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Physical properties of gasoline, isobutanol and ETBE binary blends in comparison with gasoline ethanol blends

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HIGHLIGHTS

- We measured density, RVP and distillation curves for iBtOH/ETBE–gasoline blends.
- We calculated the most relevant blends' parameters for EN 228 and ASTM D4814.
- The blends with ETBE or iBtOH have advantages over EtOH in terms of fuel properties.
- The addition of ETBE affects fuel-standards compliance less than iBtOH and EtOH.

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ABSTRACT

The addition of renewable fuels to gasoline, such as bio-alcohols or bio-ethers is required in order to be in compliance with current environmental directives. Nevertheless, they change fuel properties which could affect standards compliance, engine performance and air emissions. This paper studies the impact of ethanol (EtOH), isobutanol (iBtOH) or ethyl tert-butyl ether (ETBE) on the Reid Vapour Pressure (RVP), distillation curves, density and other related gasoline properties, which belong to the group of relevant specifications that affect engine operation. The main conclusion is that the addition of ETBE or iBtOH has important advantages over EtOH in terms of energy density, air/fuel ratio, vapour pressure, renewable content and other effects; it was also found that the addition of ETBE affects equally and linearly the properties of two kinds of base gasolines as compared with other studies.

1. Introduction

The transport sector in the E.U. accounts for 31.5% of the total energy consumption, of which almost 95% is based on fossil fuels [1–3]. The transport sector experienced an increase in the share of energy demand from 26% in 1990 to 32% in 2013 [3]. The case of the U.S. is similar with 27.6% of the total energy consumption, of which approximately 95% is based on fossil fuels [4].

The key feature to be noted is that almost 95% of total fuel usage in this sector was supplied by crude oil-based products, which has severe implications for the security of supply and greenhouse gas emissions. Biofuels or liquid fuels for transport produced from biomass are attracting considerable attention as a strategy to tackle both problems by substituting or blending petrol and diesel with biofuels [5]. In this way, the E.U., through the Directive 2009/28/EC, established a goal of at least 10% renewable energy content in fuels for transport before 2020. At the same time, some fuel regulations to permit the addition of renewable components are being developed (Directive 2009/30/EC). The typical renewable fuel alternatives for gasoline are ethanol (100% renewable) and ethyl tert-butyl ether (47% renewable, as stated in the Directive 2003/30/EC). Nevertheless, ethanol is not a problem-free fuel because, when used as a blending component in gasoline, it increases evaporative emissions, may cause corrosion and can lead to problems with phase separation in cold conditions. Also, when used at high concentrations, ethanol creates additional problems with corrosion, aldehyde emissions and startability. Ethers give better end-use properties than ethanol [6]. Therefore, the transformation of EtOH to ETBE is highly recommendable to protect engine integrity, improve performance and reduce gaseous emissions. Other alcohols such as isobutanol have many advantages compared with ethanol [7–12]: it is not as flammable as ethanol due to its higher flash point, for which reason it can be stored more safely; it has a stoichiometric air/fuel ratio that is closer to that

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of gasoline, allowing for the use of high blends when no fuel system modification has been carried out; its solubility in water is very low, reducing drastically the phase separation problem; it is much less corrosive than ethanol due to its bigger molecular size and lower polarity, allowing for blending with gasoline in the refinery and transport by oil pipeline; the azeotropic increase in RVP for low-alcohol blends of isobutanol is lower than that of ethanol, avoiding the problem of surpassing some regulation limits; etc.

The reasons why butanol was not selected instead of ethanol as a gasoline alternative in the 1970s were: lower fermentation process yields; much lower final concentration and a boiling point higher than that of water, meaning there is a lot of water to boil off, which is expensive [7]. However, the increasing interest in the use of biobutanol as a gasoline surrogate has prompted a number of companies to explore novel alternatives to traditional acetone butanol ethanol (ABE) fermentation, which would enable biobutanol to be produced on an industrial scale. The new genetically-manipulated strains of butanol-hyperproducing Clostridium bacteria, e.g. *Clostridium beijerinckii BA101* or *Clostridium saccharoperbutylacetonicum*, which have the potential for producing butanol from different substrates with elevated yields and productivities; the new integrated processes of fermentation-recovery and the in situ removal of ABE, e.g. by gas stripping or by membrane reactor, are some recent biobutanol production developments that can convert biobutanol into a competitive biofuel [8,13–15]. Costs of 0.44–0.55 $/L are feasible by applying recent developments [13,14]. Additionally, conventional ethanol plants can be retrofitted to butanol plants with small investments [6,7,9].

For all the above reasons, isobutanol and ETBE are interesting biofuels. Nevertheless, the use of these biofuels changes some important fuel properties (RVP, distillation curve, oxygen content, etc.), and therefore the gaseous emissions, the mechanical performance or the reliability of the engine [16].

Many researchers have looked into the change in these and other properties of isobutanol/ETBE and gasoline blends. Andersen [17,18] has reported distillation curves and RVP for gasoline binary blends with isobutanol and other alcohols. Petre [19] has offered experimental results concerning the effect of the blend of two gasolines with different composition and ETBE or other ethers on the RVP, distillation curves and vapour lock index (VLI). Pumphrey [20] has presented a method to predict vapour pressures of gasoline–alcohol mixtures and validate them with blends of gasoline and different oxygenates. Li [21] has measured and tested phase separation, density, low heating value, 10% evaporated temperature, kinematic viscosity, stoichiometric air/fuel ratio, octane number, copper corrosiveness and oxygen content of isobutanol–gasoline binary blends. Other researchers have studied the influence of the addition of isobutanol to gasoline on engine cold start, combustion, driveability, gaseous emissions, torque, power or fuel economy [22–26].

Thus, the current and growing interest in this matter led the authors to publish experimental data of the distillation curves, the RVP and the density of binary and ternary blends of a 'summer gasoline' with ethanol and ETBE [16,27]. Following this line, this paper claims to offer new empirical evidences, focusing on the same properties but in the case of a winter gasoline blended with isobutanol or ETBE. Together with the relevant properties (density, RVP and distillation curve), other important parameters for the technical performance of the fuels like energy density, air/fuel ratio, renewable energy content or antiknock behaviour are also considered in this study. Moreover, comparing the data of the present work with those of previous papers [16,27] the authors will be able to discuss first, if the kind of gasoline affects the impact of ETBE over the blend properties and, second, if ethanol is more or less advisable as gasoline substitute.

The measured properties, as well as the chemical compositions of the base gasoline, allow the authors to determine most of the parameters which are in the Directive 2009/30/EC and check their compliance with mandatory specifications. This information, which is not very common in the literature, is interesting as it could help researchers to foresee the engine performance when these blends are used and compare the advantages or disadvantages of all the biofuels (especially isobutanol and ETBE).

2. Materials and methods

To carry out this research, some fuels and experimental facilities that meet European standards were used.

2.1. Materials

The gasoline used as base fuel to prepare the blends was a 95-octane gasoline purchased in winter at a REPSOL fuel station in Spain. Table 1 shows how this gasoline complies with the EN 228 standard. The isobutanol was provided by Productos Químicos Manuel Riesgo S.A. It had a purity grade of 99.8%. The ETBE was provided by the REPSOL research centre in Móstoles (Madrid, Spain).

The abbreviated blend names were built with some letters (iB or ET) and a number (0–100). The letters "iB" precedes the volume percentage of added iBtOH (iBtOH) and the letter "ET" precedes the volume percentage of added ETBE (ETBE∗). For example: "iB20" means 20% of iBtOH and 80% of base gasoline; "ET20" means 20% of ETBE∗ and 80% of base gasoline. The tested blends were: iB0 to iB100 and ET0 to ET30 for RVP and distillation curves; and iB0 to iB100 and ET0 to ET100 for densities. In this study, the base gasoline had 0.00% of iBtOH, 9.76% of ETBE and 1.46% of EtOH. This composition of the base gasoline allows the influence of iBtOH from 0% to 100% to be appreciated in all tests. The influence of the addition of ETBE may be determined from the ETBE content of base gasoline (9.76% v/v) to 100% v/v, but this was not a major problem because the ETBE–gasoline blends showed a linear performance and, therefore, no conclusion will differ from that obtained with a free-ETBE base gasoline. Finally, the influence of EtOH was not studied in this work. The effect of the little EtOH content on the base gasoline lightly affects the results but does not change the conclusions of the study.

2.2. Methods: Experimental facilities and test management

The experimental facilities and test management necessary to develop the work were described in the aforementioned paper [16].

3. Results and discussion

In this section the main results obtained from the tests (RVP, distillation curves, density and composition) are shown and discussed.

3.1. Density, energy density, stoichiometric (λ_S) and relative (λ_R) air/fuel ratio and air–fuel mixture heating value

To evaluate if excess volume is relevant when gasoline and isobutanol or ETBE are mixed, the density of the binary mixtures iB0 to iB100 and ET0 to ET100 were measured. The difference between the experimental density and the ideal density was slightly different but always less than 0.34%. Thus, it could be assumed that the density of a mixture is the weighted mean by volumetric composition of the components' densities.