

Composition and Behavior of Fuel Ethanol

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Notice

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Abstract

Ethanol usage in the United States has increased due in part to the elimination of methyl tert-butyl ether from the fuel supply and to the mandates of Congress. Two samples, one each from a wet mill and a dry mill ethanol plant, were obtained before denaturing. Each of these samples contained mostly ethanol, but also low concentrations of water, methanol, and higher molecular weight alcohols (up to five carbons). The wet mill sample also contained ethyl acetate and an ether, 1,1-diethoxyethane. The allowable denaturants for fuel ethanol are similar to gasoline. Since the denaturants are immiscible with water, the ability of the denatured fuel ethanol to absorb water is limited. Experiments with E95 and E85 showed that these both began to phase separate when about 15% water was added to the E95 or E85. The gasoline was released gradually as water was added to the fuel. For E95, there is a smaller amount of gasoline in the fuel (2% to 5%) so less gasoline can be released. The changes in volume when water and ethanol or water and E85 are mixed displayed a deficit of 3% at maximum. The byproducts of fuel ethanol production are less soluble, sorb more, diffuse less readily, and are less volatile than ethanol. It's likely, however, that the increased ethanol concentration in water will increase the solubility of the byproducts, as it does the petroleum hydrocarbons. The production byproducts compose less than 1% of the mass of the fuel. Releases of fuel ethanol will be dominated by the ethanol.

Foreword

The National Exposure Research Laboratory's Ecosystems Research Division (ERD) in Athens, Georgia, conducts research on organic and inorganic chemicals, greenhouse gas biogeochemical cycles, and land use perturbations that create direct and indirect, chemical and non-chemical stresses, exposures, and potential risks to humans and ecosystems. ERD develops, tests, applies and provides technical support for exposure and ecosystem response models used for assessing and managing risks to humans and ecosystems, within a watershed / regional context.

The Regulatory Support Branch (RSB) conducts problem-driven and applied research, develops technology tools, and provides technical support to customer Program and Regional Offices, States, Municipalities, and Tribes. Models are distributed and supported via the EPA Center for Exposure Assessment Modeling (CEAM) and through access to Internet tools (www.epa.gov/athens/onsite).

Fuel composition provides the starting point for evaluation of releases to the environment. For ethanol gasolines, the composition of the fuel differs from typical gasoline by the addition of large amounts of ethanol and the presence of fermentation byproducts. Physically, the fuel can be subject to phase separation upon contact with water. This report provides basic information on usage of ethanol in U.S. gasoline, fuel ethanol production methods, analytical methods for fuel and water samples, fuel ethanol composition and properties, and phase behavior. This information forms the starting point for evaluation of potential environmental impacts and ecosystem and human exposures.

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Oil Spill Report Series

A series of research reports is planned to present data and models for oil spill planning and response. To date, these include:

1. Oil Composition

James W. Weaver, Sheldon A. Skaggs, David C. Spidle, Guthrie Stone, 2009, Composition of Fuel Ethanol, United States Environmental Protection Agency, Washington, D.C., EPA/600/R-09/037.

Zhendi Wang, B.P. Hollebone, M. Fingas, B. Fieldhouse, L. Sigouin, M. Landriault, P. Smith, J. Noonan, and G. Thouin, 2003, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 1. Composition and Properties of Selected Oils, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-03/072.

2. Dispersants

George Sorial, Subhashini Chandrasekar, James W. Weaver, 2004, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 2a. Dispersant Effectiveness Data for a Suite of Environmental Conditions – The Effects of Temperature, Volatilization, and Energy, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-04/119.

3. Simulation Models

James W. Weaver, 2004, Characteristics of Spilled Oils, Fuels, and Petroleum Products: 3a. Simulation of Oil Spills and Dispersants Under Conditions of Uncertainty, United States Environmental Protection Agency, National Exposure Research Laboratory, EPA/600/R-04/120.

As more reports are added to the series, they may be found on EPA's web site at: <http://www.epa.gov/athens/publications>.

Leaking Underground Storage Tank Assessment Report Series

A series of research reports is planned to present data and models for leaking underground storage tank risk assessments. To date these include:

1. Gasoline Composition

James W. Weaver, Sheldon A. Skaggs, David C. Spidle, Guthrie Stone, 2009, Composition of Fuel Ethanol, United States Environmental Protection Agency, Washington, D.C., EPA/600/R-09/037.

James W. Weaver, Linda R. Exum, Lourdes M. Prieto, 2008, Gasoline Composition Regulations Affecting LUST Sites, United States Environmental Protection Agency, Washington, D.C., EPA/600/R-08/xxx.

Weaver, James W., Lewis Jordan and Daniel B. Hall, 2005, Predicted Ground Water, Soil and Soil Gas Impacts from US Gasolines, 2004: First Analysis of the Autumnal Data, United States Environmental Protection Agency, Washington, D.C., EPA/600/R-05/032.

2. Simulation Models

Gorokhovski, Vikenti M. and James W. Weaver, 2007, A Catalog of Ground Water Flow Solutions for Plume Diving Calculations, United States Environmental Protection Agency, Washington, D.C.

Weaver, James W., 2004, On-line Tools for Assessing Petroleum Releases, United States Environmental Protection Agency, Washington, D.C., EPA 600/R-04/101.

3. Model Background and Evaluation

Weaver, James W. and C. S. Sosik, 2007, Assessment of Modeling Reports for Petroleum Release and Brownfields Sites, United States Environmental Protection Agency, Washington, D.C., EPA 600/R-07/101.

As more reports are added to the series, they may be found on EPA's web site at: <http://www.epa.gov/athens/publications>.

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Terminology

Following ASTM D 4806 – 08a Standard Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel.

Denaturant -- a material added to fuel ethanol to make it unsuitable for beverage use, but not for unsuitable for automotive use.

Fuel Ethanol -- ethanol with impurities common to its production including water but not denaturants.

Denatured Fuel Ethanol – fuel ethanol made unfit for beverage use by the addition of denaturants.

Higher Molecular Weight Alcohols – aliphatic alcohols of general formula $C_nH_{2n+1}OH$ with n from 3 to 8.

Following the Code of Federal Regulations (40 CFR) Part 80 – Regulation of Fuels and Fuel Additives:

Reformulated Gasoline (RFG) is any gasoline whose formulation has been certified under 40 CFR § 80.40 and which meets each of the standards and requirements prescribed under 40 CFR § 80.41.

From 1995 until 2006, RFG was required to contain 2 % by weight oxygen-containing compounds (“oxygenates”)

Conventional Gasoline (CG) is any gasoline which has not been certified under 40 CFR § 80.40.

Oxygenated Gasoline (OG) is any gasoline which contains a measurable amount of oxygenate.

Introduction

Gasoline composition has changed because of engine requirements, clean-air and energy-policy legislation, and EPA rule-making. Although ethanol has been in use in motor gasolines for many years, its usage began to increase after 2000 due to concerns over methyl *tert*-butyl ether (MTBE) pollution of ground waters and the resulting state bans of MTBE. Later Congress passed legislation that both removed the oxygenate requirement for reformulated gasoline and required increased use of renewable fuels. Thus since 2006 there has been a large increase in the use of ethanol in the U.S.

The object of this report is the composition and behavior of fuel ethanol, denatured fuel ethanol, and consumer blends (particularly the 15% gasoline-containing E85). Because of Bureau of Alcohol and Tobacco regulations, producers of fuel ethanol generally do not distribute their product in a non-denatured form. Further, analysis of denatured fuel ethanol is complicated by the addition of the numerous constituents of the typical denaturant, namely gasoline. An objective of this research was to obtain samples of non-denatured fuel ethanol. One sample each of the two main production methods – wet milling and dry milling -- was obtained for analysis. The quantity of these samples was limited so analyses were performed on slightly less limited quantities of denatured fuel ethanol (E95) and the easily obtained consumer product E85.

These samples were used to investigate composition of fuel ethanol. Literature on alcohol production for fuel and beverages was used as a guide for the possible constituents of these products. Gas chromatography (GC) coupled with mass spectroscopy (MS) was used for unambiguous identification of the constituents. Subsequent analyses using GC with a flame ionization detector (FID) and Karl Fischer

titration was used to quantify the concentrations of the constituents. Properties of the identified components of fuel ethanol were then estimated using the SPARC chemical property estimator. SPARC was used so that temperature dependence of properties could be explored.

Phase separation of E95 and E85 was studied because when spilled or released to the environment, in most cases these fuels will encounter either surface water in the form of flowing streams, creeks, or rivers; ponds, lakes or estuaries; or soil moisture and ground water. Response to incidents may vary if the fuel forms a separate phase or mixes with water. Since the fuels have a certain water tolerance, phase separation may depend on the composition of the fuel and the nature of the release to water. Ethanol and water are known *not* to mix in direct proportion to their volumes. This effect might change the behavior of the fuel/water system during releases. Simple experiments were devised to determine the volume changes in various ethanol/gasoline blends.

The report is intended to provide a brief overview of the composition and properties of ethanol fuels and contains the following sections describing four topics: composition, chemical properties, phase separation and volume changes.

Background and Literature Review

The background and literature review is divided into seven sections, each of which bears on the objectives of the report. The topics are

- Regulatory History of Gasoline,
- Ethanol Use in Gasoline,
- Gasoline Production in the United States,
- Fuel Ethanol,
- Byproducts in Fuel Ethanol,
- Analytical Methods, and
- Phase Separation and Co-solvency.

Regulatory History of Gasoline

The Clean Air Act Amendments of 1990 introduced a number of different requirements that had a major impact on gasoline composition throughout the entire United States from their implementation in 1992 and 1995 until the present. See Weaver et al. [1] for more detail. The most important factors for understanding the current usage of ethanol were the total ban on lead in gasoline, requirements for conventional gasoline (CG), reformulated gasoline (RFG), and oxygenated gasoline (OG). Both RFG and OG programs required usage of oxygenated gasoline additives, and for the first years of the programs, the most commonly used oxygenate was MTBE.

Ethanol Use in Gasoline

Because of subsurface water quality concerns from releases of fuels containing MTBE, states began in 2000 to ban MTBE and, in some cases, other ethers and alcohols

as fuel additives. Since they were actions taken by state legislatures, they did not affect federal requirements for oxygenate usage. The bans had the effect of causing ethanol usage as a fuel oxygenate to increase in the U.S. The oxygen mandate for reformulated gasoline was removed by the Energy Policy Act of 2005. The act also required usage of renewable fuels, causing another increase in ethanol usage. The Energy Independence and Security Act (EISA) of 2007 increased the mandated amounts of biofuels for 2008 through 2012 and extended the period of required use of biofuels to 2022. The EISA also required targeted amounts of advanced and cellulosic biofuels for the periods 2009 to 2022 and 2010 to 2022, respectively (Figure 1).

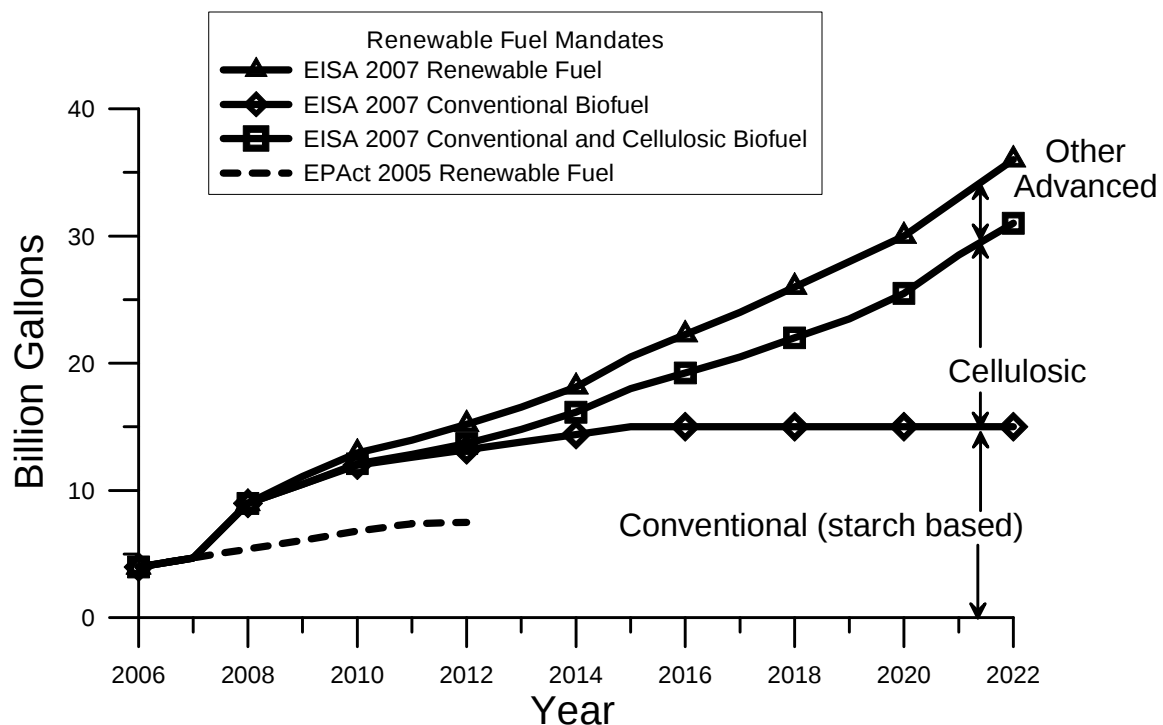


Figure 1 Renewable and biofuel mandates from the Energy Policy Act (EPAct) of 2005 and the Energy Independence and Security Act (EISA) of 2007.

Gasoline Production in the United States

Gasoline production data compiled by the Department of Energy's Energy Information Agency (EIA) documents the production and importation of conventional and reformulated gasoline [2]. These data show that production of RFG began in September 1994 shortly before the implementation of the RFG program (Figure 2). RFG replaced part of the total production of gasoline in the U.S. The remainder became conventional gasoline simply by definition (see 40 CFR §80.2). Production of both types of gasoline tended to increase, although RFG production increased faster than conventional gasoline production. Even so, conventional gasoline accounts for roughly two thirds of U.S. gasoline, a proportion that has been consistent since the beginning of the RFG/CG designation. EIA began differentiating RFG containing ether, alcohol or no oxygenate in 2004 (Figure 3). By this time most of the MTBE bans were in place so alcohol use in RFG was highest. The use of MTBE was slowly declining until the oxygenate mandate was removed by the Energy Policy Act of 2005 (EPAct 2005). In mid 2006 MTBE was abruptly removed from the fuel supply (Figure 3) and the amount of RFG made with ether decreased to a negligible amount, while the amount of RFG made with alcohol abruptly increased. The EPAct 2005 legislation also required increased use of biofuels. Conventional gasoline showed increasing amounts of alcohol, especially after mid 2007. In 2007 the Energy Independence and Security Act mandated increased levels of biofuel usage through 2022. As of March, 2009, EIA data show that 75% of the total gasoline produced in the U.S. contained alcohol.¹

¹ For the week ending March 6, 2009, there were 8539 thousand barrels produced per day of finished motor gasoline. Of this there were 2896 thousand barrels produced per day of reformulated gasoline

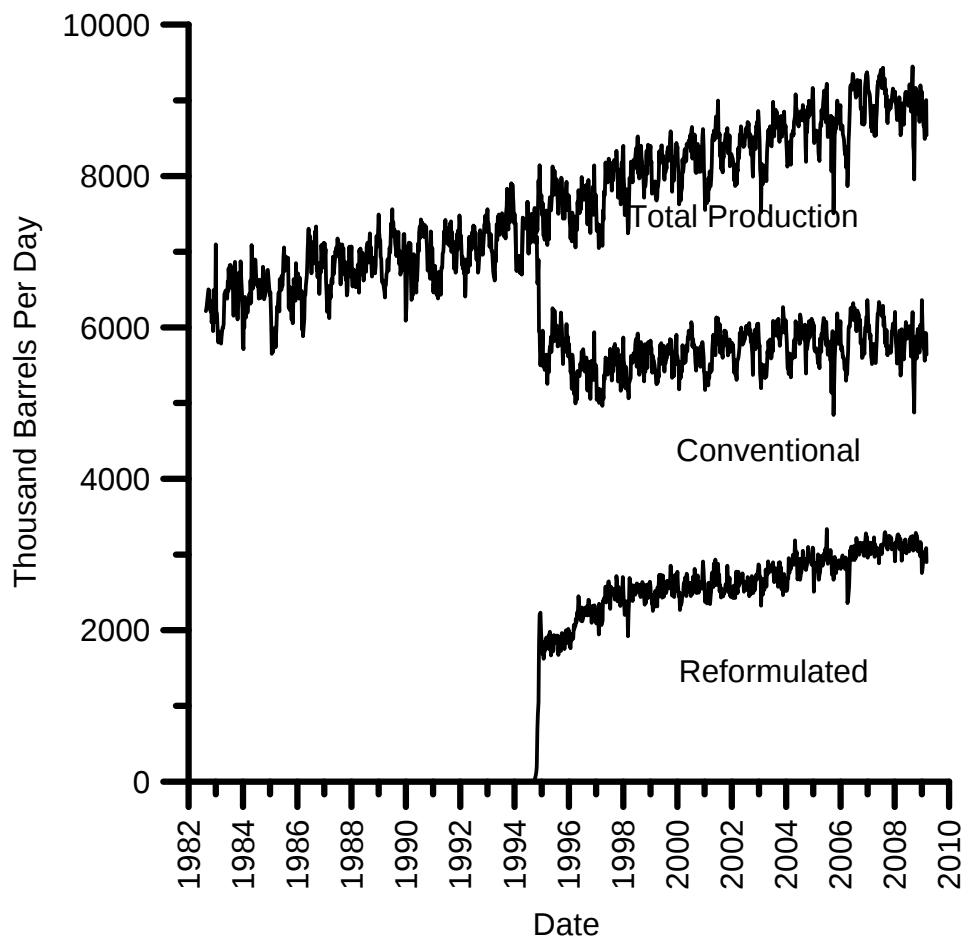


Figure 2 DOE gasoline production and importation data. Prior to the Clean Air Act Amendments, there was no distinction between conventional and reformulated gasoline. The proportion of conventional gasoline (2/3) has remained roughly constant over the period 1995 to 2007.

containing alcohol and 3549 thousand barrels produced per day of conventional gasoline containing alcohol.

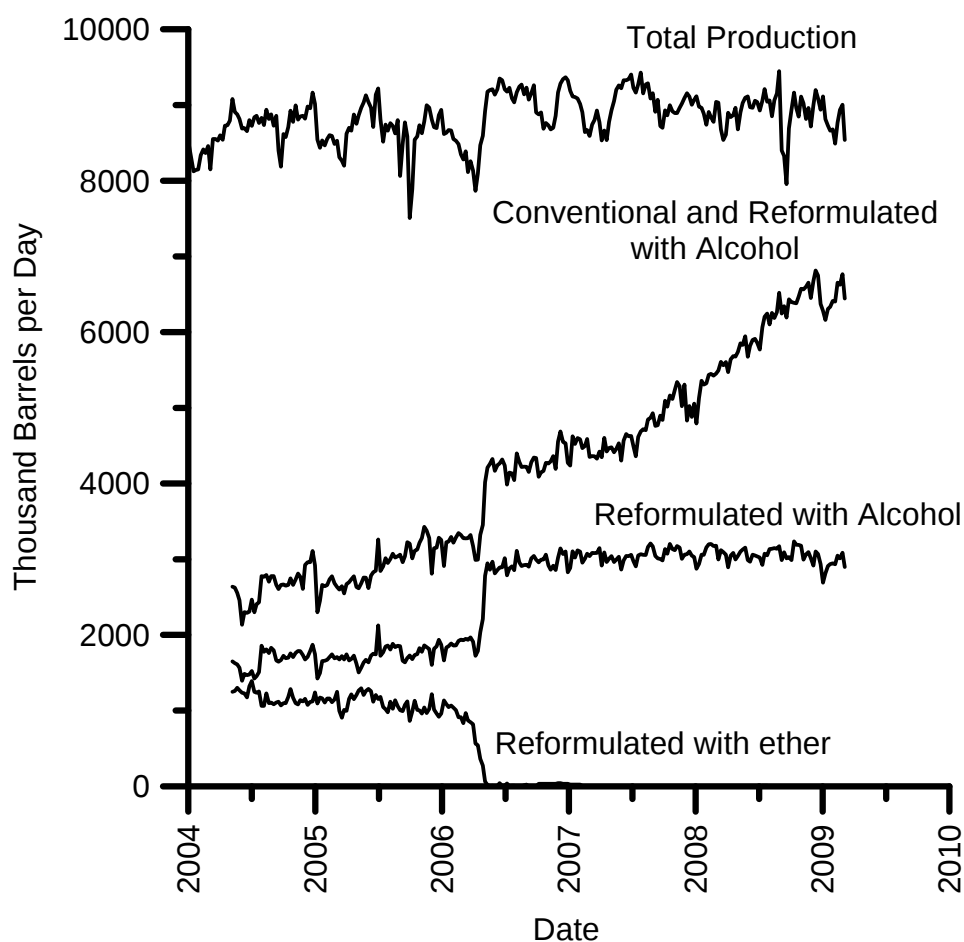


Figure 3 Production of reformulated gasoline with ether and alcohol, conventional gasoline with alcohol and total gasoline production on a weekly basis.

Petroleum product surveys are conducted annually by Northrop Grumman [3]. Samples are collected from service stations and analyzed for selected compositional and physical properties. The benzene and ethanol data presented below were determined by ASTM methods [3]. These data show the variability of ethanol content within the conventional and reformulated classes from cities representing the continental United States. The benzene data were included because it is an important gasoline component and is subject to specific regulation by the Clean Air Act.

For the summer sampling of 2007, conventional gasoline (Figure 4) contained varying amounts of ethanol with two dominant levels: about 10% and, with fewer samples, none. The samples with about 10% ethanol represent E10 and illustrate the observed variability for summer 2007. Outliers contained as much as 14.4% ethanol. Both premium (defined here as octane numbers (ON) greater than 90) and regular had ethanol contents throughout the range from 0 to 11%. Benzene levels ranged to 3.6% which is due to the benzene levels in conventional gasoline being set from 1990 producer/importer baselines [1] The summer 2007 reformulated gasoline (Figure 5) showed also showed two dominant ethanol levels: around 10% and just under 6%.. Regular and premium gasoline showed no discernable patterns, but were represented throughout the data range. Compared to conventional gasoline, benzene levels were lower in reformulated gasoline due to clean air act requirements. Most samples showed benzene levels below 1% by volume.

Conventional Gasoline

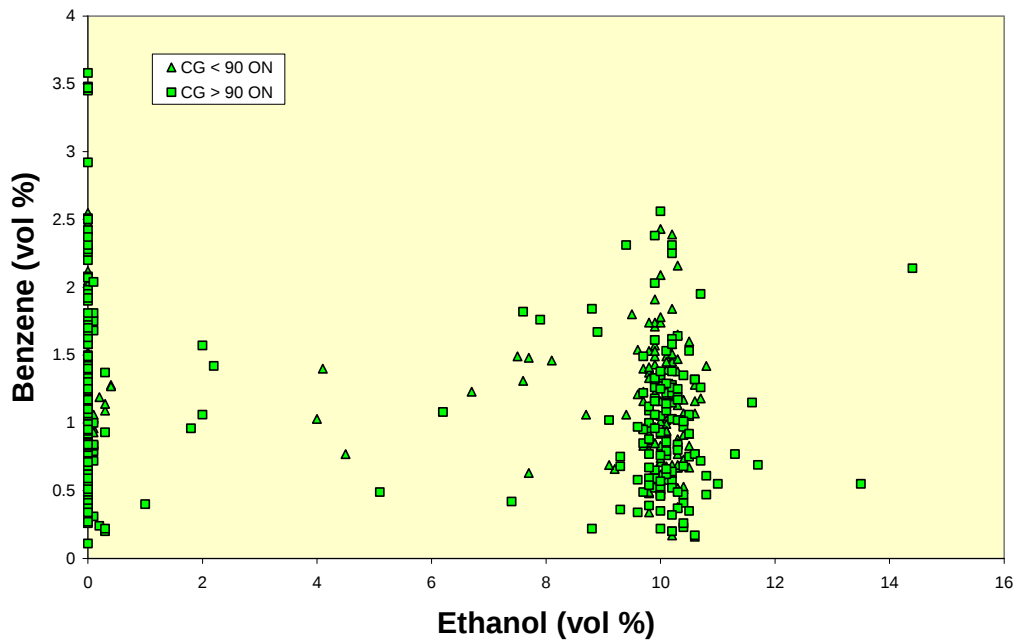


Figure 4 Benzene and ethanol content in conventional gasoline collected by Northop Grumman in 2007.

Reformulated Gasoline

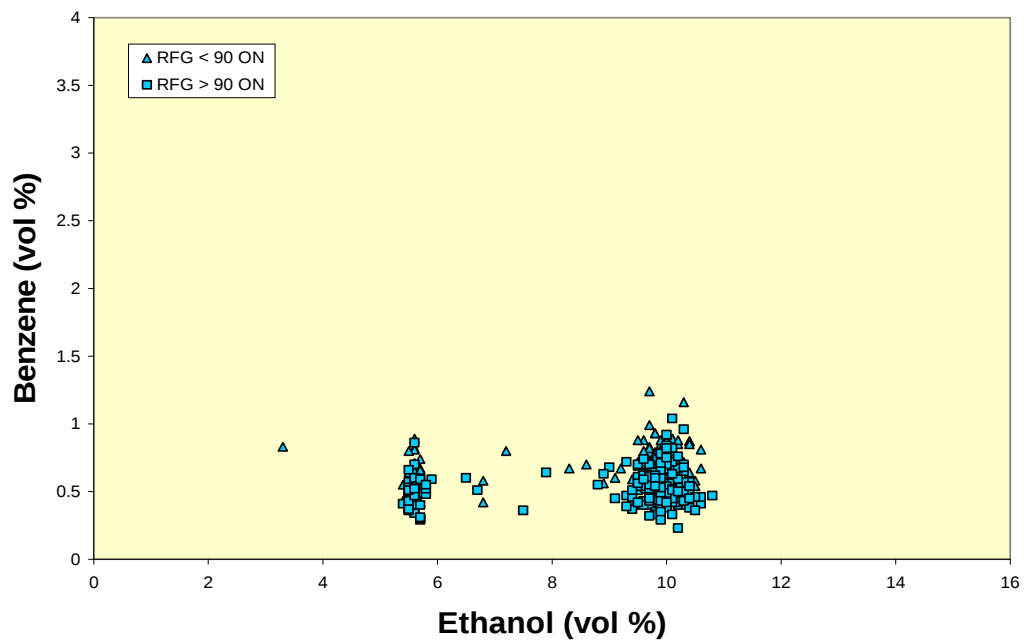


Figure 5 Benzene and ethanol content in reformulated gasoline collected by Northop Grumman in 2007.

Fuel Ethanol

Fuel ethanol is produced by several methods. The most common is the dry mill process that accounts for 75% of current production. Dry mill plants typically produce ethanol as the primary product with animal feed (called Dried Distiller's Grains with Solubles, DDGS) and carbon dioxide as co-products. In dry milling the entire corn kernel is ground and used as the feed stock for ethanol production [4, 5]. In wet milling, the corn is first separated into its components: starch, fiber, gluten and germ [4]. These plants produce ethanol as one of several food industry products including corn oil, corn syrup, and corn sugar. After fermentation the alcohol is distilled to 190 proof to reduce the water content. Afterward, molecular sieve technology is used to remove the remaining water.

For use as a fuel, ethanol is made unfit for drinking by addition of a denaturant. ASTM [6] gives requirements for fuel ethanol and acceptable denaturants for use in automobile engines. Fuel ethanol is permitted by ASTM to contain 1.76% to 5.0% denaturant. Beginning on January 1, 2009, the 2008 Food, Conservation, and Energy Act allows a full ethanol production credit only so long as the denaturant content is no more than 2% [7]. Because of measurement difficulties, the Internal Revenue Service is temporarily allowing credits as long as the denaturant(s) do not exceed 2.5% of the volume of the fuel ethanol [8]. The allowable denaturants are:

- natural gasoline,
- gasoline components, or
- unleaded gasoline.

The ethanol content, after denaturing, is to be a minimum of 92.1% at the time of blending with gasoline and the water content of the fuel ethanol is to be less than 1%.

ASTM also specifies prohibited denaturants:

- hydrocarbons with an end boiling point above 225 °C,
- methanol not meeting ASTM D1152,
- pyrroles,
- turpentine,
- ketones, and
- tars.

These substances are said to have potentially extreme adverse effects on fuel stability, automotive engines, and fuel systems. Since the typical boiling range of gasoline is 90 °C to 200 °C [9], the first prohibited denaturant listed above indicates that denaturants for fuel ethanol are intended to be very much like gasoline.

Byproducts in Fuel Ethanol

Fermentation of corn starch produces ethanol and other compounds. Although ethanol is the dominant alcohol produced, a variety of others have been documented [10]. Air emissions from a beer brewer/dry-mill ethanol plant were monitored and a number of hydrocarbons were identified. Classes of compounds included tearing agents (lacrimators), respiratory irritants and odorants. Specific examples included formaldehyde, acetaldehyde, furfural, 2-Furancarboxaldehyde, acrolein, benzene, methanol, ethanol, glycerol, styrene, lactic acid and acetic acid [11]. The complete list of compounds is given in Appendix B, although most of these have not been reported as constituents of fuel ethanol itself. The main byproducts of ethanol production are isopropyl and isobutyl alcohols, but also include methyl, amyl, iso-amyl, n-propyl,

glycerol (1,2,3-propanetriol), higher alcohols, ethers, acetic aldehyde and acids. The presence of pentoses leads to production of furfural (furan-2-carbaldehyde), which degrades rubber or elastomeric seals². Production of the byproducts can reduce ethanol production by 10%. Because of competition among microorganisms, the longer that fermentation continues, the more equilibrium shifts toward the higher alcohols, aldehydes, acids or methane [11].

For comparison purposes, the following literature on beverage alcohol production was reviewed as a related production activity might show insight into issues of fuel ethanol. In production of beverages [13] found acetals (i.e., 1-1 diethoxyethane) occurring in small quantities. The occurrence of acetals began to be significant after 4 hours of fermentation and is related to higher acidity related to infections of acid-forming bacteria. Esters are formed from organic acids and predominantly ethanol. In the first hours of fermentation ethyl and methyl esters of acetic acid were produced. In later stages of fermentation esters of higher alcohols appeared (isoamyl acetate, isobutyl acetate, and ethyl hexanoate). Other compounds produced include 2-propanol, acrolein (in the form of acrolein diethylacetal), acetic aldehyde [13] .

Production of fermentation byproducts is important to beverage producers or consumers because volatile esters impart flavors [13, 14], contaminants can be present in illegally produced alcohol [15], and reduction in some byproducts is needed for food-grade alcohol [16]. Fan and Qian found a large number of flavor imparting compounds in increased concentration in five-year old Chinese Liquor which was aged in a clay vessel [14]. In a study of contaminants of illegally-produced drinking alcohol, analysis

² Corrosion of steel is attributed to the formation of ethanol/water molecular structures as well as the amount of water itself [12].

was performed for the ethanol, isopropanol, acetone, methanol, ethylene glycol and lead contents [15]. A later summary of studies indicated analysis for ethanol, methanol, 1-propanol, iso-butanol and isoamyl alcohol were commonly analyzed in evaluation of these liquors [17].

Analytical Methods

There are common aspects of analytical methods for alcohol analyses. ASTM specifies a long nonspecific narrow-bore capillary column and direct injection to a gas chromatograph (GC) with a flame ionization detector (FID) [18]. Others have used direct injection to a CG-FID [19] using a wax column [13] or non-polar fused silica column [20]. Trace level analyses of ethanol, MTBE and other alcohols and ethers have been conducted with solid phase micro extraction (SPME) using a DVB/Carbozen/PDMS fiber, a GC equipped with a fused silica column and mass selective detector [14, 21]. Solid phase extraction was used to concentrate impurities in Brazilian ethanol prior to GC-MS identification [22].

Phase Separation and Co-solvency

Although water and gasoline are mutually immiscible, a small amount of each is soluble in the other. Typical water contents of non-ethanol gasolines are on the order of 0.01%. As the ethanol content increases, the amount of water that can be accommodated in the fuel increases. There is a limit, however, to this tolerance beyond which the fuel separates into a predominantly water phase and a predominantly gasoline phase. Phase

partitioning data that represent this phenomena are commonly represented on tri-linear phase diagrams, where a boundary separates the single- from the two-phase regions. An example phase diagram is shown in Figure 6. The solid curve on the diagram represents the boundary between a one-phase region and a two-phase region. At any point on the diagram, the amount of water, ethanol and hydrocarbon can be read from the three axes. If a mixture contained 85% ethanol, 15% hydrocarbon and no water, its location on the diagram is the beginning point of the dashed arrow. The mixture would exist as a single phase. By increasing the water content, the mixture moves in the direction of the arrow. Once the phase boundary is reached, then the mixture breaks into two phases: a predominantly aqueous/alcohol phase and an predominantly oil phase. Note, however, each of the three components is present to some degree in the two phases.

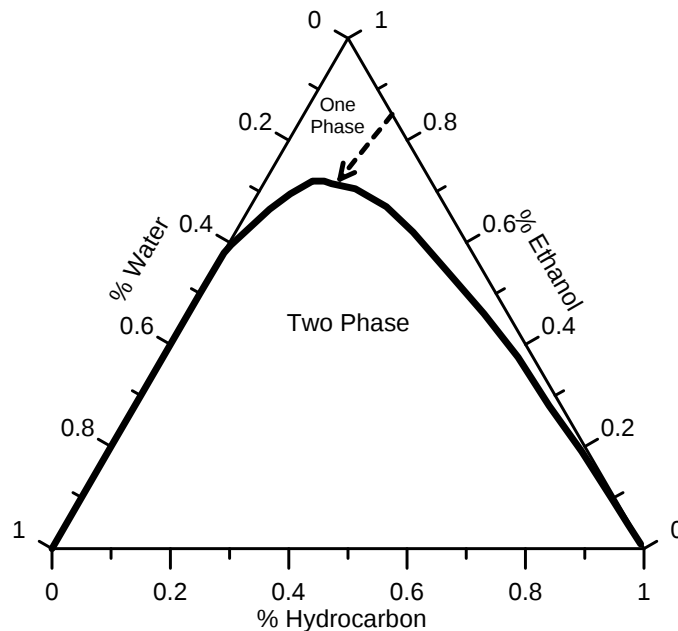


Figure 6 Methanol-Water-Hydrocarbon phase diagram.

For gasoline fuels, the tri-linear diagram has some conceptual utility, but there are many more than three species present. Regardless, the approach allows for a visual

representation of the various combinations of water, ethanol, and “gasoline” that co-exist in solution in either a single or dual phase. Letcher et al. [23] measured phase separation in gasoline-water-alcohol systems and found somewhat suppressed phase separation at higher temperatures. Phase separation was also suppressed in the order: methanol, 1-butanol, ethanol and 1-propanol. K. Y. Lee [24] compared published phase equilibrium data against predicted phase boundaries in three phase water/solvent and BTEX systems and also in systems with a mixed solvent. These showed reasonable agreement for ethanol and methanol as solvents. Nakayama [25] described phase separation in methanol-gasolines as potentially including three layers: water, emulsified water-gasoline and gasoline. Higher molecular weight alcohols were shown by H. K. Lee and coworkers [26] to have suppressed phase separation at low temperatures in methanol-surrogate gasoline blends. French and Malone [27] presented an extensive review of the effects of ethanol on gasoline, including increased vapor pressure at certain ethanol concentrations, materials compatibility and the influence of temperature on phase separation. More detail on potential impacts from subsurface releases from ethanol fuels can be found in Rixey and co-workers [28].

In multicomponent systems, ethanol has the ability to increase the apparent solubility of a partly miscible compound. For the case of the ethanol gasoline, there might be sufficient ethanol present to increase the concentration of gasoline components in water. Heermann and Powers [19] determined the equilibrium phase concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) for various amounts of ethanol in solution. Their purpose was to determine the degree of co-solvency caused by the alcohol and to identify modeling approaches for predicting equilibrium concentrations.

They concluded that the best fit consisted of a piecewise model that had a linear relationship for low ethanol contents (approximately 25% or less) and a log-linear relationship for higher ethanol contents. Data were fit to a surrogate gasoline consisting of eight compounds and then used to predict BTEX concentrations for commercial gasolines.

Estimated aqueous concentrations of benzene calculated from the method developed by Heerman and Powers are shown in Figure 7. The aqueous concentration of benzene from a gasoline mixture depends on the amount of benzene present in the fuel and the co-solvency due to the presence of ethanol in water³. As the amount of ethanol increases, so does the co-solvency, but this effect is balanced by the decline in benzene-containing blendstock used in formulating higher ethanol content fuels. A hypothetical mixture of blendstock containing 1% benzene and denatured fuel ethanol is plotted in Figure 7. The fuel ethanol was assumed to be denatured with 2% gasoline which itself contained 1% benzene. At ethanol contents below about 25 volume %, there is no increase in benzene solubility for this mixture. The aqueous benzene concentration peaks at about 85% ethanol. Higher ethanol content causes a decline in the benzene concentration due to the reduction in benzene content of the fuel. The plot shows the estimated concentration for the average parameter set and the extreme values of the fitted parameters that give the lowest and highest peak concentration. The latter are included because Heerman and Powers gave 95% confidence limits on their fitted parameters. The estimate of benzene concentration from these considerations is 645 +/- 85 mg/L at a

³ When phase separation of an ethanol blend gasoline occurs the bulk of the ethanol partitions to the water phase [23]. thus, assuming that most of the alcohol initially present in the gasoline phase moves to the water phase is reasonable. This behavior differs from mixtures where 1-propanol or 1-butanol serve as the alcohol phase. For these the bulk of the alcohol stays with the gasoline phase.

volume fraction of 87.5% denatured alcohol. This value is about 20 times the aqueous phase concentration of benzene when no ethanol is present (i.e., 33.7 mg/L).

Estimated Benzene Concentration

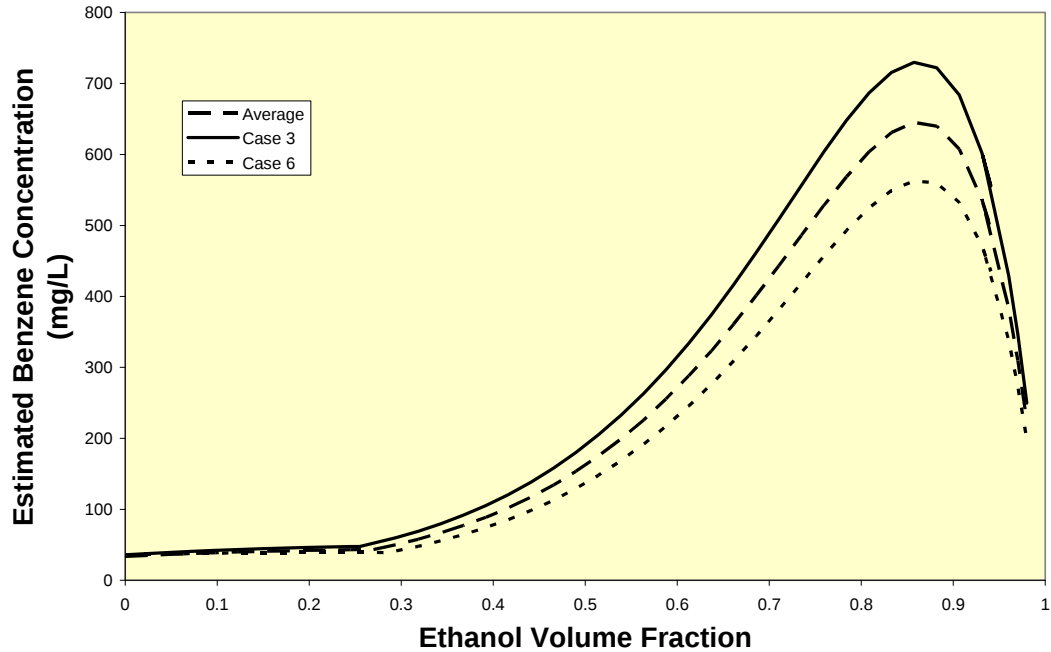


Figure 7 Estimated benzene solubility using the co-solvency relationship developed by Heerman and Powers [19]. The hypothetical mixtures consisted of blendstock containing 1 vol % benzene mixed with ethanol containing 2% of a denaturant that itself contained 1% benzene. Curves are plotted for the average parameters from Heerman and Powers [19] and their extreme parameter sets giving the lowest and highest peak benzene concentrations.

Fuel Ethanol Analyses

Two samples of corn-based, fuel ethanol (non-denatured) were obtained from their manufacturers and analyzed according to the following procedure. There was one sample each from a wet mill and dry mill process. First, gas chromatography/mass spectroscopy (GC/MS) was used to identify the unknown constituents of the samples, followed by quantitation of the concentration using GC/FID, and Karl Fischer titration of the samples for their water content. The details of the analytical methods used in this study are presented in Appendix A.

Analysis of the wet and dry mill samples showed that the fuel ethanol samples included one-, two- and three-carbon unbranched alcohols: methanol, ethanol and propanol (Table 1 and Figure 11); four- and five-carbon branched alcohols: isobutyl alcohol and the two isomers of pentanol (also known as amyl alcohol, see Figure 12): 2-methyl 1-butanol (active amyl alcohol) and 3-methyl, 1-butanol (isoamyl alcohol). The wet mill sample contained two additional compounds both known byproducts of fermentation: ethyl acetate (Figure 13) and, the di-ether, 1,1-diethoxyethane (Figure 14).

Although higher molecular weight alcohols were found in each sample, the bulk of the samples, 97.30% of the wet mill and 96.60% of the dry mill sample were composed of ethanol. The three to five carbon alcohols composed 0.26% and 0.19% of the samples, respectively. Subtracting the total weight percents of the quantitated compounds and water from 1.00, gives the amount of unidentified material as 1.28% and 3.00% respectively.

Table 1 Compounds identified by GC-MS in two samples of fuel ethanol. Concentrations were determined by retention time analysis using GC-FID.

Name	Formula	CAS. Number	Retention Time (min)	Concentration (wt. %)	
				Wet Mill Sample	Dry Mill Sample
Water ⁽¹⁾	H ₂ O	7732-18-15	n.a.	0.65	0.08
Methanol	CH ₄ O	67-55-1	2.191	0.07	0.06
Ethanol ⁽²⁾	C ₂ H ₆ O	64-17-5	2.324	97.3	96.60
1-Propanol	C ₃ H ₈ O	71-23-8	2.673	0.03	0.08
Isobutyl Alcohol	C ₄ H ₁₀ O	78-83-1	3.186	0.10	0.08
2-Methyl 1-Butanol	C ₅ H ₁₂ O	137-32-6	5.147	0.06	0.01
3-Methyl 1-Butanol	C ₅ H ₁₂ O	123-51-3	5.033	0.21	0.02
Ethyl Acetate	C ₄ H ₈ O ₂	141-78-6	3.077	0.02	--
1,1-Diethoxyethane	C ₆ H ₁₄ O ₂	105-57-7	4.958	0.28	--

⁽¹⁾ Determined by Karl Fischer titration

⁽²⁾ Determined by remainder of other compounds

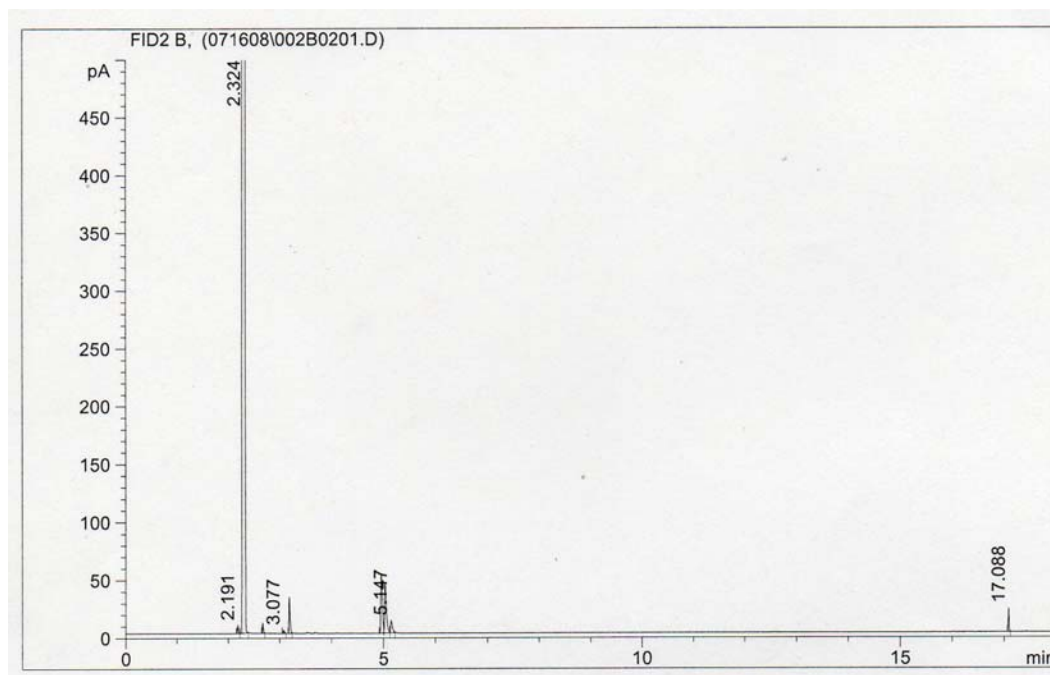


Figure 8 Wet mill sample chromatogram. Retention times are shown in Error! Reference source not found..

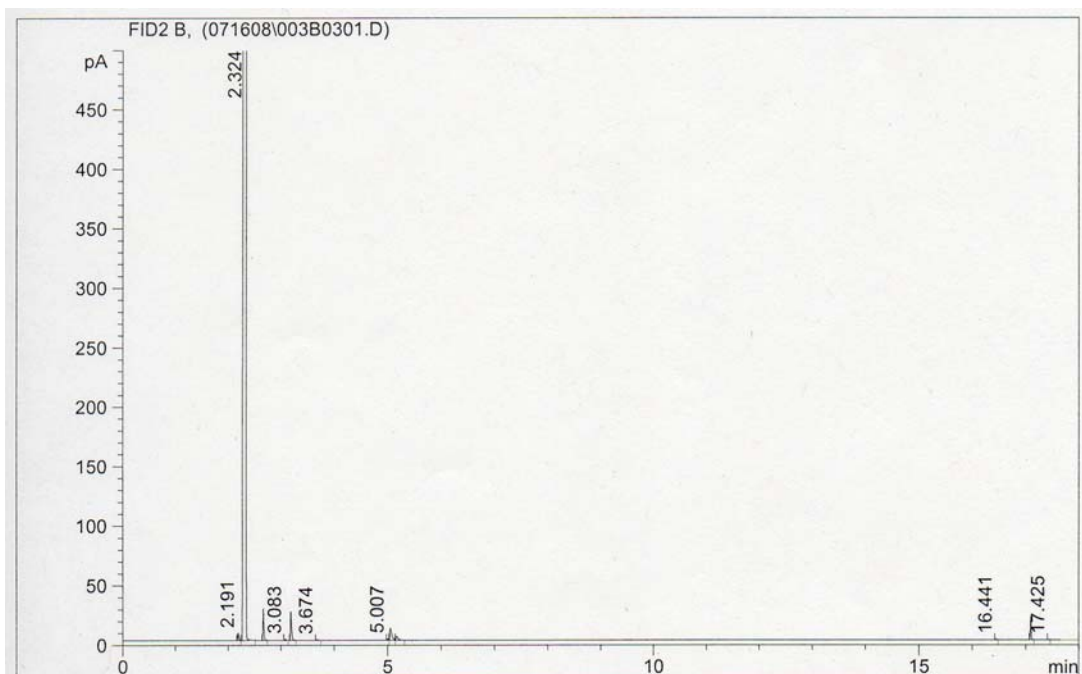


Figure 9 Dry mill sample chromatogram. Retention times are shown in Table 1.

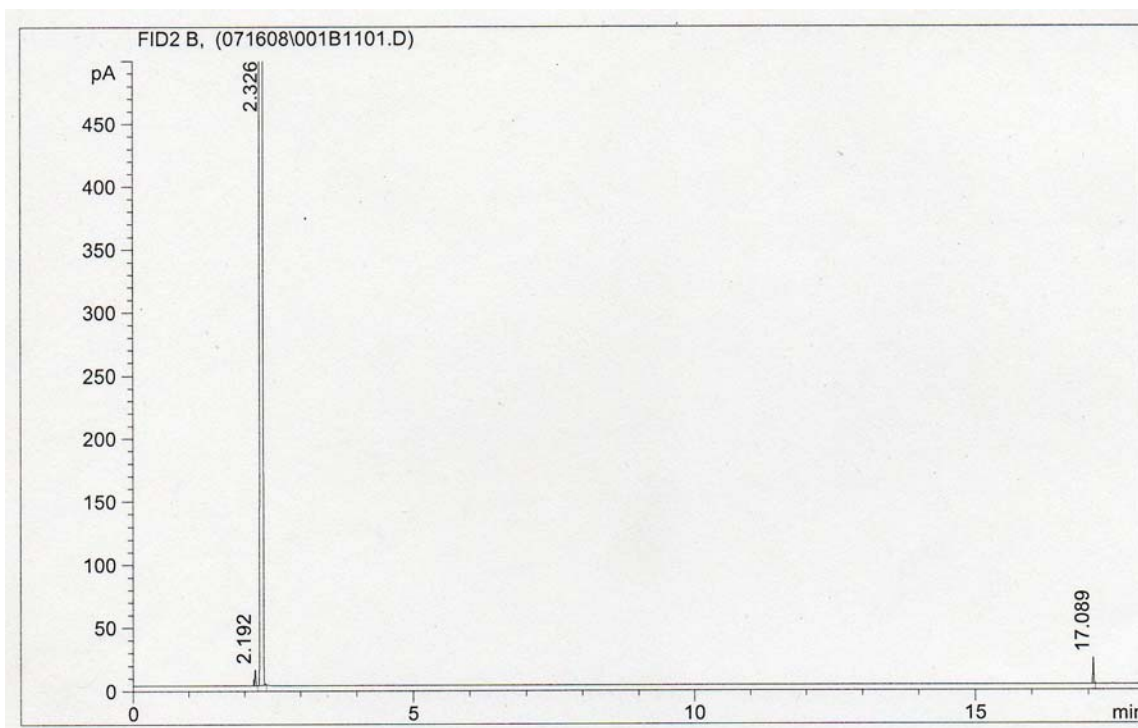
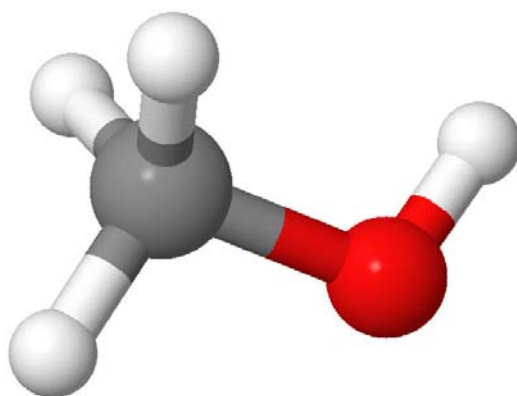
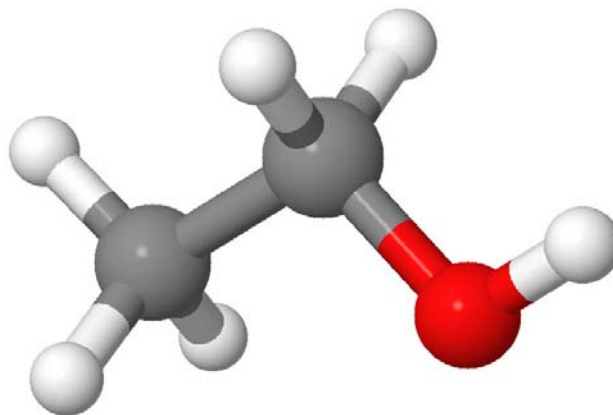


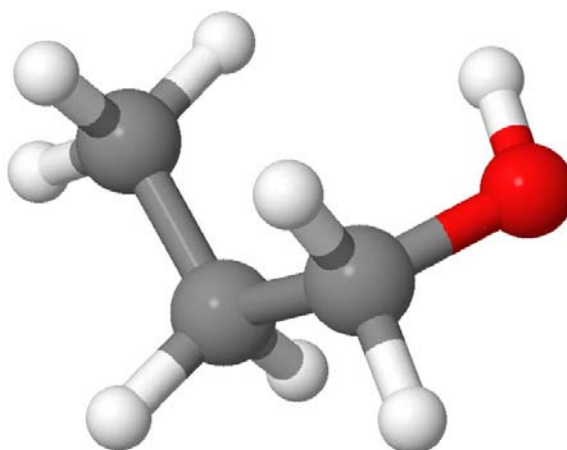
Figure 10 QA blank -- showing internal standard (1, 3-Dibromo-2-propanol with retention time of 17.089 minutes) and alcohol matrix (retention time of 2.192 and 2.326 minutes).



Jmol



Jmol



Jmol

Figure 11 Unbranched alcohols: Methanol CH_4O (top) and Ethanol $\text{C}_2\text{H}_6\text{O}$ (center) and 1-Propanol $\text{C}_3\text{H}_8\text{O}$ (bottom) molecules.

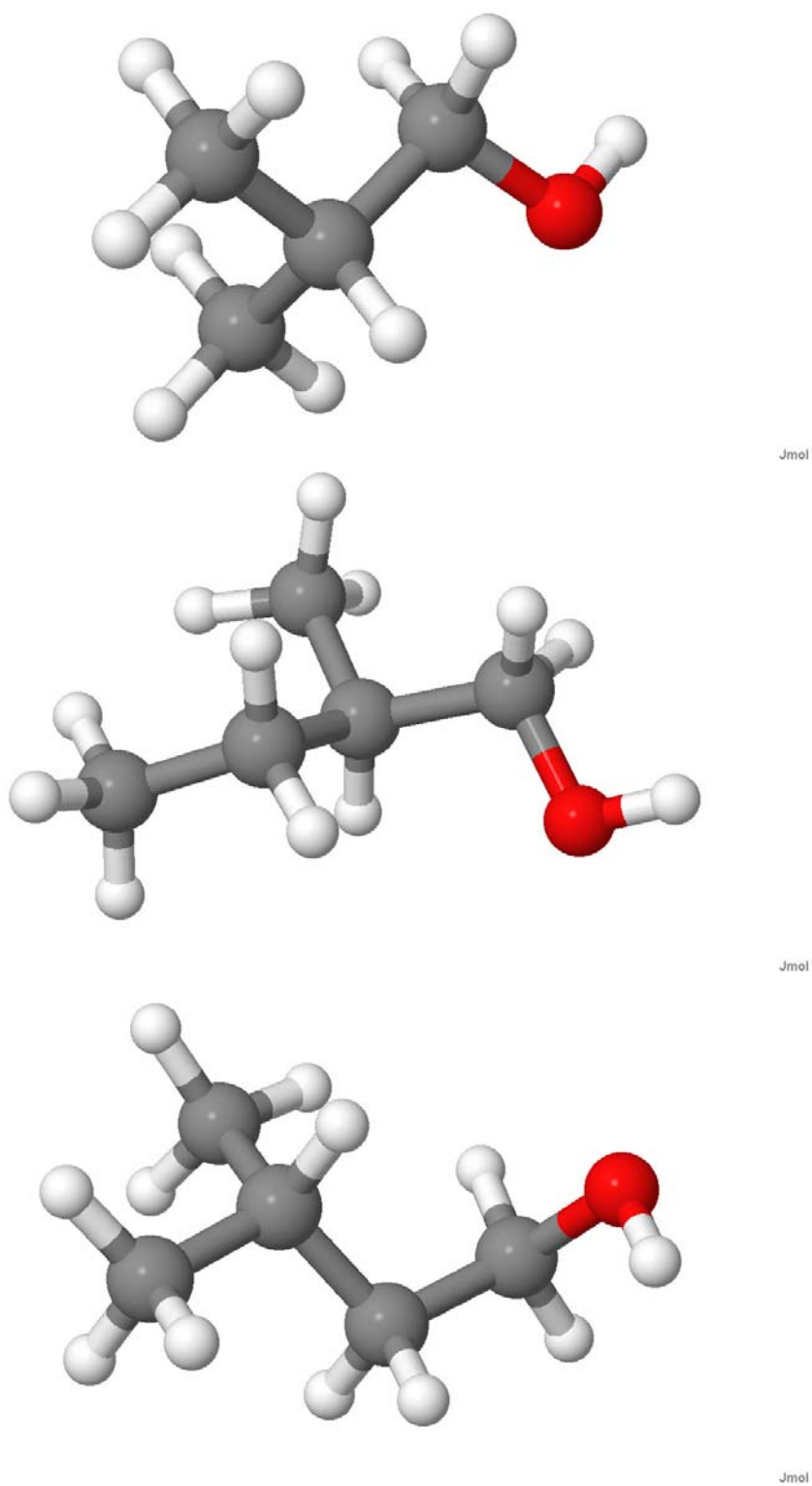
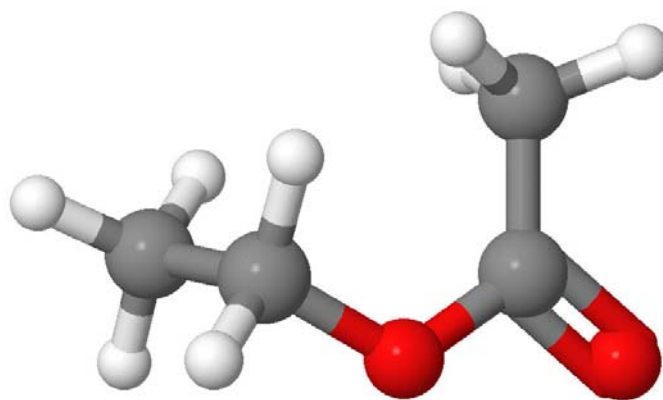
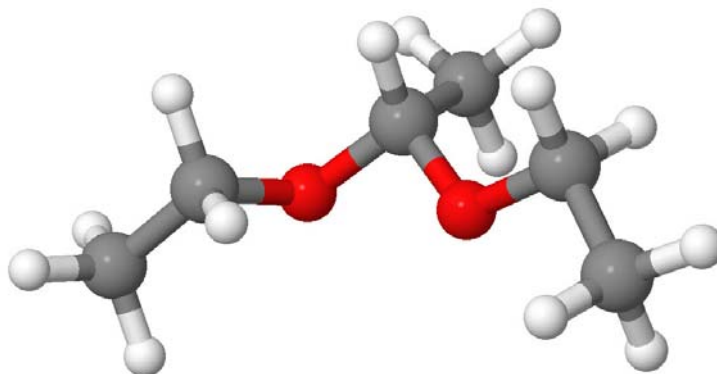


Figure 12 Branched chain alcohols: Isobutyl alcohol $C_4H_{10}O$ (top), 2-methyl 1-butanol $C_5H_{12}O$ (center) and 3-methyl 1-butanol $C_5H_{12}O$ (bottom) molecules.

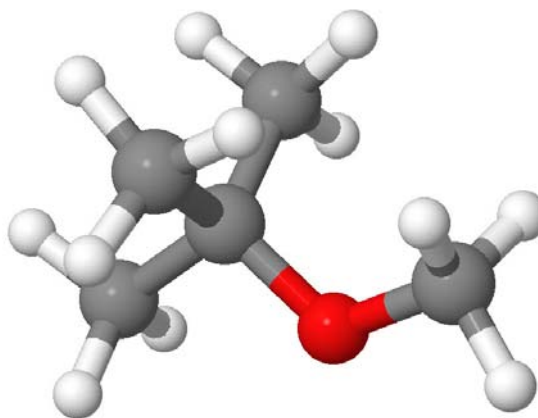


Jmol

Figure 13 Ethyl acetate $C_4H_8O_2$ molecule.



Jmol



Jmol

Figure 14 Ethers: The di-ether 1,1-diethoxyethane $C_6H_{14}O_2$ (top) and MTBE $C_6H_{12}O$ (bottom) molecules.

Phase Separation

Phase separation results for an E95 and an E85 sample are shown in Figure 15. A limited amount of E95 was available for testing so a simplified procedure was used (See Appendix A). The results show that phase separation occurs with addition of water to each of these fuels. Each fuel accommodated a certain amount of water. In both cases this was approximately 15% to 20% of the fuel volume. When the water added to the fuel increased beyond this level, gasoline was released from the fuel. The release of gasoline, however, occurred over an interval of water additions that continued until approximately 45% of the E95 volume and 50% of the E85 volume. At higher amounts of water added, the maximum amount of gasoline was released. Since the amount of gasoline in the E95 and E85 was unknown the released volumes might not have reached the presumed total (i.e, the normalized gasoline levels are below 1.0). Particularly for the E95, the volume of gasoline was very small (0.21 mL or less), so that the measurement accuracy is fairly low.

For higher levels of water added to E85, the gasoline volume was reduced from its maximum. This might have occurred because of the small volumes of gasoline released, the presence of an emulsified layer, and volume changes when E85 and water are combined. When ethanol is added to gasoline, the volume of the mixture is slightly greater than the sum of the volumes. When water is added to ethanol the volume of the mixture is less than the sum of the volumes. This phenomena occurs because some of the polar ethanol molecules are accommodated within the structure that forms from the polar water molecules [29]. The volume reduction for alcohol-water mixtures is on the order

of 5%. (See Appendix C for a discussion of the physical chemistry of these ethanol-water volume effects.)

Figure 16 shows the volume changes observed when water was added to E85. Here the average values from the four experiments plotted in Figure 15 were used to determine the average volume of the aqueous phase (solid line), the average volume of the gasoline phase and the total volume (dot-dash line). These are compared against the total volume added during the experiments (upper dashed line). The figure shows that the total volume resulting from the addition of water to E85 is less than the sum of the water and E85 combined (upper dashed line). The deficit of volume was about 3% for these experiments. Figure 17 shows experimental and theoretical results for the volume of mixtures of water and ethanol. The theoretical calculation was made from the theory presented in Appendix C and the data published by Pečar and Doleček [30]. The maximum reduction found in both the experiment and theoretical calculation of about 3.5% roughly corresponds to the reduction in volume observed for mixtures of E85 and water (Figure 16).

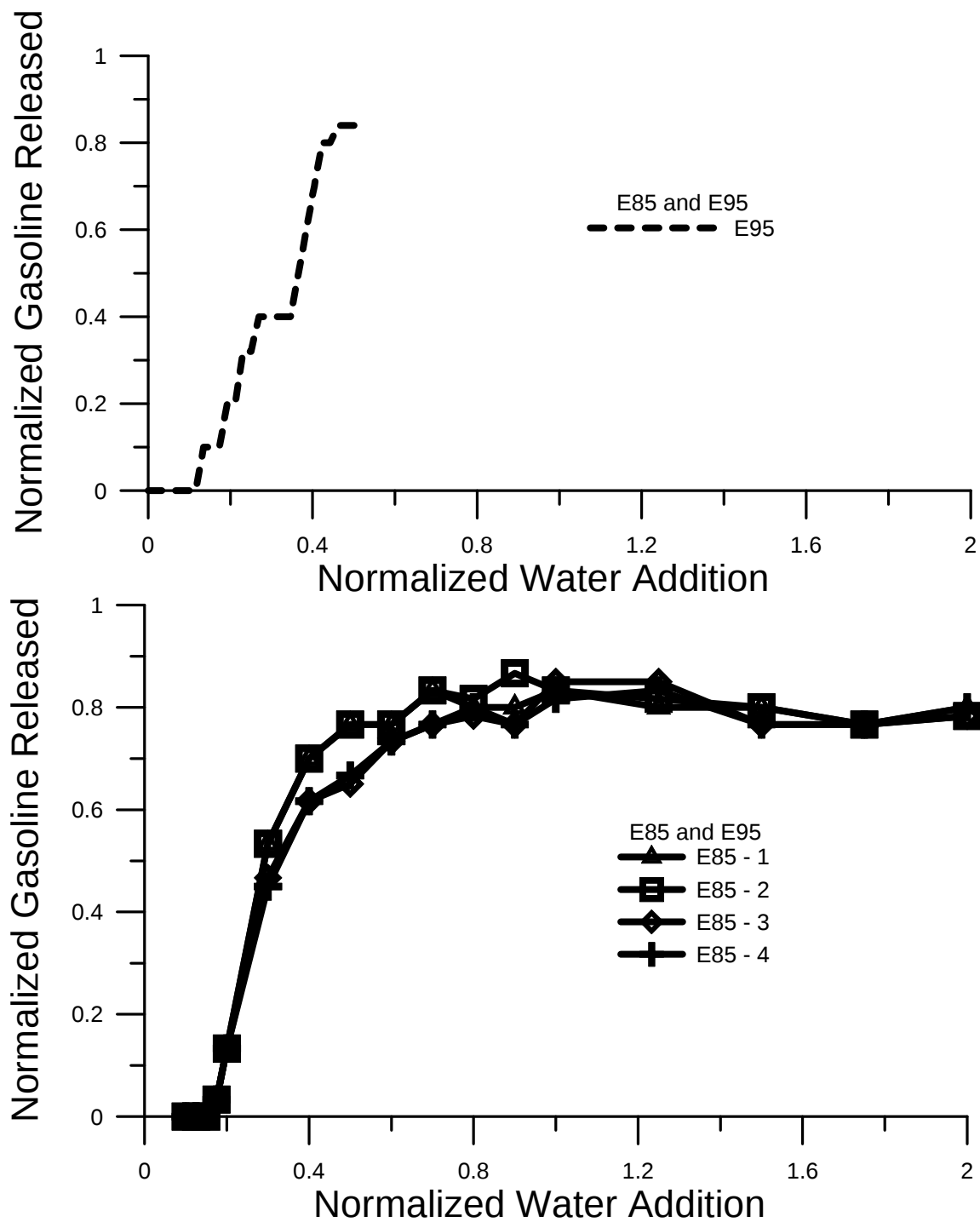


Figure 15 Release of gasoline from E95 (top) and E85 (bottom) at varying amounts of water added. The gasoline is normalized to the nominal amount of gasoline in the E95 (5% of 7 ml) or E85 (15% of 20 ml). The water is normalized to the volume of E95 (7 ml) or E85 (20 mL).

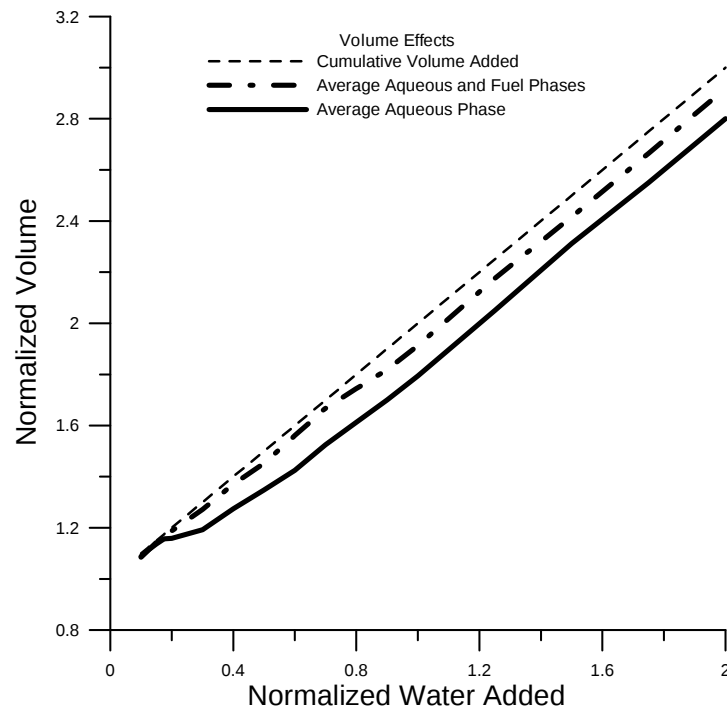


Figure 16 Volume changes as water is added to a sample of E85. All the volumes are normalized to the volume of E85 (20 ml).

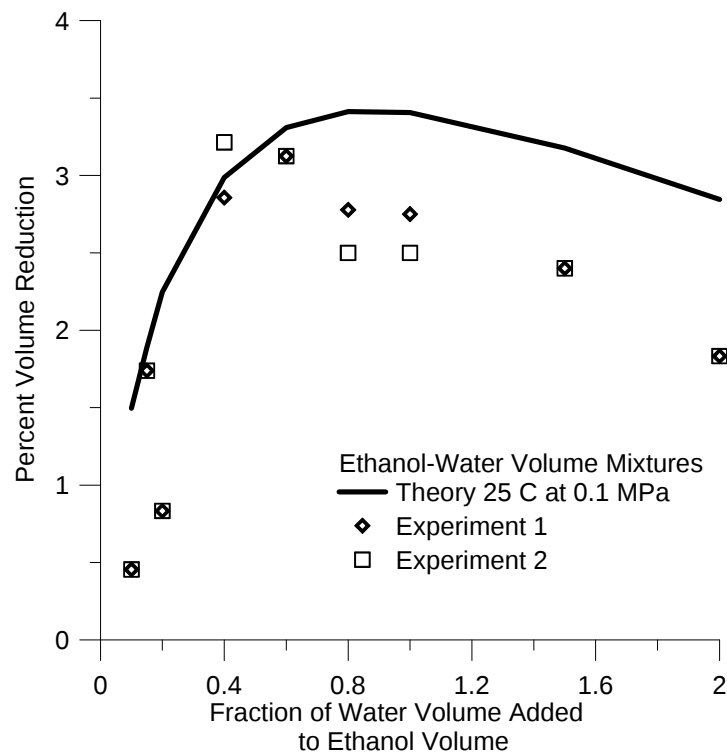


Figure 17 Total volume reduction during addition of water to ethanol.

Fuel Ethanol Component Properties

The properties of the chemicals found in the fuel ethanol samples were estimated using the SPARC calculator [31] that is available for use via the Internet.⁴ These estimates were used, because all parameters were not found in the literature for all chemicals and, more importantly, measured values are not available for all temperatures of interest (5 °C to 45 °C). For comparison purposes, properties of benzene and methyl *tert*-butyl ether (MTBE) were also estimated from SPARC. Appendix D contains a comparison of SPARC-generated and EPI SuiteTM-generated properties, along with an estimate of error in SPARC properties.

Table 2 shows the results for 15 °C from SPARC for solubility, Henry's constant, vapor pressure, the air phase diffusion coefficient, the water phase diffusion coefficient, and the octanol-water partition coefficient. The compounds are ordered first by number of oxygen atoms (one or two) and then by number of carbon atoms. Table 3 shows the same 15 °C results ordered by parameter value.

Solubility

Solubility can be viewed as a direct measurement of hydrophobicity or the tendency of water to exclude a substance from solution. The solubility is the maximum concentration which an aqueous solution will tolerate before the onset of phase separation [32]. Ethanol and methanol are infinitely soluble in water. Any amount of ethanol or methanol can be dissolved in water without forming a separate phase. All of the other

⁴ <http://ibmlc2.chem.uga.edu/sparc/>

compounds found in the samples have finite solubility. Alcohols, though, have a greater affinity for water than either benzene, MTBE or the 1,1-diethoxyethane. Benzene is non-polar (observe the symmetric structure with no oxygen in Figure 18) so it's solubility is the lowest of this group. Figure 21 and Figure 22 show the variation in solubility from 5 °C to 45 °C.

The actual water phase concentrations resulting from partitioning of these compounds or other constituents of gasoline are significantly lower than these solubilities. In effect the concentration obtained from a mixture depends on the solubility of a component *and* the amount present in the mixture [33]. Consequently the solubilities presented in Table 2, Table 3, Figure 21 and Figure 22 are much greater than the concentrations that would be observed in water contacted with gasoline.

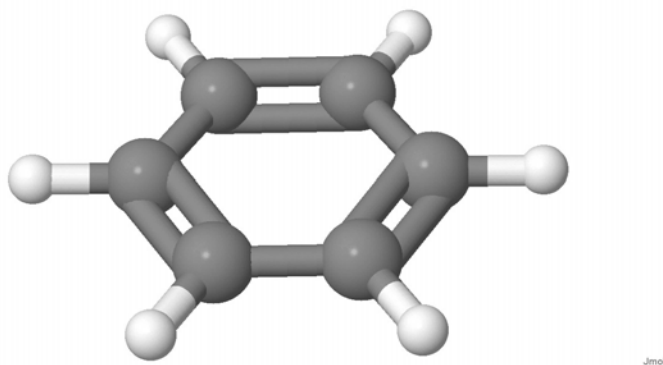


Figure 18 Benzene C₆H₆ molecule.

Octanol-Water Partition Coefficient

The octanol-water partition coefficient, K_{ow} , is a measure of the tendency for a chemical to preferentially partition from water to organic matter [34]. This coefficient is generally inversely related to solubility and provides information similar to the compound's solubility—albeit in an inverse sense. The most soluble compounds have the least degree of partitioning to octanol. The SPARC results show almost a direct reversal from solubility. In the environment the octanol-water partition coefficient corresponds to the tendency to partition to soil organic matter or animal tissues.

Water and Air Phase Diffusion Coefficients

The diffusion coefficients for water and air are measures of the ability of the molecule to diffuse through intermolecular collisions [34]. Generally, the air phase diffusion coefficients are roughly four orders of magnitude higher than the water phase diffusion coefficients. Obviously, diffusion through air occurs much more readily than diffusion in water (similarly diffusion coefficients in solids are again much lower than those for water). Generally smaller molecules diffuse more readily than larger molecules and this trend is evident in the SPARC results for both water and air.

Vapor Pressure

Vapor pressure is a measure of the maximum possible concentration of a compound in the gas phase at a given temperature. This quantity represents equilibrium partitioning of an organic chemical between the gaseous phase and compound itself

(liquid or solid). It provides information on the attractive forces among the compound's molecules in the condensed phase [35]. Table 3 shows that at 15 °C the vapor pressures of the alcohols were inversely related to their molecular weight. Therefore methanol had the highest vapor pressure and 3-methyl 1-butanol the lowest.

Henry's Constant

The Henry's Constant measures equilibrium partitioning between air and water. Table 3 shows that for the alcohols the Henry's Constants increase with increasing molecular weight. The ordering is generally inverse to that for the solubility, as the higher the water solubility the less tendency to partition to the air.

Property Variation with Temperature

The SPARC calculator provides prediction of temperature-dependence of all its estimated property values. The variation over the range of 5 °C to 45 °C of the properties discussed here are presented in Appendix E.

Table 2 Solubility, Henry's Constant, Vapor Pressure, Air Phase Diffusion Coefficient and Octanol-Water Partition Coefficient estimated by the SPARC calculator for fuel ethanol components, benzene and MTBE at 15 C.

Name	Formula	SPARC ⁽¹⁾ estimated properties at 15 C					
		Solubility (mg/L)	Henry's Constant (atm m ³ /mol)	Vapor Pressure (torr)	Air Diffusion Coefficient (cm ² /s)	Water Diffusion Coefficient (cm ² /s)	Octanol-Water Partition Coefficient (dimensionless)
Methanol	CH ₄ O	Infinite	3.4 x 10 ⁻⁶	77	0.150	1.3 x 10 ⁻⁵	0.24
Ethanol	C₂H₆O	Infinite	5.4 x 10⁻⁶	46	0.110	1.0 x 10⁻⁵	0.74
1-Propanol	C ₃ H ₈ O	2.2 x 10 ⁵	7.3 x 10 ⁻⁶	15	0.094	8.7 x 10 ⁻⁶	3.31
Isobutyl Alcohol	C ₄ H ₁₀ O	9.3 x 10 ⁴	9.0 x 10 ⁻⁶	7	0.081	7.7 x 10 ⁻⁶	8.51
2-Methyl 1-Butanol	C ₅ H ₁₂ O	2.8 x 10 ⁴	1.1 x 10 ⁻⁵	3	0.072	7.0 x 10 ⁻⁶	23.40
3-Methyl 1-Butanol	C ₅ H ₁₂ O	1.9 x 10 ⁴	1.2 x 10 ⁻⁵	2	0.071	6.9 x 10 ⁻⁶	33.11
Benzene	C₆H₆	1.0 x 10³	7.0 x 10⁻³	69	0.085	8.7 x 10⁻⁶	147.91
MTBE	C₆H₁₂O	1.8 x 10⁴	1.2 x 10⁻³	190	0.074	6.5 x 10⁻⁶	34.67
Ethyl Acetate	C ₄ H ₈ O ₂	4.3 x 10 ⁴	1.5 x 10 ⁻⁴	54	0.080	7.4 x 10 ⁻⁶	7.08
1,1-Diethoxyethane	C ₆ H ₁₄ O ₂	2.1 x 10 ⁴	1.8 x 10 ⁻⁴	24	0.062	5.8 x 10 ⁻⁶	34.67

(1) SPARC estimates were generated from May 2008 release w4.2.1405-s4.2.1408, <http://ibmcl2.chem.uga.edu/sparc/> on 8/30/2008 and 8/31/2008

Table 3 SPARC estimated properties at 15 °C ranked from lowest to highest.

Solubility g/L		Octanol-Water Partition Coefficient (dimensionless)		Water Diffusion Coefficient cm ² /s	
name	value	name	value	name	value
<i>Benzene</i>	<i>1.0x 10³</i>	Methanol	0.24	1,1-Diethoxyethane	5.8 x 10 ⁻⁶
<i>MTBE</i>	<i>1.8 x 10³</i>	<i>Ethanol</i>	<i>0.74</i>	<i>MTBE</i>	<i>6.5 x 10⁻⁶</i>
3-methyl 1-butanol	1.9 x 10 ⁴	1-Propanol	3.31	3-methyl 1-butanol	6.9 x 10 ⁻⁶
1,1-Diethoxyethane	2.1 x 10 ⁴	Ethyl Acetate	7.08	2-methyl 1-butanol	7.0 x 10 ⁻⁶
2-methyl 1-butanol	2.8 x 10 ⁴	Isobutyl Alcohol	8.51	Ethyl acetate	7.4 x 10 ⁻⁶
Ethyl acetate	4.3 x 10 ⁴	2-Methyl 1-Butanol	23.40	Isobutyl alcohol	7.7 x 10 ⁻⁶
Isobutyl alcohol	9.3 x 10 ⁴	3-Methyl 1-Butanol	33.11	<i>Benzene</i>	<i>8.7 x 10⁻⁶</i>
1-Propanol	2.2 x 10 ⁵	1,1-Diethoxyethane	34.67	1-Propanol	8.7 x 10 ⁻⁶
<i>Ethanol</i>	<i>Infinite</i>	<i>MTBE</i>	<i>34.67</i>	<i>Ethanol</i>	<i>1.0 x 10⁻⁵</i>
Methanol	infinite	<i>Benzene</i>	<i>147.91</i>	Methanol	1.3 x 10 ⁻⁵

Table 3 (continued) SPARC estimated properties at 15 °C ranked from lowest to highest.

Henry's Constant atm m ³ /mol		Vapor Pressure torr		Air Diffusion Coefficient cm ² /s	
name	value	Name	value	Name	value
Methanol	3.4 x 10 ⁻⁶	3-Methyl 1-Butanol	2	1,1-Diethoxyethane	0.062
<i>Ethanol</i>	<i>5.4 x 10⁻⁶</i>	2-Methyl 1-Butanol	3	3-Methyl 1-Butanol	0.071
1-Propanol	7.3 x 10 ⁻⁶	Isobutyl Alcohol	7	2-Methyl 1-Butanol	0.072
Isobutyl Alcohol	9.0 x 10 ⁻⁶	1-Propanol	15	<i>MTBE</i>	<i>0.074</i>
2-methyl 1-Butanol	1.1 x 10 ⁻⁵	1,1-Diethoxyethane	24	Ethyl Acetate	0.080
3-methyl 1-Butanol	1.2 x 10 ⁻⁵	<i>Ethanol</i>	<i>46</i>	Isobutyl Alcohol	0.081
Ethyl Acetate	1.5 x 10 ⁻⁴	Ethyl Acetate	54	<i>Benzene</i>	<i>0.085</i>
1,1-Diethoxyethane	1.8 x 10 ⁻⁴	<i>Benzene</i>	<i>69</i>	1-Propanol	0.094
<i>MTBE</i>	<i>1.2 x 10⁻³</i>	Methanol	77	<i>Ethanol</i>	<i>0.110</i>
<i>Benzene</i>	<i>7.0 x 10⁻³</i>	<i>MTBE</i>	<i>190</i>	Methanol	0.150

Discussion and Conclusions

Ethanol usage in the United States has increased due in part to the elimination of methyl tert-butyl ether from the fuel supply and to the mandates of Congress. Required amounts of ethanol in fuel will increase the total through the year 2022. Current data show that 75% of U.S. produced gasoline contains ethanol. For the year 2007, the amounts in conventional gasoline ranged from none to 10.5%, with outliers at higher concentration. Premium gasoline showed two maximums one near 6% and the other at about 10%. Two samples of non-denatured fuel grade ethanol, one each from a wet mill and a dry mill ethanol plant, were obtained before denaturing. Each of these samples contained mostly ethanol, but also low concentrations of water, methanol, and higher molecular weight alcohols (up to five carbons). The wet mill sample also contained ethyl acetate and an ether, 1,1-diethoxyethane. These two compounds might have been present due to the difference in production method, as wet milling is intended to produce a wide range of products from the components of corn.

The allowable denaturants for fuel ethanol are similar to gasoline. Unleaded gasoline, gasoline range hydrocarbons, natural gasoline or condensate can be used for this purpose. Since pure ethanol, the primary constituent of fuel ethanol is miscible in water, a large amount of water can be accommodated in fuel ethanol. Since the denaturants are immiscible with water, the ability of the denatured fuel ethanol to absorb water is limited. Experiments with E95 and E85 showed that these both began to phase separate when about 15% water was added to the E95 or E85. The gasoline was released gradually as water was added to the fuel. Because about 50% water was needed for complete phase

separation of the E95 and E85, phase separation effects in flowing water can be estimated: If the flow in the receiving water body is 50% or greater than the release rate of the E95 or E85 phase separation is a likelihood. In these cases an “oil” slick composed of gasoline should be expected. For E95, there is a smaller amount of gasoline in the fuel (2% to 5%) and the slick would be less massive than for the same spill of E85. The changes in volume when water and ethanol or water and E85 are mixed displayed a deficit of 3% at maximum. For example, a fuel spill that caused a release to a creek would increase the flow volume by its volume less 3%. This phenomena for is unlikely to be environmentally significant.

The byproducts of fuel ethanol production are less soluble, sorb more, diffuse less readily, and are less volatile than ethanol. It’s likely, however, that the increased ethanol concentration in water will increase the solubility of the byproducts, as it does the petroleum hydrocarbons. The byproducts compose less than 1% of the mass of the fuel so releases of fuel ethanol will be dominated by the ethanol. Increased solubility of petroleum hydrocarbons is possible when the ethanol fraction is greater than about 20%. The solubility of benzene could increase by a factor of 20 due to the presence of the ethanol.

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Appendix A Analytical Methods

Fuel Ethanol Analysis

The undenatured fuel ethanol samples were directly injected into an Agilent 6890 GC with a 5973 MSD. The 2.0 μL injected sample was split in the injector at a 200:1 ratio with the injector temperature at 250°C. Separation of the compounds was achieved with a 30m Restek Rtx-200 MS column with an ID of 250 μm , film thickness of 0.5 μm , and a flow rate of 0.7 mL / minute. Initial oven temperature was 40°C for 4 minutes, followed by a 1°C / minute temperature ramp to 50°C. A final temperature ramp of 30°C / minute to 250°C was used to elute late boilers and clean the column. Once reaching 250°C, there was a final hold time of 5.33 minutes. Total run time was 26 minutes. The transfer line to the MSD was kept at 280°C, the MS source at 230°C, and the MS quadrupole at 150°C for the entire analysis. The sample was ionized as it entered the MSD by electron impact. The MSD was turned on after a 1 minute solvent delay, and scanned from 15 to 550 M/Z.

Subsequently, chemical standards were obtained and three calibration curves were developed for an Agilent 6890 gas chromatograph with a flame ionization detector (GC-FID). For all the compounds except ethanol 1.0 μL was injected and the split ratio and temperature programs were the same. Ethanol analysis was achieved by first diluting the sample in acetone to 0.5% of the starting concentration and only splitting the sample 50:1. Compound separation was achieved with a 30m J&W HP-5 column with an ID of 320 μm , film thickness of 0.25 μm , and flow of 0.5 mL per minute. Calibration curve points were 2.0%, 1.0%, 0.5%, 0.2%, 0.1%, and 0.05% by volume of each suspected

compound. Linear correlation lines were compared to area counts from the fuel samples to determine the percentages of compounds in the samples. Because of overlapping retention times, 3-Methyl 1-Butanol and ethanol were calibrated separately from the rest of the compounds. An internal standard of 0.1% by volume of 1, 3-Dibromo-2-propanol was spiked into every sample.

The Karl Fischer (KF) coulometric method was used to determine the water content in the ethanol samples [36]. Samples were analyzed using a Brinkman Metrohm Titrino 831 KF Coulometer with Coulomat AG reagent. This system detects trace amounts of water by titrating the sample to a bipotentiometric end point and is selective to water. One to three milliliters of sample was weighed to the nearest 0.0001 g. The sample was then injected into the titration vessel, and the sample weight was entered into the titrator software. The sample was automatically titrated by the instrument and the water content calculated by the software which was displayed to the nearest 0.01%. Water content values were manually recorded into a laboratory notebook.

Phase Separation

Separation experiments were conducted by adding various amounts of deionized water to a fixed amount of E-85 fuel at ambient temperature. E-85: water ratios included 5:0.5, 5: 0.625, 5:0.75, 5:0.875, 5:1, 5:1.5, 5:2, 5:2.5, 5:3, 5:3.5, 5:4, 5:4.5, 1:1, 1:1.25, 1:1.5, 1:1.75, and 1:2. First, 20 ml of E-85 was transferred by class “A” volumetric pipette into a separatory funnel that was appropriately sized for the total volume expected. Amounts of deionized water were then added to the E-85 to the desired ratio by class “A” volumetric pipette. The separatory flask was then gently shaken and vented

three times before allowing the mixture to remain undisturbed for five minutes in order to allow separation to occur. After five minutes the aqueous (bottom) phase was slowly and carefully drained into an appropriately sized graduated cylinder. The remaining oil (top) phase was then slowly and carefully drained into an appropriately sized graduated cylinder. The volume of the liquid in each cylinder was then recorded for each phase.

A screening method was developed for rapid assessment of phase separation potential, that was particularly useful since the available volume of sample was limited. Measured portions of three commercial ethanol/gasoline mixed samples (E10, E85, and E95) were placed in a 10 ml graduated cylinder. A burette was used to deliver 0.1 ml of deionized water at set increments. Sample mixing was obtained by a continual stirring of a magnetic stir bar at the base of the graduated cylinder. Emulsions were allowed to stir for five minutes before any readings were taken. The affects of the addition of the water (emulsion and/or the presence of two phase behavior) was noted after each addition. The volume of the bottom phase (assumed to be ethanol/water) was read from the markings on the graduated cylinder. Shrinkage of the total volume was also noted by reading the total volume of the solution in the graduated cylinder compared to the initial ethanol/gasoline volume plus the added water volume. Synthetic samples of approximately E25 and E35 were created by adding 1 ml and 2 ml of 100% Ethanol to 5 ml of E10. These were tested in the same manner as the E10.

Appendix B Detected and tentatively identified chemicals from an ethanol plant in Minnesota [10].

Chemical Detected	Chemical Tentatively Identified	Chemical Tentatively Identified
<i>Plant Location: DDGS Dryer Stack</i>		
Methanol	1,3-butadiene	2-methyl-butanal
Ethanol	1,3-butadiene, 2-methyl-	2-methyl-furan
Toluene	1,3-pentadiene	2-methylpropenal
Ethylbenzene	1-2-propadiene	2-pentyl-furan
Acetone	1-4-pentadiene	2-propen-1-ol
Formaldehyde	1-decene	2-propenal
Acetaldehyde	1-dodecene	3-methyl-butanal
Acrolein	1-heptene	6-heptenoic acid
Benzene	1-hexene	acetaldehyde
Styrene	1-methy-2-cyclopropene	benzaldehyde
Lactic Acid	1-nonene	ethanol
Acetic Acid	1-octene	furan
Furfuraldehyde	1-undecene	hexanal
	2-butanone	Nitro-methane
	2-butenal	nonanal
	2-furancarboxaldehyde	propene
	2-heptenal	
	2-methyl-1-pentene	
	2-methyl-2-propenal	

Chemical Detected**Chemical Tentatively Identified**

Plant Location: Distillation Dryer Stack

Methanol	1 butanol 3-methyl
Ethanol	1 butanol 3-methyl, aceta
Carbonyl Sulfide	1-butanol, 3methyl- (S)
Formaldehyde	1-butanol, 3methyl- aceta
Acetaldehyde	butane
MEK/Butyraldehydes	butane, 2, 2-dimethyl
m,p-Tolualdehyde	butane, 2, 3-dimethyl
	butane, 2-methyl
	cyclopentane, methyl-
	ethanol
	ethyl acetate
	heptane
	hexane
	hexane 2-methyl
	hexane, 3-methyl
	pentane
	pentane, 2 methyl
	2-methyl-1-pentene
	2-methyl-2-propenal

Chemical Detected**Chemical Tentatively Identified**

Plant Location: Fermentation Scrubber

Methanol	1 butanol 3-methyl
Ethanol	1 butanol 2-methyl
Carbonyl Sulfide	1 butanol 2-methyl (s)
Formaldehyde	1-butanol, 3methyl- aceta
Acetaldehyde	1,3-pentadiene
Hydrogen Sulfide	1-propanol
Dimethyl Sulfide	1-propanol, 2-methyl
	acetaldehyde
	dimethyl sulfide
	ethanol
	ethyl acetate
	formic acid
	pentane
	propanoic acid

Appendix C Ethanol and Water Mixtures

When water and ethanol form a mixture, a unique volumetric effect occurs: the resulting volume is less than the sum of the individual water and ethanol volumes. This phenomenon of contracting volume is a result of interstitial packing and molecular interaction (hydrogen bonding) between water and ethanol molecules in solution. Because the volume of the solution depends on its composition, it is convenient to discuss volumetric effects of ethanol-water mixtures in terms of partial molar volume.

The partial molar volume, V_i , is defined as follows:

$$V_i = (\partial V / \partial n_i)_{T,p,n_j}$$

The equation above can be stated by saying that V_i is the change in total volume per mole of “i” added, when some amount of “i” is added to the mixture at constant temperature, pressure and amount of other substances [37]. Using partial molar volumes, the total volume of a solution can be given by the following equation:

$$V_T = V_1 n_1 + V_2 n_2 + \dots + V_N n_N$$

$$V_T = (\partial V / \partial n_1)_{T,p,n_j} * n_1 + (\partial V / \partial n_2)_{T,p,n_j} * n_2 + \dots + (\partial V / \partial n_N)_{T,p,n_j} * n_N$$

The total volume of the solution can be discovered by determining the partial molar volumes of ethanol and water, as well as the mass fractions of the mixture. Partial molar volumes of water and ethanol can be found using the equation below [30].

$$V_e = \left(v + \omega_w (\partial V / \partial \omega_e)_{T,p,n_j} \right) M_e \quad \& \quad V_w = \left(v + \omega_e (\partial V / \partial \omega_w)_{T,p,n_j} \right) M_w,$$

In this equation, v refers to the specific volume of the solution, ω represents the mass fraction, M is indicative of molecular weight, and the subscripts “e” and “w” refer to

water and ethanol, respectively. The densities of 54 different water-ethanol mixtures are given by Pecar and Dolecek along with their respective mole fractions of ethanol. The mass fraction of ethanol and its corresponding specific volume are calculated using the data provided for these different mixtures. Specific volumes are plotted against the mass fraction of ethanol and the best fit curve is applied to the data-plot by the third degree polynomial. Then, the derivative of this polynomial is deduced, and the partial molar volume can be determined. The total volume of solution can then be predicted using the following equation:

$$V_T = (\partial V / \partial n_e)_{T,p,n_j} * n_e + (\partial V / \partial n_w)_{T,p,n_j} * n_2$$

By assuming that 1 mole of solution is present, n_e & n_w can be set equal to the mole fractions of ethanol and water, respectively.

Using the equations above and data provided by Pecar & Dolecek it can be shown that approximately one mole of ethanol and a relatively small amount of water has a total volume nearly equal to the molar volume of ethanol. However, when significant amounts of both water and ethanol are present in a mixture, the total volume is less than the individual volumes of ethanol and water standing alone. A table illustrating these volumetric effects is provided with a maximum contraction of -3.4% occurring at an ethanol mole fraction of 0.2745.

Appendix D Comparison of results from the EPI Suite™ calculator and SPARC for K_{ow} for 5 °C and 25 °C.

Figure 19 shows a comparison of $\log K_{ow}$ results from SPARC at 5 °C and 15 °C, EPI-Suite™, and experimental data reported by EPI-Suite™. Generally good agreement was seen among these sources. The SPARC results show more variation with temperature at higher K_{ow} s than for the low values. Figure 20 shows assumed variability of one-half log unit in SPARC K_{ow} results on both log-log and linear scales. Note that as the value of K_{ow} increases so does the variability on the linear scale.

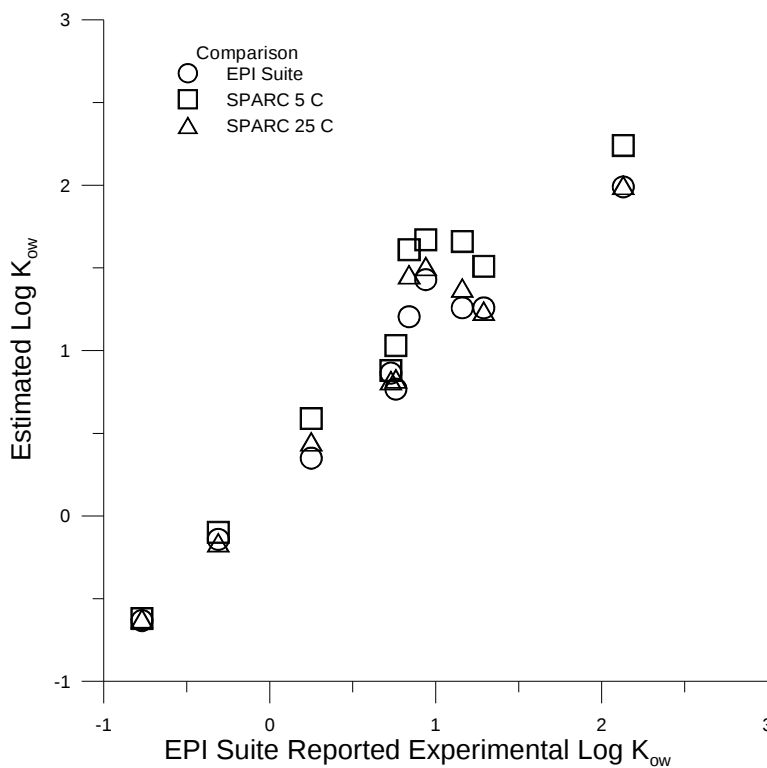


Figure 19 Estimates from the EPA EPI Suite calculator, SPARC at 5 °C and 25 °C plotted against experimental results reported with EPI Suite results.

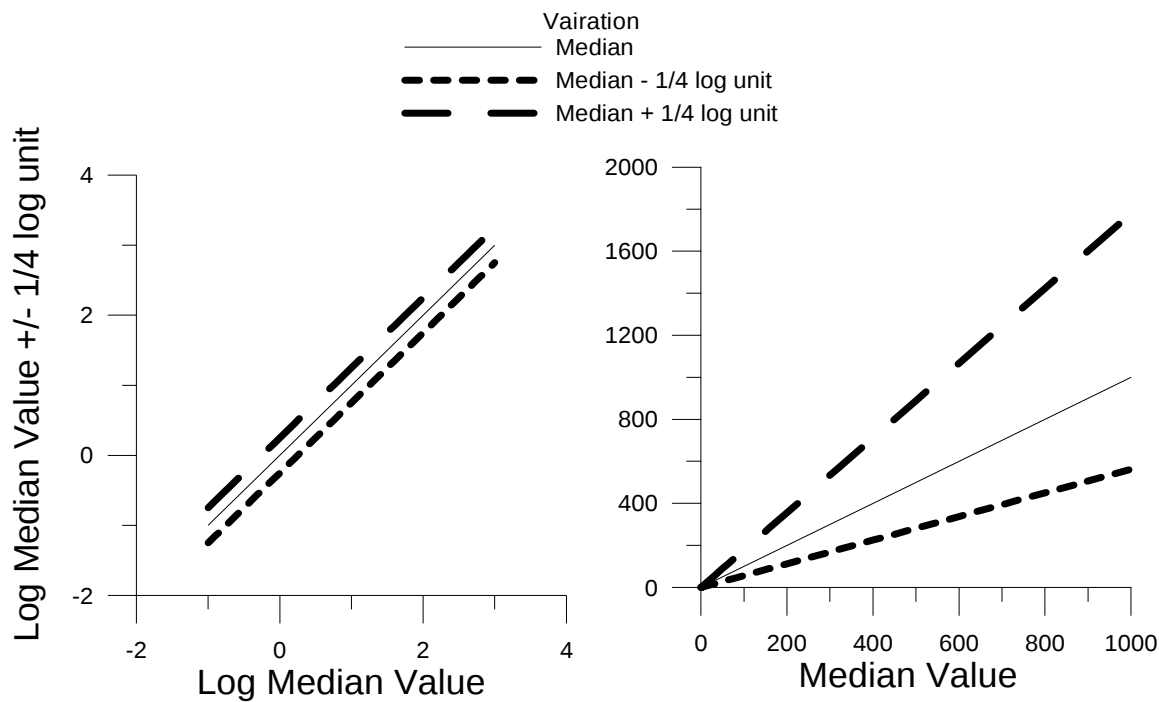


Figure 20 Example of variation in SPARC results given an assumed variability (error) of one-half log unit. The left hand graph shows results on a log-log scale. The right hand graph shows the same variation on a linear scale.

Appendix E SPARC Property Results for 5 °C to 45 °C

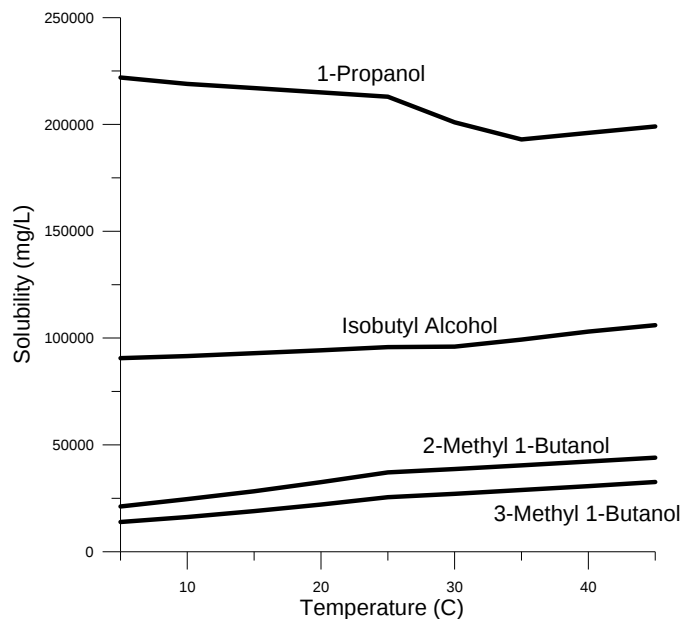


Figure 21 Solubility of the alcohols found in the wet and dry mill samples. Ethanol and methanol do not appear because their solubility is infinite.

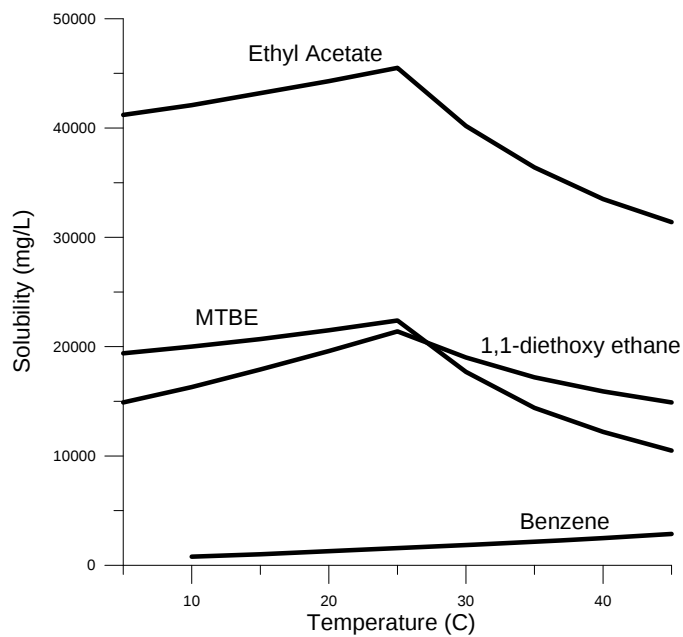


Figure 22 Solubility of ethyl acetate and 1,1-diethoxy ethane, compounds found in the wet mill sample. Solubilities of benzene and MTBE are plotted for comparison.

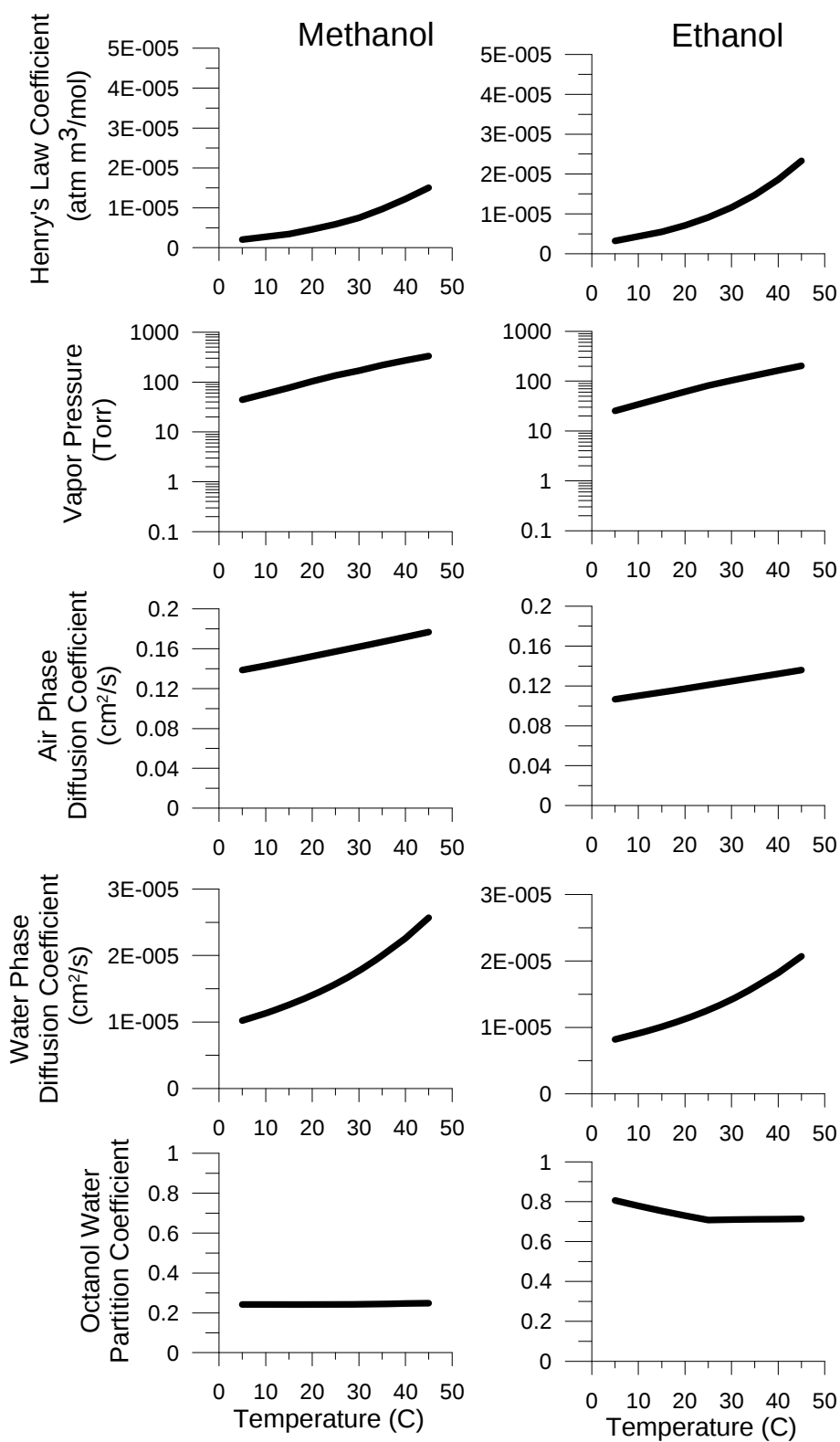


Figure 23 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for methanol and ethanol estimated by the SPARC calculator.

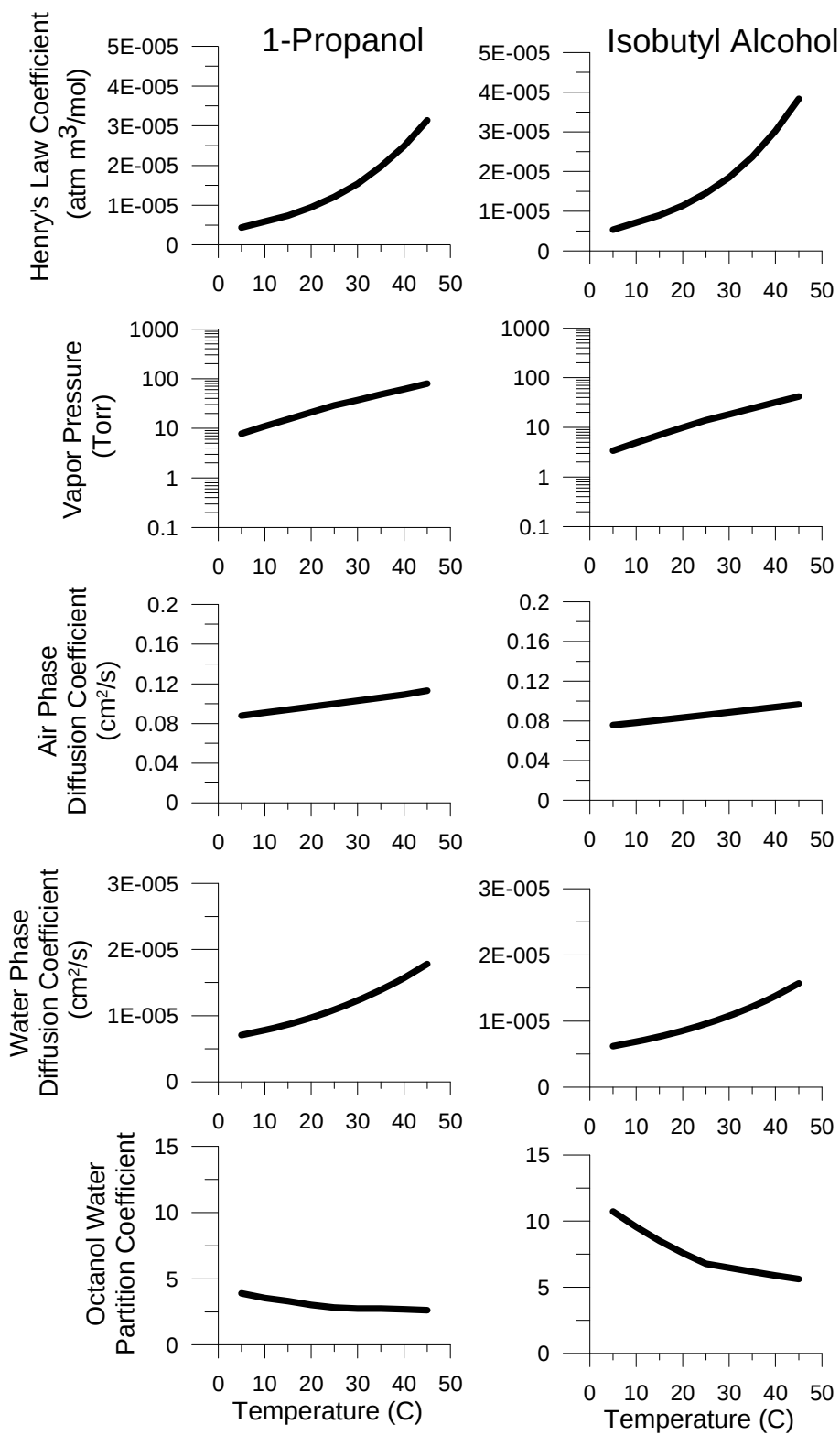


Figure 24 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for 1-propanol and isobutyl alcohol estimated by the SPARC calculator.

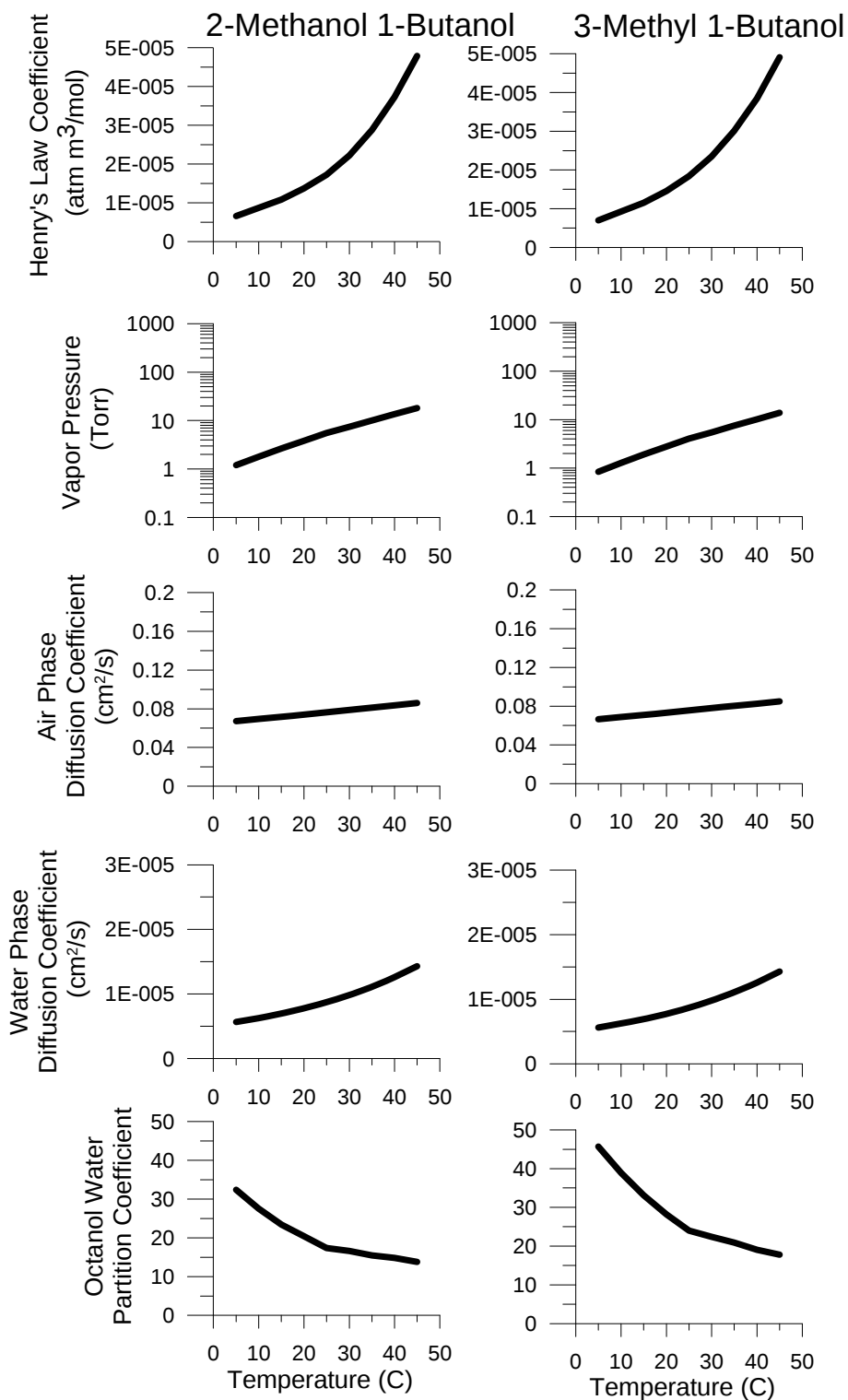


Figure 25 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for 2-methyl 1-butane and 3-methyl 1-butane estimated by the SPARC calculator.

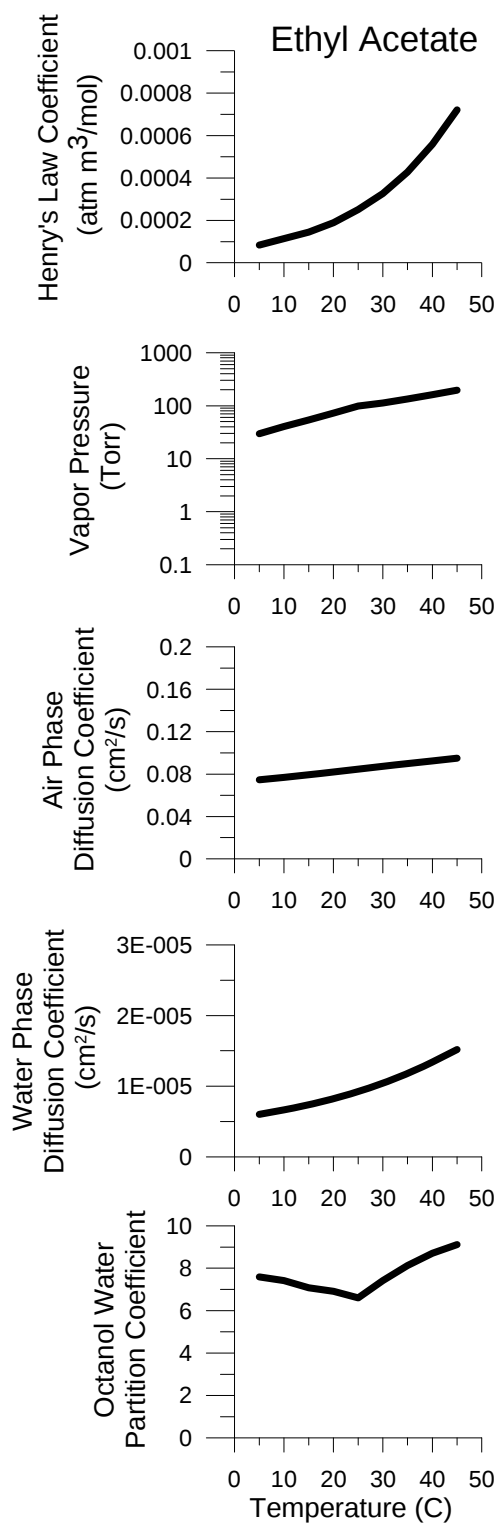


Figure 26 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for ethyl acetate estimated by the SPARC calculator.

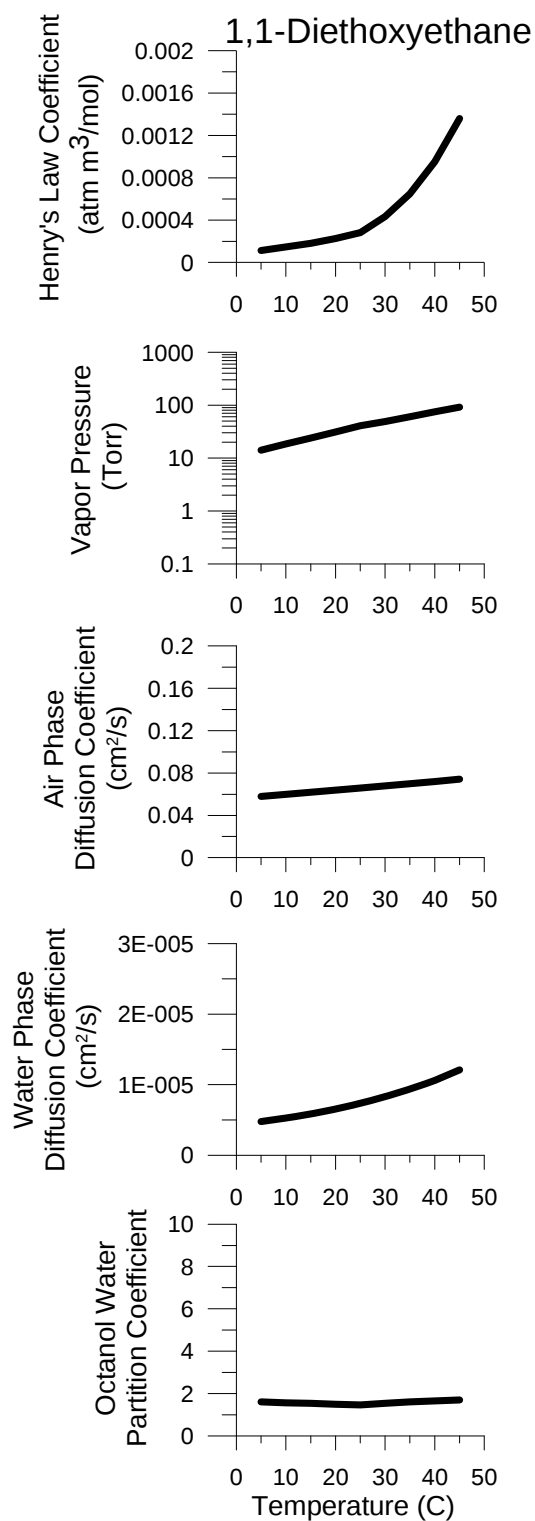


Figure 27 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for 1,1-diethoxyethane estimated by the SPARC calculator.

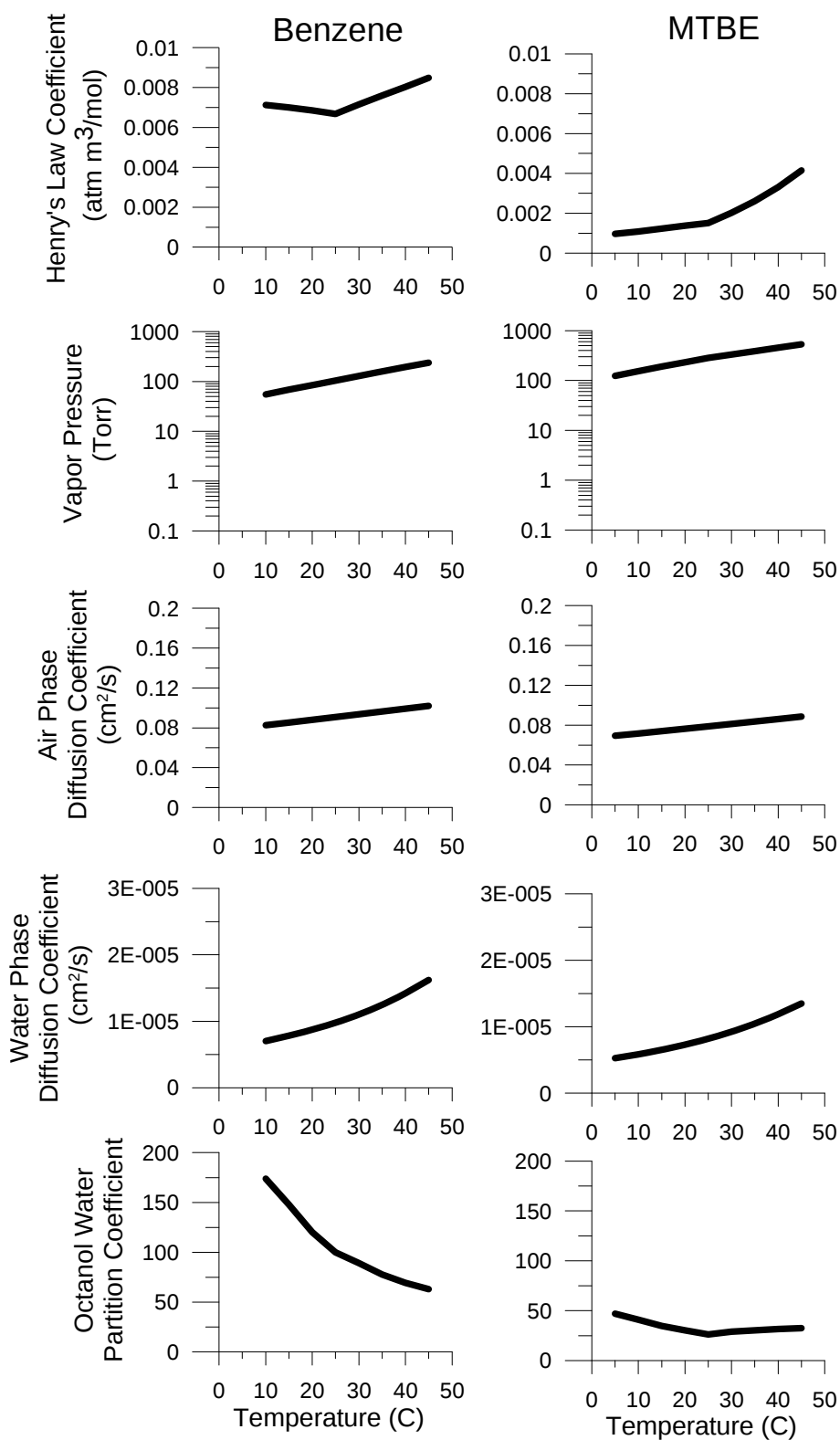


Figure 28 Properties (Henry's Law coefficient, vapor pressure, air phase diffusion coefficient, octanol/water partition coefficient) for benzene and methyl *tert*-butyl ether (MTBE) estimated by the SPARC calculator.



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