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The influence of ester additives on the properties of gasoline

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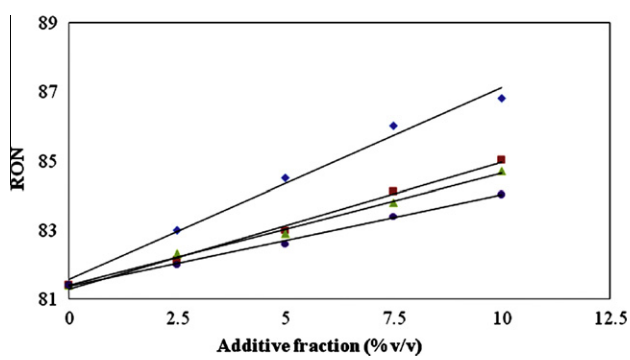
HIGHLIGHTS

- ▶ Performance of two new oxygenated additives.
- ▶ The measured RON and RVP values were compared with those of ethanol and MTBE additives.
- ▶ Drivability index was reduced for both additives.
- ▶ The RON of gasoline was increased with the addition of the oxygenated compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of two new oxygenated additives, ethyl acetate and methyl acetate was evaluated on the Reid Vapor Pressure (RVP), distillation curves, Drivability Index (DI), density and Research Octane Number (RON) of two types of gasoline with different chemical compositions and well defined characteristics (density, volatility and octane number). The measured RON and RVP values were compared with those of ethanol and MTBE additives. Gasoline was blended with four different percentages (v/v) of the additives, i.e. 2.5%, 5%, 7.5% and 10% ethyl acetate or methyl acetate. The RON of gasoline was increased and RVP remain unchanged with the addition of the oxygenated compound. Drivability index was reduced for both additives.

1. Introduction

Gasoline is one of the most important and profitable fraction of petroleum refining industry. It consists of numerous compounds that can be broadly classified into the hydrocarbon groups of paraffins, aromatics, and olefins [1,2]. These hydrocarbons have different physical and chemical characteristics that effect combustion processes and emissions in the internal combustion engines [3].

Gasoline contains over 500 hydrocarbons that may have between 3 and 12 carbons, and most gasoline have boiling range from 30 to 220 °C at atmospheric pressure. The boiling range is narrowed as the initial boiling point is increased, and the final boiling point is decreased (for environmental reasons) [4]. In general; their composition varies from refinery to refinery. There is no single criterion that can characterize gasoline purity and quality [5]. The properties of gasoline depend on the origin of the crude oil, the refinement processes and the presence of additives in gasoline [6,7]. The most important problems in oil refining are to improve the performance and environmental characteristics of the gasoline [8]. Compared with other fuels, gasoline has average well-to-wheel

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energy consumption in light-duty vehicles (LDVs). Gasoline cars have relatively low well-to-wheel NOx emissions and relatively high CO emissions [9].

Automobiles powered by gasoline are a major source of air pollution because it contains leadalkyls, which are normally added to gasoline in order to increase its octane number and, thus, increase the performance of the engine. The intense search for an effective and economical octane boosting alternative to lead has continued. Oxygenates have emerged as alternative for improving the octane number and the oxygen content in gasoline [10].

The combustion of tetra ethyl lead with oxygenate as a fuel additive almost goes back to the 1990s. The addition of oxygenates to gasoline became widespread after the elimination of the tetraethyl lead compounds [6,11].

The removal of alkyl–lead compounds has been gaining momentum due to environmental and public health reasons, oxygenated compounds has been increasingly important components in the formulation of automotive gasolines to enhance octane ratings [11,12], good replacement of toxic tetraethyl lead and as reducers of CO [13].

Gasoline is a complex mixture containing various hydrophobic moeity needed to improve physical and chemical properties and performance. The quality of gasoline depends upon hydrophilic additives, such as various alcohols and tertalkyl methyl ethers which are used often in small quantities. Oxygenates cannot provide energy, but their structure provides a reasonable antiknock value, thus they are good substitutes for aromatics, they may also reduce the smog-forming tendencies of the exhaust gases including carbon monoxide [14].

In 1995, the hydrocarbon fraction was significantly modified. These gasolines are called "reformulated gasolines" (RFGs), and there are differing specifications for different countries; however all require oxygenates to provide octane. Generally, most regulations only reduce vapor pressure and benzene directly, however reduction of aromatics are required to meet emissions criteria [15]. The commonly used oxygenates in recent gasolines include aliphatic alcohols and methyl ethers containing one to six carbons. Typical examples are methanol, ethanol, methyl tert-butyl ether (MTBE) and tert-amyl methyl ether (TAME) while propanols and butanols are primarily added as co-solvents. [16,17]. The oxygenate added to a gasoline are only effective if the hydrocarbon fractions are carefully modified to utilize the octane and volatility property of the oxygenate. If the hydrocarbon fraction is not correctly modified, oxygenate increases the undesirable toxic emissions. In this context, the most important properties of the oxygenate is the octane blending values and the vapor pressure [16].

Dorn et al. [18] investigated the relationship between the physical and chemical properties and performance of gasoline. The emphasis was placed on the effects of oxygenates when used as gasoline blending components. Incremental octane gain, emissions, and water tolerance were investigated for oxygenates blends [10].

Recently, Magnusson and Nilsso reported substantial increase (up to 44-fold) in total carbonyl emission (11, 11, 8.9 and 7.8 g/kW h, respectively) than use of both aliphatic and regular gasoline (2.1 and 2.6 g/kW h, respectively) by the addition of ETBE, ethanol, methanol (The major drawback of ethanol and methanol as fuel additive is the hygroscopic nature) and MTBE to the fuel. Significant amounts of formaldehyde and acetaldehyde were produced from the oxygenated fuels methanol or MTBE and ethanol or ETBE, respectively; while acetone and methacrolein were formed from both MTBE and ETBE [19]. Chen and co-workers reported addition of methyl ester to ethanol–diesel fuel to prevent separation of ethanol from diesel [20]. Stickney reported a blend of gasoline mixed with numerous alcohols and various substituted esters [21]. Very recently, Ray reported (US patent) the use of ethyl acetate as fuel, fuel additive and reducer of cloud point of biodiesel [22].

The goal of this study was to examine for the first time the effect of two new oxygenate additives (methyl acetate and ethyl acetate) on the quality of gasolines manufactured by the Isfahan refinery. The main advantages of these two additives as octane booster are to increase the octane content without increasing the Reid Vapor Pressure (RVP). These ester additives have several other advantages over ethanol and ethers. First, they are not toxic. Second, they have pleasant odor. Third, they do not produce aldehydes, ketons, and carbon monoxide (due to high oxidation state). Fourth, the low cost of production in compare to ETBE and MTBE. Fifth, lower volatility and the ease of handling.

2. Experimental

2.1. Composition of the base gasolines (Gas 1 and Gas 2)

The two base gasoline compositions (here in, referred to as Gas 1 and Gas 2) were used to evaluate the effect of the gasoline formulations containing oxygenates (ethyl acetate, methyl acetate, ethanol and MTBE). These gasolines with different octane rating and RVP values were obtained from the Isfahan Oil Refinery located in the Isfahan, Iran. Gas 1 contains a large proportion of isoparaffins and n-Paraffins with a broad range of distillation from 43 to 164 °C, low octane rating and low RVP. The average compositions are shown in Table 1. Gas 2 is composed basically of isoparaffins and aromatics, with a range of distillation 41–178 °C, high octane rating and high RVP (Table 2). The main physicochemical characteristics of the base gasolines, Gas 1 and Gas 2, are summarized in Table 3, Figs. 1 and 2.

2.2. Materials

The pure ethyl acetate (Merck, 99.9%), methyl acetate (Merck, 99%), ethanol (Merck, 99.8%) and MTBE (Aldrich, 99.8%) were purchased from Merck and Aldrich Chemical Companies. The pure components were stored in glass containers protected from sunlight and at constant humidity and temperature. Fuel (additives)

Table 1
Average composition of Gas 1 by group type and number of carbons.

	n-Paraffins	Iso-paraffins	Aromatics	Naphthenes	Olefins
C4	–	–	–	–	–
C5	11.3	10.4	–	2.65	–
C6	8.0	12.1	1.8	1.45	1.77
C7	3.7	7.47	7.1	2.1	1.0
C8	3.3	8.0	8.5	1.1	0.5
C9	–	0.73	4.4	–	–
C10	–	–	2.1	–	0.04
C11	–	–	0.1	–	–
Total	26.3	38.7	24	7.3	3.31

Table 2
Average composition of Gas 2 by group type and number of carbons.

	n-Paraffins	Iso-paraffins	Aromatics	Naphthenes	Olefins
C4	–	1.97	–	–	0.02
C5	–	15.26	–	0.59	–
C6	–	16.37	2.81	3.26	0.05
C7	0.37	10.66	12.52	2.60	0.05
C8	0.19	5.61	13.76	0.69	0.02
C9	–	2.58	5.27	1.16	0.13
C10	–	0.01	2.95	0.64	0.04
C11	–	–	–	–	0.01
Total	0.56	52.46	37.30	8.94	0.32