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RESEARCH ARTICLE

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## Study of water tolerance in hydrous ethanol-gasoline blends

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**Abstract:** Water tolerance of ethanol-gasoline blends of various proportions is investigated using co-solvents such as TBA (tert-butyl alcohol), cyclohexane, heptane, acetone, iso-octane, and toluene at 300 K. Miscibility was studied using a simple experimental method for various proportions of water-ethanol-gasoline blends with and without co-solvents. Results of water tolerance for each co-solvent are presented in this paper for stable mixture at room temperature.

**Keywords:** Blended fuel, Co-solvents, Ethanol, Ethanol-gasoline, Hydrous ethanol, Oxygenates, Phase-separation, Water-tolerance, and Wet ethanol.

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**1. Introduction:** In 1925, Ford told the New York Times reporter that ethyl alcohol was “*the fuel of the future*” [1]. Today, Ethanol is an octane booster and a potent oxygenate. Also, it has been in use for over 30 years in Brazil as a fuel. Use of ethanol results in reduction of greenhouse gas emissions, reduction in carbon monoxide, reduction of oxides of nitrogen and un-burnt hydrocarbon emissions, increase in combustion efficiency, reduction in fuel cost and provides rural employment [2]. Ethanol has replaced other oxygenates such as MTBE (methyl-tertiary-butyl-ether) in many regions of the world. Other octane boosting components are not environmentally friendly such as lead, an additive which is a toxic air pollutant and poisons catalytic converter catalyst, benzene is carcinogenic, aromatics and olefins which cause smog and MTBE is a potential ground water pollutant.

The use of ethanol and ethanol-gasoline blended fuel reduces dependence on imported oil and helps mitigate increasing oil prices. Use of higher percentage of ethanol in gasoline blended fuel depends on price of anhydrous ethanol. Large scale productions of ethanol from bio-refineries are from the following biomass sources: corn, sugarcane and lingo-cellulosic biomass. Bio-conversion of starches to sugars with enzymes, fermentation of sugars with yeast yields a mixture of ethanol and water, followed by distillation and dehydration of ethanol [3]. Dehydration of ethanol amounts to 14% of the net energy [4]. Therefore, use of hydrous ethanol drastically reduces the ethanol cost in hydrous ethanol-gasoline blended fuel.

The use of hydrous ethanol-gasoline blended fuel has the following challenges:

- **Phase separation:** Forms two layers upon addition of very small amounts of water. Resulting in loss of ethanol to aqueous phase and reduction in octane number of the blended fuel. Phase separation is a serious technical problem associated with ethanol-gasoline blends [5].
- **Volatility properties:** Addition of ethanol to hydrocarbon significantly affects the volatility properties. Commingling of ethanol fuel can potentially lead to off-spec gasoline [5].

- **Materials compatibility:** Plastics, elastomers and non-metals are not recommended for use with ethanol-gasoline blends due to problem of swelling [5].
- **Corrosion:** Corrosion in hydrous ethanol is of three types: General, Dry and Wet corrosion. General corrosion is due to ionic impurities, dry corrosion is due to properties of ethanol, and wet corrosion is caused by azeotropic formation of ethanol and water, which oxidizes most metals [2].
- **Performance of the engine:** Water-Ethanol phase may damage the engine due to lack of lubrication.

Hydrous ethanol is a cheap alternative to anhydrous ethanol, but blending with gasoline can cause the technical problem of phase separation, resulting in separation of heavier aqueous phase at the bottom and an upper gasoline rich phase at the top. Ethanol mixes uniformly with gasoline, but upon addition of small amount of water the ethanol-gasoline blend will absorb water due to hydrogen bonding of water-ethanol molecules [5, 6]. When the amount of water added exceeds the solubility limit it separates into ethanol-rich aqueous phase.

Water tolerance in blends is defined as the volume percentage of water that a blend can retain in solution, i.e. “tolerate” at a given temperature without phase separation [7]. Water tolerance can be improved by adding co-solvents such as: TBA (tert-butyl alcohol), cyclohexane, heptane, acetone, iso-octane, and toluene in hydrous-ethanol gasoline blends.

The addition of co-solvents can improve the water tolerance; a hydrous ethanol containing 5 vol% of water can be used without the problem of phase separation at room temperature, i.e. 25°C – 30°C. For higher water content of 6- 10 vol% in ethanol i.e. wet ethanol, a biomass adsorption process needs to be designed for dehydration of ethanol [3].

The aim of present study is to determine what proportion of water-ethanol-gasoline mixture with co-solvents will yield a stable mixture at room temperature.

## 2. Experimental:

Miscibility studies: The miscibility characteristic of hydrous ethanol was studied in two parts:

1. Water-Ethanol-Gasoline miscibility characteristic without co-solvents
2. Water-Ethanol-Gasoline miscibility characteristic with co-solvents

Part 1 of the experiment was studied for various proportions of water (1-5% vol) and anhydrous ethanol (5-25% vol) in gasoline in trial 1-5 for temperatures: 4°C, 30°C, 35°C, 40°C, and 45°C. And trial 10-40 is the study of wet ethanol of various proportions of water (10-40% vol) and anhydrous ethanol (5-25% vol) in gasoline for temperatures: 4°C, 30°C, 35°C, 40°C, and 45°C.

Experimental set-up for Part 1 consists of prepared blended fuel in a glass beaker covered with aluminum foil and stirred in a Magnetic stirrer with hot plate as shown in Figure 1. Temperatures were set using switch in the Magnetic stirrer and were measured for the various trials using laboratory thermometer. The sample was collected in a 50 ml graduated centrifugal tube and kept in the refrigerator for observing phase separation at low temperature (4°C). Measurement of aqueous phase was observed at regular intervals for various trials in 50 ml graduated centrifugal tube as shown in Figure 2.



Figure 1: Blended Fuel in the Magnetic Stirrer with hot plate for Part 1 experiment, a 10 ml glass cylinder was used for Part 2 experiment.



Figure 2: Measurement of aqueous phase in 50 ml graduated centrifuge tube

Part 2 of the experiment was studied for various proportions of water (1-5 %vol) and anhydrous ethanol (10-50 %vol) in gasoline with co-solvents (1-25 %vol) that is, Toluene, Cyclohexane, Heptane, Iso-Octane, Acetone and TBA (t-butyl alcohol) at room temperature (300 K). One set of trial per co-solvent was conducted for 1 %vol water, 10 %vol anhydrous ethanol, and 1-25 %vol co-solvent in gasoline at room temperature (300K), and another set of trials was conducted keeping 10 %vol co-solvent fixed for various proportions of water (1-5% vol) and anhydrous ethanol (10-50 %vol) in gasoline.

Experimental set-up for Part 2 is simple and rudimentary in approach, (see Figure 1). First, the blend is prepared in a 10 ml graduated cylinder by first adding gasoline of given proportion and then adding co-solvents (1-25 %vol), anhydrous ethanol (10 %vol) and water (1 %vol) in gasoline at room temperature (300 K). The second set of blend is prepared keeping the co-solvents proportion constant i.e. (10 %vol) and by adding various proportion of water (1-5 %vol) and anhydrous ethanol (10-50 %vol) in gasoline at room temperature (300 K). Any phase separation observed is noted with measurement of aqueous phase in the 10 ml glass cylinder.

Properties of blended fuels and co-solvents: Anhydrous ethanol used in the experiment is absolute ethanol (200 proof), Gasoline used is commercial gasoline purchased from Bharat Petroleum of specification MS 91/MS 95 as per IS 2796-2008 for motor gasoline and water used in the experiment is distilled/deionized water.

#### Co-solvents:

Toluene sulphur free,  $C_7H_8$ : Grade LS for synthesis (organic and inorganic)

Cyclohexane,  $C_6H_{12}$ : Grade LR for synthesis (organic and inorganic)

Heptane (Fraction from petroleum) 95%: Grade LR for synthesis (organic and inorganic)

Iso-Octane (2, 2, 4-Trimethylpentane,  $C_8H_{18}$ ): Grade LR for synthesis (organic and inorganic)

Acetone, C<sub>3</sub>H<sub>6</sub>O: Grade LR for synthesis (organic and inorganic)

TBA (tert-Butyl Alcohol, C<sub>4</sub>H<sub>10</sub>O): Extra-pure AR

The aim of blending co-solvents in ethanol-gasoline fuel is [8]:

- To improve solubility of water in ethanol-gasoline blend
- To help lower the phase separation temperature
- To reduce the transfer of ethanol to aqueous phase

Blending sample measurement: An adjustable volume pipettors (100 µl - 1000 µl) with disposable plastic tips were used to blend samples of different samples based on following nomenclature: for example, 1EW10CH1 represents 1 %vol of water, 10 %vol of ethanol and 1 %vol of cyclo-hexane (co-solvent) in gasoline. Similarly, 5EW10 represents 5 %vol of water and 10 %vol of anhydrous ethanol in gasoline.

Experimental errors: Observations of phase separation were measured visually using the graduated glass cylinder or centrifugal tube. There was loss of gasoline/ethanol vapour at temperatures above 30°C, which is not accounted in the measurement. There was negligible change in phase separation at lower temperatures, while observed in the refrigerator at 4°C. There could be errors in measurement based on wait time for phase separation.

### 3. Results:

The results of Part 1 of the experiment i.e. without co-solvents showed that by adding water of 1%vol to 5%vol in various proportions of anhydrous ethanol (5-25%vol) and gasoline blends show phase separation for temperatures: 4°C, 30°C, 35°C, 40°C, and 45°C. For higher concentration of water (10-40%vol) high ethanol-rich aqueous phase was found in most samples resulting in ethanol-deficient gasoline layer at the top of the sample as seen in figure 2. From the above experiments it clearly shows that an ethanol-gasoline blend undergoing phase separation when small amount of water is added to the blend has preferential partition for ethanol resulting in ethanol-rich aqueous phase at the bottom and ethanol-gasoline phase at the top. The ethanol-rich aqueous phase observed during the experiments had larger share of the volume which may be due to aromatic hydrocarbons in commercial gasoline that are soluble in ethanol when adding water of higher concentration.

The results of Part 2 of the experiment with co-solvents showed that by adding water of 1 %vol in 10 %vol anhydrous ethanol for various proportions of co-solvents (1-25 %) in gasoline resulted in phase separation for the following co-solvents at 300 K: Toluene, Cyclohexane, Heptane, Iso-Octane and Acetone. However, co-solvents TBA (tert-Butyl Alcohol) showed promising water tolerance for the following samples: 1EW10TBA20 (i.e. 10 %vol ethanol and 20 %vol TBA in gasoline) and 1EW10TBA25 ((i.e. 10 %vol ethanol and 25 %vol TBA in gasoline) showed 1%vol water tolerance as shown in Table 6.

Table 1-6 below shows water tolerance of different co-solvents used of 10 %vol in various proportion of anhydrous ethanol (10-50 %vol) in gasoline at 300 K. The results showed that water tolerance of 1-5 %vol were achieved at higher concentration of anhydrous ethanol in gasoline blend i.e. 50 %vol of anhydrous ethanol for the following co-solvents as shown in the Table 1-4 for Toluene, Cyclohexane, Heptane and Iso-Octane. The water tolerances of 1-5 %vol were achieved at 30-40 %vol of anhydrous ethanol for Acetone and TBA. The water tolerance of 1%vol was only achieved for 10 %vol anhydrous ethanol with higher concentration of TBA, i.e. 20-25 %vol TBA in ethanol-gasoline blends as shown in Table 6. The number of replications done for each stable sample was three. The results presented below (Table 1-6) are for the samples which showed stable mixture without phase separation at room temperature (300K).

Table 1: Experimental results of Toluene at 300 K.

Sample	Toluene vol%	Ethanol vol%	Water tolerance vol%
1EW40T10	10	40	1
5EW50T10	10	50	5

Table 2: Experimental results of Cyclohexane at 300 K.

Sample	Cyclohexane vol%	Ethanol vol%	Water tolerance vol%
4EW50CH10	10	50	4

Table 3: Experimental results of Heptane at 300 K.

Sample	Heptane vol%	Ethanol vol%	Water tolerance vol%
5EW50H10	10	50	5

Table 4: Experimental results of Iso-Octane at 300 K.

Sample	Iso-Octane vol%	Ethanol vol%	Water tolerance vol%
5EW50IO10	10	50	5

Table 5: Experimental results of Acetone at 300 K.

Sample	Acetone vol%	Ethanol vol%	Water tolerance vol%
1EW30A10	10	30	1
2EW40A10	10	40	2
5EW50A10	10	30	5

Table 6: Experimental results of TBA (tert-Butyl Alcohol) at 300 K

Sample	TBA vol%	EtOH vol%	Water tolerance vol%
1EW10TBA20	20	10	1
1EW10TBA25	25	10	1
2EW30TBA10	10	30	2
5EW40TBA10	10	40	5
5EW50TBA10	10	50	5

As can be seen, the above results show that TBA is effective at improving water tolerance in comparison to other co-solvents. The results follow the trend cited by other researches in the literature. Rajan et al. [9-10] investigated the amount of water in ethanol that can be tolerated before phase separation. The blends obtained from the study were referred as “limit blends”, since these were the limits characterizing the miscibility of water-ethanol-gasoline blend. Gramajo de Doz et al. [6] studied water tolerances and ethanol concentrations at equilibrium in the upper gasoline-rich phase for several gasoline-ethanol-water multi-component systems at temperatures of 283.15, 293.15 and 313.15 K. Osten, David W et al. [11] studied phase separation at low temperature by varying the percentage of blending agents such as TBA(ter-Butyl alcohol) and IPA (isopropyl alcohol).

**4 Discussion:** The experimental methods used here in the study are similar to a classroom demonstration of water induced phase separation of alcohol-gasoline blends [12]. This simple method of

demonstration can help us discuss the most serious problem associated with ethanol-gasoline blends such as i) ethanol-water phase separation and ii) properties of mixtures- solubility.

As can be seen, from the above experiment that addition of small amount i.e.0.1 ml (1 % vol) of distilled water in ethanol-gasoline blends results in phase separation. However, our aim of using hydrous ethanol as a cheap alternative fuel without phase separation requires the understanding of partition preference of ethanol into the aqueous phase and the tie-line in the ternary phase diagram for ethanol-gasoline-water mixture [5, 12-14]. Blending hydrous ethanol-gasoline blend with blending agents i.e. co-solvents at higher temperatures might partially solve the problem for water content of 1-5%vol and blending agent such as TBA (tert-butyl alcohol) certainly improves the water tolerance at higher concentration of TBA. But for higher concentration of water (10 %vol) in ethanol and for hydrous ethanol-gasoline blend at lower temperatures it might require a solution outside the ternary phase diagram for ethanol-gasoline-water. One of the possible avenues is dehydration of ethanol using fixed bed biomass adsorption, which needs to be explored [15].

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#### References:

- [1] Henry Ford Predicted Hemp Cars Powered by Biofuel, Available: <http://greenlivingideas.com/2009/09/09/74-years-henry-ford-predicted-hemp-cars-powered-biofuels/>.
- [2] Surisetty, Venkateswara Rao, Ajay Kumar Dalai, and JanuszKozinski, "Alcohols as alternative fuels: An overview." *Applied Catalysis A: General* 404/1 (2011) 1-11.
- [3] Huang, Hua-Jiang, ShriRamaswamy, U. W. Tschirner, and B. V. Ramarao, "A review of separation technologies in current and future biorefineries" *Separation and Purification Technology* 62/1 (2008) 1-21.
- [4] Larsen, Ulrik, Troels Johansen, and Jesper Schramm, "Ethanol as a fuel for road transportation" Main Report. IEA-AMF report 100 (2009).
- [5] French, Raymond, and Patrick Malone, "Phase equilibria of ethanol fuel blends" *Fluid phase equilibria* 228 (2005) 27-40.
- [6] Gramajo de Doz, Mónica B., Carlos M. Bonatti, and Horacio N. Sólomo, "Water tolerance and ethanol concentration in ethanol-gasoline fuels at three temperatures" *Energy & fuels* 18/2 (2004) 334-337.
- [7] Green, Gary J., and Tsoung Y. Yan, "Water tolerance of gasoline-methanol blends" *Industrial & engineering chemistry research* 29/8 (1990) 1630-1635.
- [8] Mužíková, Zlata, Milan Pospíšil, and JaroslavČerný, "Water tolerance of petrol-ethanol blends." *Gorivaimaziva* 47/1 (2008) 44-53.
- [9] Rajan, S. "Water-ethanol-gasoline blends—Physical properties, power, and pollution characteristics" *Journal of Engineering for gas Turbines and Power* 106/4 (1984) 841-848.
- [10] Rajan, Suri, and Fariborz F. Saniee, "Water-ethanol-gasoline blends as spark ignition engine fuels" *Fuel* 62/1 (1983) 117-121.
- [11] Osten, David W., and Nancy J. Sell, "Methanol-gasoline blends: blending agents to prevent phase separation" *Fuel* 62/3 (1983) 268-270.
- [12] Hammond, Robert M., "A Classroom Demonstration of Water-Induced Phase Separation of Alcohol–Gasoline Biofuel Blends" *Journal of Chemical Education* 86/9 (2009) 1045.
- [13] Peschke, Nicole, and Stanley I. Sandler, "Liquid-liquid equilibria of fuel oxygenate+ water+ hydrocarbon mixtures" *Journal of Chemical and Engineering Data* 40/1 (1995) 315-320.

- [14] Wagner, George, and Stanley I. Sandler, "Liquid-liquid equilibria of fuel oxygenate+ water+ hydrocarbon mixtures - Effect of temperature" *Journal of Chemical and Engineering Data* 40/5 (1995) 1119-1123.
- [15] Ladisch, Michael R., and Karen Dyck, "Dehydration of ethanol- New approach gives positive energy balance" *Science* 205/4409 (1979) 898-900.

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