatics.

Table 1. Main characteristics of Gasoline A and B.

Property	Gasoline A	Gasoline B
Aromatics, vol %	40.3	36.3
Olefins, vol%	8.6	3.2
Saturates, vol%	51.1	60.5
Water content, ppm	127.91	89.53

The following reagent grade oxygenates purchased from the Carl Roth Company have been used in the blends: methanol, ethanol, isopropanol and tert-butanol. The alcohols have been used without additional purification.

The blends have been successively prepared by mixing the base gasoline A and B with 2, 5, 8, respectively 10 vol% of each alcohol. Stored in the insulated recipients and controlled atmosphere, certain volume of distilled water has added into the samples. After vigorous mixing, each sample was kept in Thermo Scientific Neslab refrigerated circulating bath at different temperatures (268, 273, 283, 293, 303 K). By keeping at constant temperature for 30 minutes, the thermodynamic equilibrium between two

phases is reached and the phase separation occurs: upper organic phase and down aqueous phase.
The retained water volumes in base gasoline and reformulated gasoline have been determined by Cou-Lou Karl Aquamax apparatus through the volumetric Karl Fischer volumetric titration analysis method. A small amount of aqueous solution is taken with a scaled syringe from organic phase with the retained water content.

3. Results and Discussions

The analysis of resulting data in terms of the effect of temperature, the influence of content and type of alcohol on the retained water amount in organic phase have been revealed. Figure 1 (a, b, c) indicates the comparative study regarding the water tolerance over gasoline A with 2, 5, 8, 10 vol% of various oxygenates (methanol, isopropanol, tert-butanol) and gasoline A with same percent volume of ethanol at different temperatures.

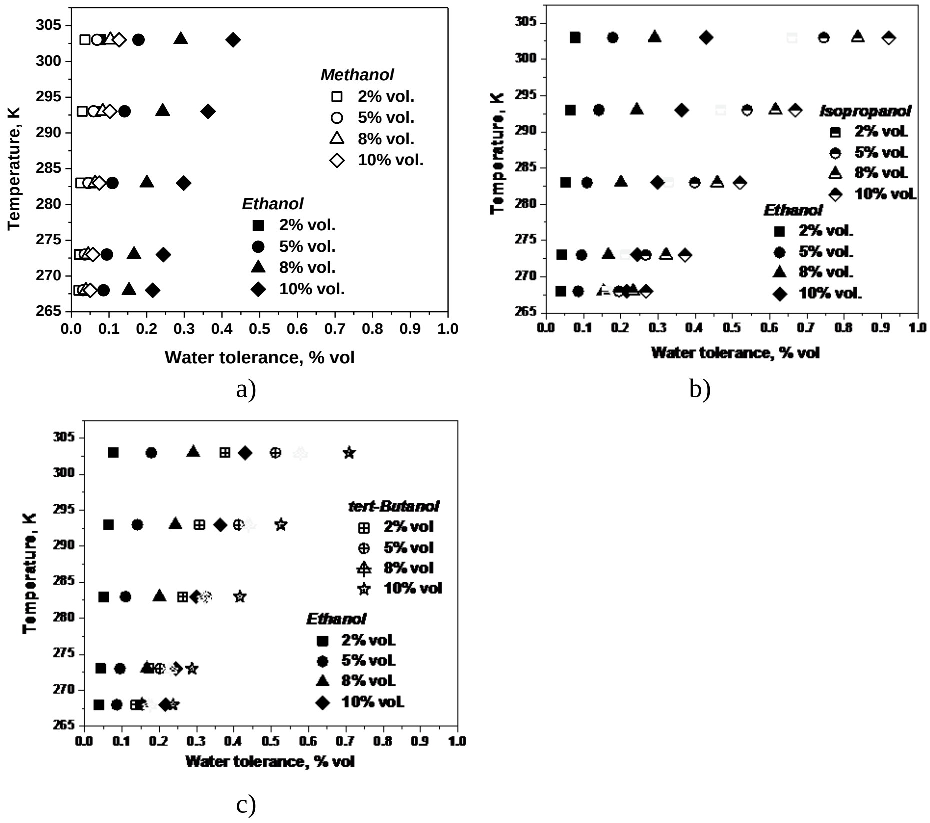

Figure 1: Water tolerance (vol%) as a function of temperature over gasoline A blended with methanol (a), isopropanol (b) and tert-butanol (c) compared with ethanol.

As shown below, by increasing the proportion of alcohols in reformulated gasoline, the water solubility in the organic phase of gasoline A-alcohols blends increases. Due to their hydrophilic behavior, the alcohols have tendency to pass in aqueous phase and enough amount of alcohol remains also in organic phase. As a consequence, the water content in the organic phase is directly proportional to its alcohol content and equilibrium temperature.

At 303 K, the solubility of water with 10 vol% ethanol is roughly 2.4 times higher than with gasoline with 5 vol% ethanol. High solubility of water in gasoline-A-alcohol blends also could be explained by the polar characteristics of the ethanol component, its ability to form hydrogen bridges and maybe the hydrocarbon content of the base gasoline. Our results are in good agreement with other studies (Mužíková et al. 2008).

A decrease of temperature indicates the lower water solubility in the organic phase for all types and alcohol contents (Figure 1). For example, a change of temperature day/night with 293 K deviation can cause the phase separation effect by means that water solubility decreases of 69.5 vol% for gasoline with 10% ethanol followed by a decreasing of 58.68 vol% for gasoline A with 10 vol% tert-butanol and 56.5 vol% for gasoline A with 10 vol% isopropanol (see Figure 2a).

One consequence of the temperature decrease is the presence of a ”new” aqueous phase or increasing of volume of existing phase which can affects the distribution and fuel storage system. As previously mentioned, based on water solubility in reformulated gasoline with different alcohols, a certain amount of alcohol appears in aqueous phase, but also a greater amount remains in organic phase.

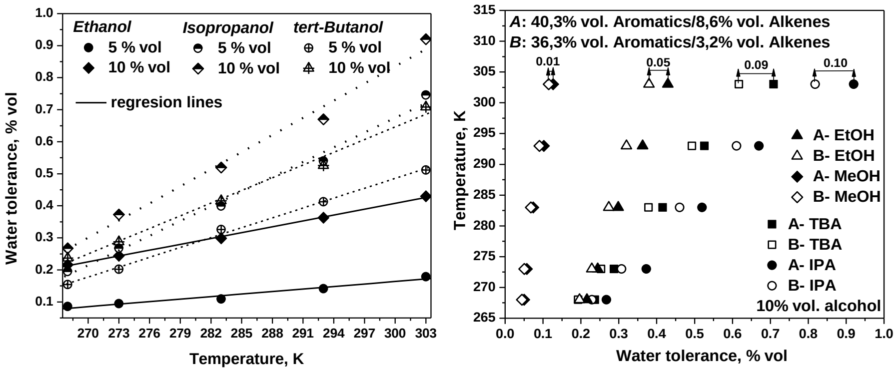

Figure 2: Water tolerance (vol%) as function of temperature-comparison between various proportions of ethanol, isopropanol and tert-butanol (a), The effect of unsaturated hydrocarbons over the water tolerance in reformulated gasoline A and B (b).

Following Figure 2a and based on the chemical structure of the alcohols, at same temperature and same alcohol content in the reformulated gasoline, the solubility in water decreases by increasing of number of carbon atoms, therefore isopropanol tends to remain in the organic phase compared with ethanol and methanol due to its branched chain structure. As tertiary alcohol, the presence of tert-butanol in the organic phase suggests a special behavior also due to its structure with high number of carbon atoms. This chemical aspect determines the increase of its solubility in water. A reformulated gasoline with 10 vol% tert-butanol will retain 1.65 times more water amount at 303 K than reformulated gasoline with 10 vol% ethanol but less than reformulated gasoline with 10 vol% isopropanol.

Aromatics and alkenes are miscible with water molecules through **π** bonds compared to saturated hydrocarbons. It is obvious that gasoline A by its content of unsaturated hydrocarbons keeps more water than gasoline B. Based on Figure 2b, by substitution of each starting gasoline with 2, 5, 8, 10 vol% methanol, ethanol, isopropanol, tert-butanol, different results regarding the proportions of water in organic phase have been obtained (see in plot the difference between these two gasoline with 10% vol methanol or ethanol, compared with isopropanol or tert-butanol).

4. Conclusion Remarks

The water content in both analysed gasoline types is influenced by the aromatic compounds. Regarding the chemical nature of primary alcohols, from the experimental results, it can be concluded that water content in the organic phase is directly proportional to its alcohol content and equilibrium temperature.

Overall, the experimental data and their analysis indicate that the reformulated gasoline with higher alcohols leads to lower aqueous phase separation in storage or distribution system than ethanol in case of temperature change due to the summer/winter or day-night period. These advantages can be coupled with another, namely: isopropanol or tert-butanol can substitute larger amounts of base gasoline than ethanol, without exceeding the maximum oxygen amount of 2.7 wt% according to the EN 228. However, isopropanol and tert-butanol also have a disadvantage. In the near future their production from renewable raw materials is difficult to achieve on industrial scale. Thus, high production cost could be expected relative to using ethanol. The accessibility of bioethanol at lower production cost and the positive impact on the octane number of reformulated gasoline are the major benefits compared with the water tolerance. In order to balance this inconvenience regarding its behavior in terms of water tolerance, higher alcohols such as isopropanol or tert-butanol could be used as co-solvents in equal proportions with ethanol. This aspect still remains as an objective for further research.

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