

## **HIGH PERFORMANCE OXYFUELS**

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### **ABSTRACT**

Alcohols and ethers are being used increasingly in gasoline blends because they provide economic octane enhancement (important because of phase-out of lead) and because they decrease CO levels in auto emissions. Gasoline containing oxygenates at the 2% O level is mandated in six metropolitan areas. Methyl-tertiary-butyl ether, (MTBE) and ethanol each constitutes 1% of overall U. S. gasoline usage. The criteria for synfuels are not cents per MM Btus but are based on their performance values.

Opportunities for improvements for conversion of syngas to oxygenates are catalysts which 1) have higher selectivity to molecular species useful as high performance fuels and which eliminate methane formation, 2) operate at lower temperatures and pressures, thus lowering plant costs, 3) integrate coal gasification and oxygenate synthesis, 4) improve fuel use.

Promising research includes catalytic concepts of dual functionality; controlled metal particle size; bimetallics, zeolites; organometallic precursors; enzymes; melt and slurry systems; catalysts design by expert systems (AI). Likewise, research on surface structure and reaction mechanisms is providing critical guidance in development of these concepts.

### **MOTIVATION FOR OXYFUELS**

In the past, the principal tool for energy policy has been the market place. Recently however, social and political issues have become important in determining policy, particularly those which concern environmental protection and balance of trade/national security. Gasoline and diesel fuels manufactured from petroleum resources have been our traditional transportation fuels. However, importation of foreign oil has been rising rapidly and now

accounts for about 50% of our petroleum usage, contributing greatly to our 12 digit balance of trade deficit. Further, due in large part to automobile exhaust emissions, many parts of the US have major ozone problems and as many as 65 metropolitan areas have not attained federal CO standards (1).

Oxyfuels, particularly alcohols and ethers, can help alleviate these problems (2). Oxyfuels can be made from natural gas and from abundant coal resources. There are two immediate benefits from the use of oxyfuels. First, concern for the environment has led to the phase-out of lead in gasoline which has created a need for octane enhancement of the gasoline pool. Blending in oxyfuels can provide needed octane enhancement. Secondly, blending of oxygenates can lower CO emissions and reduce active hydrocarbon emissions which lead to ozone formation. Six metropolitan areas, Denver, Albuquerque, Los Angeles, Las Vegas, Phoenix, Reno and Tucson, require that gasoline contain oxygenates corresponding to 2% oxygen. This can be met by use of about 11% MTBE or 6% ethanol. Consideration is being given to increase requirements to about 3% O.

A further motivation for oxyfuels is provided by the Alternative Motor Fuels Act (PL 100- 494, 1988). This act gives American automobile companies a real incentive to start building cars powered by alternative fuels by adjusting the Federally mandated average fuel economy rating to reflect gasoline saved by those vehicles.

Because of their favorable performance in automobile use, oxyfuels are now valued, not on the basis of their heats of combustion, that is, cents per MM BTU, but on their values in contributing to environmental protection and octane enhancement. It is on the basis of their favorable performance that oxyfuels have a potentially large future. This future can be enhanced by improved technology for fuel manufacture and use. Improved technology has been the subject of intensive research, the main topic of this paper.

## **STATUS**

Oxygenates of interest as fuels are shown in table 1 (2). Most are manufactured by a two step process. First, synthesis gas, a mixture of hydrogen and carbon oxides, is

made from methane, coal or petroleum fractions including residua. Then the synthesis gas is reacted over a catalyst which directs the hydrogenation of the carbon oxides to the desired products. These may be hydrocarbons as in SASOL, South Africa, or oxygenates, particularly methanol or mixed alcohols.

Fuel ethanol is produced by fermentation of corn or sugar cane. Isopropanol and sec-butyl alcohol are made by hydration of propylene and butylenes, respectively. Tert-butanol is a byproduct in the manufacture of propylene oxide. Fuel ethers are manufactured by reacting the appropriate alcohol with either isobutene or isopentene.

Oxygenates have penetrated the 300 million gallon per day motor fuel market in the U.S. to an increasing extent. At present, ethanol and MTBE each are being used to the extent of 3 million gallons per day. The growth in the use of MTBE has been phenomenal. The first MTBE plant was built in Italy in 1973. The growing U.S. manufacture and use is shown in table 2. Note that MTBE represents an indirect but straightforward method of using methanol in gasoline. MTBE is regarded as a more satisfactory method of using methanol in gasoline blends because of its better compatibility with gasoline compared with methanol.

Another recognition of the value of MTBE is seen in the action by ARCO to manufacture and distribute 'emission control gasoline', EC-1. This reformulated gasoline contains MTBE and is designated for use in autos which are not equipped with catalytic converters. EC-1 contains a minimum of 1% oxygen by weight.

#### **IMPROVED TECHNOLOGY FOR OXYFUELS**

There are significant opportunities for improvements in the manufacture of fuel oxygenates from syngas (3). Promising catalytic research results have been reviewed in a report (4) prepared for the International Energy Agency, sponsored in part by D.O.E. A variety of new concepts have been investigated with the aim of improved synthesis of fuel oxygenates. Included are: catalysts derived from alloys, catalyst designed by artificial intelligence, base catalysts systems, dual function catalysts, enzymes, hybrid catalysts, melt systems, multimetal components, organometallic precursors, partial poisoning, particle size

control, Raney metals, ship-in-a-bottle fabrication, and slurry systems.

The application of these catalytic concepts can provide four types of improvements:

- I) Higher selectivity to molecular species useful as high performance fuels; elimination of methane formation.
- II) Lower plant investment and operating costs.
- III) Savings by integration of gasification and synthesis.
- IV) Improved fuels use.

## **I. IMPROVED SELECTIVITY**

Mixed alcohols are desired as fuels because, when blended in gasoline, they raise octane ratings and also decrease CO emissions from autos. The distributions of alcohols for mixed-alcohol processes which have been developed are shown in table 3. It would be desirable for the synthesis reaction to provide a larger proportion of ethanol and less methane formation.

### Particle size control of selectivity.

An interesting approach to selectivity control is through the use of control of the catalyst metal particle size. As shown in figure 1 (5), using Rh/SiO<sub>2</sub> catalysts, methanol is produced selectively at high Rh dispersion, while C<sub>2</sub> oxygenates are favored by larger particle size, for example 0.35 nm. Methane formation increases with decreased dispersion. The rationale for this catalysts structure/performance relationship can be understood on the basis of the concept that for formation of methane and higher alcohols, the catalysts must possess a multiplicity of sites, presumably neighboring, so as to accommodate simultaneous dissociative chemisorption of CO and of H<sub>2</sub>. Larger ensembles of metal atoms are more likely to be able to provide these multisites than smaller crystallites and hence larger crystallites favor formation of methane and higher alcohols.

### Multimetallic catalysts for selectivity control.

The impetus for research utilizing supported Rh catalysts can be traced to the discovery at Union Carbide that selectivity to ethanol can be improved by adding small amounts of modifying metals such as Fe (6). Recently, Arakawa and co-workers (7) have extended this research area

in a systematic way and have classified promoters of Rh-based catalysts according to those which increase or decrease metal dispersion, and those which accelerate CO dissociation. The suggested effects therefore on selectivity to oxygenate synthesis are depicted schematically in figure 2 (7).

#### Dual functionality for selectivity control.

The concept of dual function catalysts capable of balanced acceleration of two different types of chemical reactions has been used successfully, for example in naphtha reforming (8). Recently, dual functionality has been shown to operate in an important way in CO hydrogenation in which CO and H<sub>2</sub> are activated on separate but related catalytic sites. An important feature of the recognition of dual functionality is that it permits an understanding of consequent fabrication of catalysts of superior capabilities. Dual functionality is illustrated by recent research results obtained with molybdenum-containing catalysts containing added a) group VIII metal or b) alkali metal.

Rh/Mo/Al<sub>2</sub>O<sub>3</sub>. Supported Rh catalysts have been known to hydrogenate CO to oxygenates and, as mentioned above, selectivity can be increased by addition of small amounts of modifying metals. However, recently it has been discovered that the addition of large amounts of molybdena increases greatly activity for CO hydrogenation (9, 10, 11, 12, 13). Selectivity to oxygenates is also increased. Pertinent research results obtained at the University of Delaware are now discussed. A 3% Rh/Al<sub>2</sub>O<sub>3</sub> catalyst was tested at 250° (all temperatures are °C) using a H<sub>2</sub>/CO=2 mixture at 30 MPa. 28% of the CO was hydrogenated. However with the addition of 7.5% Mo (in oxide form), activity was increased 12-fold (same conversion at 36,000 GHSV). Selectivity to oxygenates increased to 66%.

The number of Rh sites active for CO activation were identified by CO chemisorption. It was found that CO chemisorption decreased from 112 micromoles per gram of the Rh/Al<sub>2</sub>O<sub>3</sub> catalyst to 28 micromoles for a Rh/15% Mo/Al<sub>2</sub>O<sub>3</sub> catalyst whilst activity for CO hydrogenation increased 38-fold. Thus activity per Rh site (identified by CO chemisorption) the turn-over frequency was increased 150-fold by the addition of the molybdena!

In other experiments (ethylene hydrogenation) it was established that CO inhibits the hydrogenation capability of Rh/Al<sub>2</sub>O<sub>3</sub> catalyst but this inhibition does not occur with Rh/Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. Additional insight was gained from kinetic measurements. It was also found that CO inhibits CO hydrogenation capability of Rh/Al<sub>2</sub>O<sub>3</sub> but not of Rh/Mo/Al<sub>2</sub>O<sub>3</sub>.

These and other characterization measurements have led to the concept that a dual site mechanism operates in which CO is activated by Rh metal and H<sub>2</sub> by Mo in a +5 or +4 oxidation state (12). a spill-over effect occurs (10) with activated H migrating to react with activated CO Fig. 3 (12). Increased activity is believed to be due to increased hydrogenation capability, previously limiting. An important feature is that H<sub>2</sub> activation occurs on Mo sites which are not inhibited by CO. CO inhibits H<sub>2</sub> chemisorption on Rh sites. The increased oxygenates and decreased methane formation are due to the increased hydrogenation of activated, undissociated CO.

It was determined that the apparent E<sub>activation</sub> for methanol formation (18Kcal/mole) is much lower than that for methane formation (34 Kcal/mole). This also attests to the difference in mechanism for formation of these two C<sub>1</sub> chemicals. Differences in E<sub>act</sub> for methane and methanol also provides for control of selectivity by operation at lower temperatures for higher selectivity to oxygenates (14).

The importance of these results is that they provide a guide for the design of better catalysts through an understanding of catalyst structure/performance. Of particular promise is the guidance provided in the search for the best Rh-Mo inter relationship, an opportunity highlighted by the 150-fold increase in activity per site. How to make more of these super-active sites!

Alkali-MoS<sub>2</sub>-Support. Bifunctionality has also been identified for Mo-containing catalysts comprised of alkali-MoS<sub>2</sub>-support that catalyze CO hydrogenation to oxygenates. It has been proposed (15) that CO is activated by the alkali and H<sub>2</sub> is dissociatively activated by MoS<sub>2</sub>. Large



observed with Cs/Cu/ZnO catalysts which minimizes the formation of ethanol due to chain growth by rapid beta addition rather than CO insertion.

Mixed alcohols synthesis over MoS<sub>2</sub> catalysts, including those doubly promoted with alkali and group VIII metal, has been the subject of a substantial development effort. High yields of ethanol were demonstrated over K/CoS/MoS<sub>2</sub>, table 3 (16). Of particular importance is the observation that homologation of alcohols occurs to a significant extent. This was taken as an explanation for the great deviation from the Anderson-Shulz-Flory distribution pattern (16). As pointed out, the commercial significance is that methanol, the lowest value alcohol in the mixed alcohol product, can be adjusted via recycle to any desired level and/or that inexpensive purchased methanol could be fed along with syngas dramatically increasing reactor productivity.

#### Isoalcohols/MTBE

It should be pointed out that higher alcohols synthesized over Cu/ZnO/A<sub>2</sub>O<sub>3</sub> catalysts have a branched chain structure. Of the butanols synthesized in the Lurgi process, 70% are isobutanol (2-methyl-propanol) (no tertiary butanol). This has a number of implications. One is that the isobutanol can be dehydrated to form isobutylene which can then be reacted with the methanol to form MTBE. Thus, valuable MTBE can be synthesized entirely from syngas. Reactions for MTBE are given in Fig. 4. This suggests the possibility that through research a way could be devised to manufacture MTBE from syngas either in a single step or at least in fewer steps.

## **II LOWER PLANT COSTS**

Although the conversion of syngas to methanol is highly selective, 99%, its manufacture can be improved by improving thermal efficiency and/or by reducing recycle and purification costs. This has led to engineering ideas for process improvements which could lower plant investment and operating costs.

Slurry catalysts. For instance, a major effort is underway to develop a liquid-phase methanol synthesis process in which catalyst particles are suspended in an inert liquid

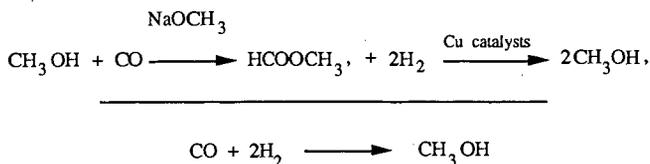
medium. This system prevents excessive temperature increases and so permits higher syngas conversion per pass, reducing expensive recycle. The catalyst is also able to provide shift reaction in which CO reacts with water to produce H<sub>2</sub> and CO<sub>2</sub>. This permits the use of less expensive syngas having lower H<sub>2</sub>/CO ratios. The so-called LPMEOH process has been operated at 8 tons per day production rate and construction and operation of a commercial plant has been proposed (17).

Integrated Synthesis/Separation. A novel approach to circumvent thermodynamic equilibrium limitations to CO hydrogenation is to remove methanol from the reactor as it is formed (18). A trickle flow principle has been demonstrated in which synthesis catalyst pellets form a stationary bed and solid adsorbent trickles downward over (through) the packed bed. This Gas-Solid-Solid-Trickle-Flow-Reactor has been demonstrated; synthesis conversion proceeds to complete conversion.

#### Ultra high-activity catalysts.

Alloys. A still different approach is to search for catalysts so active that CO hydrogenation can be carried out at much lower temperatures, say 175°, than is used conventionally, about 250°. Perhaps the research on dual function catalysts can lead to such a catalysts. Catalysts derived from an intermetallic copper/Thx alloy precursor have been discovered by researchers at the BuMines at Reno (19) to exhibit extraordinary high activity for methanol synthesis by CO hydrogenation. Workers at ICI (20) extended this discovery and demonstrated that a catalyst derived from CuCe<sub>0.5</sub> precursor is active for synthesis as low as 100°. Moreover, a stable activity of 25 moles of methanol per Kg catalyst per hour was obtained. However, this catalyst is irreversibly deactivated by small amounts of CO<sub>2</sub> in the syngas. This presents a challenge to understand the reaction mechanism and to utilize this discovery in practical process technology.

Base catalysts. An entirely different liquid phase catalytic system for methanol manufacture involves the reaction of CO with a strong base such as sodium methoxide. As shown in the following equations, methyl formate can be prepared, followed by catalytic hydrogenation of the methyl formate to methanol.



The synthesis reaction is carried out at 80° and 3 MPa, whilst the hydrogenation is operated at 110-180°. To be economic, it is deemed essential that the synthesis and hydrogenolysis be combined. Thus, a hydrogenation catalyst which is active at a lower temperature is needed. Some success has been obtained using highly active Raney copper (21).

A 1984 report (22) by scientists at Brookhaven describes a novel approach to methanol synthesis. Two catalyst components are in the liquid phase, a metal (molybdenum) carbonyl that activates CO and a hydride that hydrogenates the carbonyl to methanol and is regenerated by reaction with hydrogen. A further improvement was reported in which synthesis temperature of 100° were used indicating extraordinary activities for methanol synthesis. Technical information has not been made public.

### III INTEGRATED GASIFICATION-OXYFUEL SYNTHESIS: IG-OS

The objective of IG-OS is the conversion of the crude hydrocarbon feed stocks to oxygenates in one step or at least, without separation, in one reactor. This may or may not involve the intermediate production of CO and H<sub>2</sub>. Intensive research efforts are underway to convert methane by direct oxidation to alcohols or to ethylene which can be hydrated to ethanol. It is proposed that the direct conversion of coal to oxygenates may also be possible. Related to this concept is the observation that methane formation occurred in the Synthane process of coal gasification. This led to the suggestion of IGHS, integrated gasification/hydrocarbon synthesis (23). Actually it has been demonstrated that by the addition of a nickel catalyst during coal gasification, a considerable amount of methane can be synthesized. However, the nickel catalyst became deactivated by sulfur. Coal gasification

usually occurs at temperatures above 800°. However, the gasification temperature can be lowered by the use of alkali catalysts. The synthesis of methanol occurs usually at 250° and for higher alcohols temperatures of 350° + can be used. For integrated coal gasification/oxygenate synthesis it will be necessary to develop combination catalytic systems which perform gasification and oxysynthesis at the same temperature. The combination catalyst system may include capability for oxidation, steam/carbon reaction and synthesis. The synthesis catalyst must be sulfur stable, not believed to be impossible considering the success of MoS<sub>2</sub> catalysts in alcohol synthesis.

#### **IV CATALYSTS FOR IMPROVED FUEL USE**

The value of a fuel should be judged in terms of effectiveness in the system: fuel manufacture/fuel use. Catalysis can contribute to more efficient use of oxyfuels. Syngas can be made available as a fuel by the catalytic decomposition of methanol or by catalytic reaction of methanol with steam. There is a gain in fuel efficiency if waste heat is used to carry out the endothermic conversion of methanol to syngas fuel. When waste exhaust heat is used (available on-board an auto or power plant) a gain in efficiency of 15-20% is predicted to be possible (24) although in actual tests fuel consumption benefits have been lower.

Catalysts for improved diesel fuel use is also possible. Diesel engines are more efficient because of the high compression ratio at which they operate. However, use of hydrocarbon diesel fuels is recognized as causing pollution, a situation which could be improved by the use of methanol. However, the combustion characteristics of heat methanol are not favorable for diesel (non-spark plug) use. The use of an additive such as AVOCET - termed a "chemical spark plug" - is being developed (25). An additional opportunity would be to develop in-cylinder catalysts which would provide for favorable methanol combustion under diesel conditions.

Finally, it should be said that many believe that methanol will become a major fuel not only as an alternative for diesel, but also for gasoline as well. This is being recognized in two recent events. The first is the

marketing in California by Arco and Chevron of M-85 which contains 85% methanol. The second is the extensive testing being carried out with flexible fuel vehicles, FFV, which can operate on gasoline, methanol or any combination of these (2).

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Table 1. FUEL OXYGENATES PROPERTIES

	METHANOL	ETHANOL	ISOPROPYL ALCOHOL	SECONDARY BUTYL ALCOHOL	TERTIARY BUTYL ALCOHOL	MIXED ALCOHOLS	MTBE METHYL TERTIARY BUTYL ETHER	ETBE ETHYL TERTIARY BUTYL ETHER	TAME TERTIARY AMYL METHYL ETHER	GASOLINE
	MeOH	EtOH	IPA	SBA	TBA	MAS*	MTBE	ETBE	TAME	GASO
Blending Octane RON + MON 2	101	101	106	99	100	106	108	111	102	87
Heat of Combustion Thousands BTU's Per Gallon	64.5	76.5	94.6	101.4	101.1		108.5	116.5	111.9	124.8
Density	0.79	0.79	0.79	0.80	0.80	0.80	0.75	0.74	0.77	0.74
Pounds Per Gallon	6.6	6.6	6.6	6.8	6.8	6.7	6.3	6.2	6.4	6.2
Boiling Point Degrees C	64.6	78.5	82.4	99.5	82.6	range	55.4	72.8	86.3	range
Production In USA, 1987 Millions of Gallons/Day	3.0	2.9	0.6				2.8			300

Fuels of 0.79 density weigh 6.6 pounds per gallon, 277 pounds per barrel of 42 US gallons; 1 ton contains 7.2 barrels or 303 gallons.

Table 2. U.S. production of MTBE and methanol consumption for MTBE millions of gallons per year

Year	MTBE	Methanol
1982	190	65
1983	250	85
1984	370	130
1985	430	150
1986	830	290
1987	1030	360
* 1989	1530	534
** 1989	2010	700

\* Capacity  
 \*\* Capacity +  
 planned

Table 3. Composition of fuel alcohols from syngas

Alcohol, %	C1	C2	C3	C4	C5+	Other oxvgenates	Catalyst
MAS (SEHT)	69	3	4	13	9	2	K/Zn/Cr
Substifuel (IFP)	64	25	6	2	2.5	0.5	K/Cu/Co/Al
Octamix (Lurgi)	62	7	4	8	19	--	alkali/ Cu/Zn/Cr
AS (Dow)	26 <sup>a</sup>	48	14	3.5	0.5	8	CoS/MoS <sub>2</sub> / K

<sup>a</sup> Methanol can be recycled to extinction, increasing ethanol %.

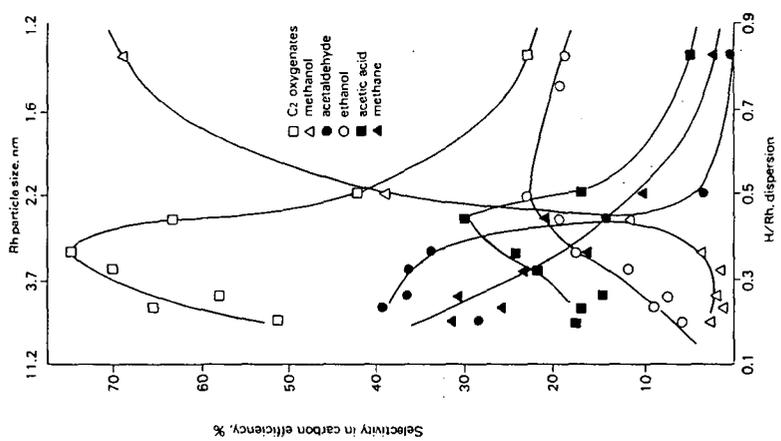


Figure 1. Relationship between dispersion and selectivity

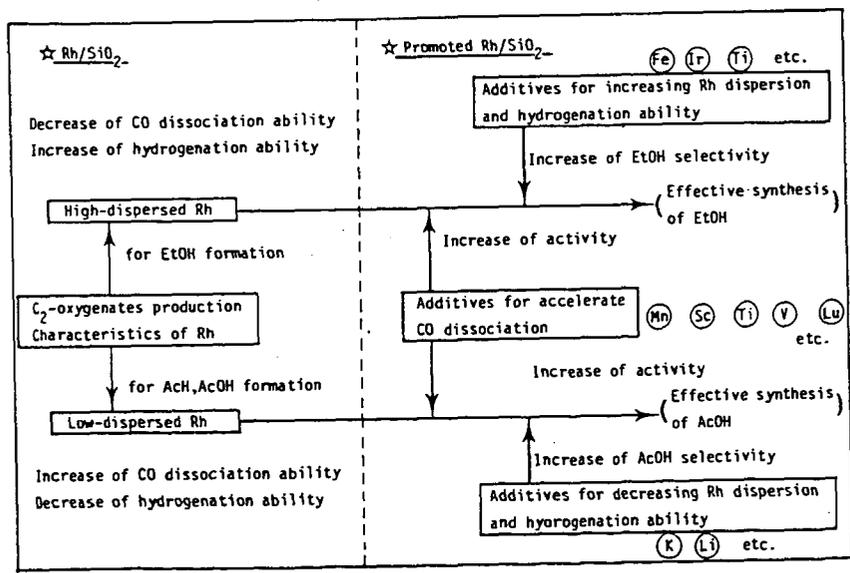


Figure 2. The roles of additives for effective synthesis of EtOH and AcOH.

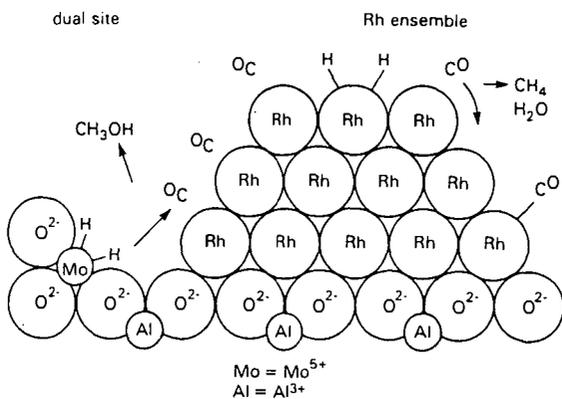


Figure 3. Proposed structure/reactivity scheme, rhodium-molybdena-alumina catalyst

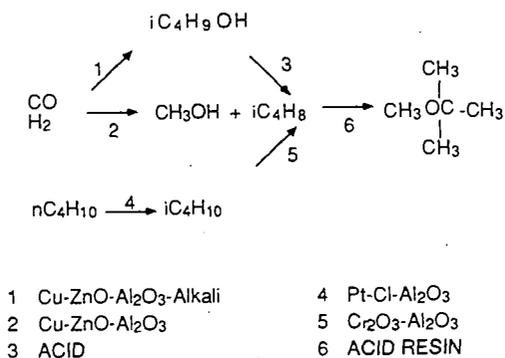


Figure 4. Synthesis of Methyl-tertiary-butyl ether, MTBE

## PERFORMANCE ASSESSMENT OF NOVEL SUBSTITUTE GASOLINE COMPONENTS

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### INTRODUCTION

During the last several years there has been an increasing interest in the European Economic Community in the savings of crude oil through the use of substitute fuel components in gasoline, which was officially expressed by EEC regulation 536/1985 and other regulations that are currently in effect. When this regulation was initially conceived in 1982, the principal impetus was concern over the availability of imported crude oil in the Community; as time went by, however, environmental considerations assumed major importance. Given this interest, which is also manifest in other parts of the world, it is important to obtain an accurate understanding of the effects of the substitute fuel components on engine efficiency and pollution abatement. The major difference between traditional gasoline and the substitute fuels under consideration lies in their chemical structure and particularly the oxygen content of the latter.

The first problem that must be solved in testing for increased fuel performance in gasoline engines is the nature of the base fuel to which the additives and extenders will be blended. Most of the research work that has been reported [1-6] employs full range, unleaded gasoline or specific refinery streams, such as reformates [7]. The physical characteristics of these fuels (such as vapor pressure, RON, MON, distillation behavior, proportion of saturates, olefins and aromatics) are usually specified; nevertheless, this does not permit exact duplication or extension of the reported work because it is impossible to procure the exact fuel that was initially employed. To overcome this problem, API-45 [8] used a 60:40 mixture of iso-octane and n-heptane as a base fuel, whereas other workers [9] employed either pure iso-octane or 80 octane PRF. This latter method does permit duplication of experiments but suffers from unrealistic (usually too high) BRON estimates, because of the dissimilarity of the base fuels to actual gasoline. As an example of the disparities that can be encountered, the case of MTBE may be mentioned, whose BRON is listed as 148 in API-45 [8] although in actual practice [10] it ranges between 110 and 120 for most types of gasoline.

Our approach in this matter has been to prepare a series of base fuels which are blends of pure hydrocarbons so as to have reproducible compositions, but which at the same time are complex enough to approach actual gasoline in behavior. It should be remembered, of course, that the high cost of pure hydrocarbons places an economic limit on the complexity of the mixture and the choice of components.

Table 1 contains the compositions and octane numbers of all base fuels that were prepared and tested during the course of this work, along with the RON and BRON values of the individual

constituents, as reported in API-45 [8].

In order to be able to evaluate the results quickly, a relative effectiveness scale was introduced, by which all fuels were compared to the performance of MTBE, both on a molar and on a weight basis; the effectiveness of the latter was taken as unity. The results so far are encouraging, since some useful conclusions can be drawn following this systematic approach.

#### NOVEL FUEL COMPONENTS: SYNTHETIC ASPECTS

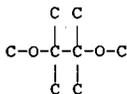
The aim of the chemical synthesis component of the research program is to make available, for testing and correlation purposes, structures that appear promising but at the same time can be easily prepared from readily available starting materials; exotic compounds and intricate synthetic procedures are considered to be outside the scope of our current effort.

In this vein, the procedures that were selected included the Leuckart reaction (preparation of substituted amines), acid catalyzed additions (preparation of ethers and dioxolanes) and simple condensation of amines with formic acid (preparation of substituted formamides), along with classical etherification and Mannich condensation.

An intriguing molecule, which in principle should be an effective oxygenate component in gasoline, is pinacol dimethyl ether (PDME); it is structurally similar to MTBE, except that it contains two of each of the active molecular centers (tertiary carbons and methyl ethers) per molecule:



MTBE



PDME

Another attractive feature of PDME is that it can in principle be derived from acetone via the pinacol reduction and trapping of the intermediate di-anion. Attempted formation of PDME by methylation of the magnesium salt of pinacol that is formed under the classical conditions [13] failed because of the extreme lack of solubility of the salt. In a second attempt, the more soluble aluminum salt [14] was employed instead, but again very little of the desired product was formed. Very recently, PDME was finally prepared by the Williamson etherification of the di-sodium salt of preformed pinacol, but its antiknock activity has not yet been measured.

#### NOVEL FUEL COMPONENTS: ANTI-KNOCK PERFORMANCE AND STRUCTURE-ACTIVITY CORRELATIONS

##### Comparison of activity of oxygen atom with nitrogen atom in the same molecular environment

From the results that are depicted in Table 2 it can be seen that aliphatic amines are definitely more active anti-knock additives than the equivalent alcohols; this holds true as long as there is at least one hydrogen attached to the amine nitrogen. On

the contrary, tertiary amine groups have a very strong pro-knock effect; an extreme example is N,N,N',N'-tetramethylethylenediamine, whose two tertiary nitrogens transform it into what is probably the most pro-knock simple amine. An even more striking performance is displayed by the commercially available tetrakis-dimethylaminoethylene, whose four tertiary nitrogens lower its BRON to a value of about -1000. This behavior of aliphatic tertiary amines is in sharp contrast to that of aromatic amines; thus, in the benzene series, tertiary amines (e.g. N,N-dimethylaniline) have no effect on the octane rating of the fuel [11] and in the fulvene series compounds like 6-dimethylaminofulvene are among the most active non-metallic antiknock additives that have been described so far [4]. Another interesting observation from the results in Table 3 is that the known anti-knock activity of the tert-butyl group is matched or in some cases surpassed by that of the iso-butyl group.

In the case of cyclic structures, whose performance is shown in Table 4, the contrast between secondary and tertiary amines is again quite remarkable; the replacement of pyrrolidine by N-methylpyrrolidine at the same concentration (3%) in the same fuel reduces the octane rating by a full 8 RON units! It was also decided to test these two groups in direct comparison and a molecule that contains both of them, N-methyl piperazine, was selected. The effect of the tertiary nitrogen was stronger and N-methylpiperazine displayed proknock behavior.

Other conclusions that can be drawn from the data on Table 4 are that heterocyclic five-membered rings are better performers than equivalent six-membered rings; this is in agreement with the higher activity of cyclopentane (API BRON 141) when compared with cyclohexane (API BRON 110). In addition, the presence in the molecule of the oxymethylene group C-O-CH<sub>2</sub>-C leads to pro-knock behavior. This again is in agreement with the reported [5] pro-knock activity of compounds that contain the oxy-methylene group, such as methylal and dimethyl ether; by contrast, antiknock ethers such as MTBE and TAME are devoid of this structural feature.

#### Furan derivatives

The furan moiety has been known [8,14] to be an antiknock molecular feature. Furfuryl alcohol is one of the most readily available and inexpensive furan derivatives which, upon testing, displayed high antiknock performance, having a higher BRON rating than MTBE and being about 50% more effective on a weight and molar basis. It is noteworthy that furfuryl alcohol is the only alcohol tested thus far that has a higher antiknock performance than its equivalent amine (cf. results in Table 5). The other advantage of this material is its derivation from non-petroleum sources, i.e. from renewable agricultural by-products. Its major drawback lies in its limited solubility in hydrocarbon fuels (maximum solubility in BF-1 is about 1.5% by volume). The next higher homolog,  $\alpha$ -methyl furfuryl alcohol, possesses much higher solubility while retaining the anti-knock performance.

It is noteworthy that the methyl ether of furfuryl alcohol, which was also synthesized and tested, displayed proknock behavior, having a BRON of only 66. In hindsight this result should have been expected, given that furfuryl methyl ether, unlike its parent alcohol, possesses the strongly proknock structural feature C-CH<sub>2</sub>-O-C. Another furan derivative that was tested was benzofuran, which was also found to possess significant antiknock activity.

Finally, a novel additive was designed and synthesized; this was N-t-butylfurfurylamine (NTBF), which was expected to possess good activity since, in addition to the furan ring, it incorporates a secondary amine and a tert-butyl group. Indeed, as can be seen in the data of table 5, this easily accessible compound possesses one of the highest blending octane numbers among non-aromatic amines and is about six times as effective an additive as MTBE on a molar basis.

#### Substituted Phenols and Derivatives

Substituted phenols have long been known to possess antiknock activity. Their effectiveness increases by having them undergo the Mannich reaction, which adds an aminomethyl moiety at the ortho position, thus transforming them to 2-hydroxybenzylamines (HBA). The very high activity of the HBA's (and even more so of their salts) was observed by one of us several years ago [5] and was later extensively investigated by Burns [1,15]. As shown in Table 5, the improvement in performance that occurs in going from the parent phenol to the corresponding HBA is highest among di-substituted phenols (xylenols). Creosote, a phenolic mixture that is derived from wood tar, displays an antiknock activity similar to that of MTBE. Upon transformation to the corresponding HBA mixture via the Mannich reaction, a large BRON increase is observed, which is consistent with the high xylene content of creosote.

#### POLLUTANT EMISSIONS AND ENGINE PERFORMANCE

The effect of oxygenate additives on pollutant emissions from gasoline engines has been extensively studied, and it is generally accepted that they offer tangible benefits on CO and hydrocarbon emissions, while not significantly affecting NOx emissions; the aldehyde content in the exhaust, however, is usually higher. When any nitrogen-containing material is added to the fuel, there is concern that NOx emissions may increase.

Tests that were run on the CFR engine showed that NOx emissions were independent of fuel nitrogen content but dependent on air-fuel ratio. However, we do not consider these results as representative because the CFR engine has a single cylinder and operates under relatively mild conditions when compared to actual automobile engines.

A parallel research project that is being conducted at the Department of Mechanical and Process Engineering of Sheffield University [16] is looking into the performance and emissions of standard spark-ignition engines that run on gasoline that incorporates oxygen and/or nitrogen containing additives. The engine which is used at Sheffield is a fully instrumented four-cylinder standard production unit, which is coupled to an appropriate dynamometer. The additives that have been tested were blended with unleaded premium gasoline and included MTBE, methanol, furan, furfuryl alcohol, anisole, and t-butylamine among several others. Fuel economy on an energy basis was improved by amounts that ranged from 3.5% (furfuryl alcohol) to 0.9% (anisole); representative results are shown in Table 6.

As far as exhaust emissions were concerned, oxygenates generally tended to follow the pattern mentioned above, except that materials containing the furan ring appeared to lower NOx emissions. Additionally, it was observed that one of the factors

that influence the NOx content of the exhaust gases was the concentration of the additive; small amounts of additives actually decreased NOx emissions in comparison to the base gasoline. After a certain concentration threshold was reached, however, NOx emissions increased. Nitrogen-containing additives behaved in similar fashion, except that threshold concentrations were lower than those of oxygenates.

The novel additive NTBF was also tested in the engine under similar conditions but to a limited extent because of the small quantities that were available. Preliminary results show that this material improves fuel economy to an extent similar to other additives that contain the furan ring; a single test showed that, at a concentration of 1%, NOx emissions were lower than those of the base gasoline. Furthermore, it was observed that NTBF lowers the aldehyde content of the exhaust gases, which is a rather unexpected behavior for an oxygen-containing material.

#### CONCLUSIONS

The screening of over one hundred blends of base fuels with potential additive candidates allows the following conclusions to be made regarding the relation of molecular structure with anti-knock activity:

- a. Amines are usually more effective anti-knock additives than the equivalent alcohols.
- b. The presence in the molecule of a tertiary nitrogen atom imparts a strong pro-knock effect.
- c. The presence of five-membered rings leads to better performance than six-membered rings.
- d. The structural group C-O-CH<sub>2</sub>-C is a pro-knock feature in the molecule.
- e. The biomass derived phenolic mixture known as creosote has good antiknock activity, which is greatly enhanced by its transformation to HBA via the Mannich reaction.
- f. Molecules designed on the basis of the activity of their constituent groups can lead to superior anti-knock performance. (e.g. N-t-butyl furfurylamine)

#### ABBREVIATIONS AND DEFINITIONS

API-45	American Petroleum Institute Research Project 45 (see ref.8)
BF1-BF5	Base fuels for octane number determinations (for compositions refer to Table 1)
BRON	Blending Research Octane Number
HBA	Hydroxy Benzyl Amine
MON	Motor Octane Number (according to ASTM D-2700)
MTBE	Methyl tert-Butyl Ether
NTBF	N-t-butyl furfurylamine
PRF	Primary Reference Fuel
RON	Research Octane Number (according to ASTM D-2699)
TAME	tert-Amyl Methyl Ether
THF	Tetrahydrofuran

BRON is defined by the formula:  $B = [M-F(1-V)]/V$  where:

- B = BRON of a given fuel component
- M = RON of the fuel blend
- F = RON of the base fuel
- V = Concentration of the component in the blend (vol/vol)

#### ACKNOWLEDGEMENT

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TABLE 1

COMPOSITION OF BASE FUELS  
(Compositions given in percent by volume)

COMPONENT	API	BRON	API	RON	BF-1	BF-2	BF-3	BF-4	BF-5
n-Hexane	19		24.8		20	15	25	28.5	19.2
Cyclohexane	110		83.0		-	15	15	19.0	-
n-Heptane	0		0.0		5	15	-	-	4.8
iso-Octane	100		100.0		55	20	20	9.5	52.8
Diisobutylene	168		105.3		-	5	5	-	-
Toluene	124		120.1		15	15	15	28.5	14.4
Xylenes*	144		117.2		5	15	20	9.5	4.8
Methanol					-	-	-	1.7	-
Isopropanol					-	-	-	3.3	-
MTBE					-	-	-	-	4.0
RON					90.5	85.5	93.4	93.3	91.9

\* The composition of the xylenes mixture, as determined by vapor phase chromatography, was 3.7% o-xylene, 72.3% m-xylene, and 23.9% p-xylene.

**TABLE 2**  
Antiknock performance of simple alcohols and amines  
(Results at 3% vol. concentrations in BF-1)

Compound	$\Delta$ RON	BRON	Relative Effectiveness (MTBE=1)	
			Molar	Weight
MTBE (5%)	1.8	126	1.00	1.00
Methyl t-octyl ether (2%)	0.7	125	1.52	0.88
i-Butanol	0.8	117	0.57	0.68
i-Butylamine	2.9	187	2.24	2.71
di-(i-Butyl)amine	1.8	151	2.43	1.65
t-Butanol (5%)	1.2	114	0.53	0.63
t-Butylamine (5%)	2.6	143	1.27	1.53
t-Butyldimethylamine	-0.2	84		pro-knock
t-Octylamine	0.8	117	1.04	0.68
t-Octyldimethylamine	0.1	94	0.15	0.07
N,N,N',N'-Tetramethyl- ethylenediamine	-5.5	-93		pro-knock
Tetrakis-dimethylamino- ethylene (1%)	-11.6	-1070		pro-knock

**TABLE 3**  
Antiknock performance of cyclic oxygen and nitrogen compounds  
(Results at 3% vol. concentrations in BF-1)

Compound	$\Delta$ RON	BRON	Relative Effectiveness (MTBE=1)	
			Molar	Weight
THF	0.2	97.2	0.12	0.16
Pyrrrolidine	4.9	287.2	3.80	4.70
N-Methylpyrrrolidine	-3.0	-9.5		pro-knock
Piperidine	1.9	154	1.46	1.50
Morpholine	-0.5	73.8		pro-knock
N-Methylpiperazine (2%)	-1.0	40		pro-knock
Trimethylidioxolane (1%)	0.1	101	0.29	0.23

**TABLE 4**  
Antiknock performance of furan derivatives

Compound	BRON	Relative Effectiveness (MTBE=1)	
		Molar	Weight
Furan	190	1.40	1.81
Furfuryl alcohol (1.5%)	170	1.66	1.49
Methylfurfuryl alcohol (2%)	171	1.86	1.71
Furfuryl methyl ether (2%)	66		pro-knock
Benzofuran (1%)	144	1.50	1.13
Furfurylamine**	153	3.29	2.98
N-t-Butylfurfurylamine (1%)	250	6.06	3.49
"best amine"***	174	~3.8	

- \* Data from API-45
- \*\* Data from ref. [12]
- \*\*\* Data from ref. [7]

**TABLE 5**  
Antiknock performance of substituted phenols  
and corresponding HBA's

Compound	BRON	Relative Effectiveness (MTBE=1)	
		Molar	Weight
4-cresol (2%)	221	3.41	2.79
HBA (2.5%)	287	8.37	4.20
4-t-butylphenol(0.5%)	173	2.91	1.76
HBA (1%)	247	8.02	3.34
4-t-octylphenol (1%)	128	1.87	0.80
HBA (0.5%)	176	5.10	1.83
3-cresol (2%)	191	2.62	2.14
HBA (0.5%)	292	8.05	4.30
3,5-xylenol (0.5%)	124	1.01	0.72
HBA (0.5%)	271	7.80	3.84
2,5-xylenol (0.5%)	169	2.32	1.68
HBA (0.5%)	332	10.41	5.16
Creosote (2%)	121	--	0.65
HBA (2%)	234	--	3.06

**TABLE 6**  
Change in fuel economy [energy basis] caused by added components  
(Net power test, wide open throttle)

Component	Improvement in fuel economy (%)
MTBE	3.1
Methanol	1.6
Anisole	0.9
Furan	1.4
2-Methylfuran	3.1
Furfuryl alcohol	3.5
tert-Butylamine	2.9

Component concentration: 2% vol.  
Base gasoline: unleaded premium  
Spark timing: minimum for best torque

A NEAR INFRARED REGRESSION MODEL FOR OCTANE  
MEASUREMENTS IN GASOLINES WHICH CONTAIN MTBE

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INTRODUCTION

Near infrared (NIR) spectroscopy has emerged as a superior technique for the on-line determination of octane during the blending of gasoline. This results from the numerous advantages that NIR spectroscopy has over conventional on-line instrumentation.

From an analytical standpoint the NIR is advantageous because the spectral data is related to chemical structure. The NIR is also a region of the spectrum where Beer's Law can be used to quantify results. This allows multiple regression analysis to be performed on wavelengths which correlate with chemical functionalities and a dependent variable like octane. Additionally, the technique is fast, has good repeatability, is objective, and can easily be adapted for continuous on-line operation.

The increasing use of oxygenates as gasoline blending components has posed a special problem for NIR spectroscopists. This stems from the fact that oxygenates are only present in a small, but increasing, percentage of the blends a refinery produces. This can result in substantial errors in octane determinations by NIR on gasolines which contain oxygenated components.

Methyl t-butyl ether (MTBE) is currently the oxygenated blending component of choice. MTBE is advantageous because it has a high blending octane, a low Reid vapor pressure, is relatively cheap, and does not form peroxides (1).

The goal of this project was to develop a NIR regression model that could be used to predict pump octanes regardless of whether they contained MTBE.

EXPERIMENTAL

Approximately 175 samples were submitted to the Ashland Petroleum Automotive and Products Applications Laboratory for octane analysis by ASTM Methods D2623 and D2699 (2).

One hundred and forty-three samples were used to form a box car distribution. The box car consisted of a minimum of five samples within each 0.5 octane numbers across the pump (R+M/2) octane range of 84.5 - 94.0. The remaining samples were used to evaluate the performance of the knock engine laboratory.

A NIRSystems model 6500 near infrared spectrometer was used for all data collection. The spectra were co-added and represented an average of 100 signals.

The spectrophotometer was connected to an IBM PS-2 model 50 computer for signal processing. The PC was also capable of transferring data to Ashland's Lexington Data Center.

A thermostatic temperature controller was used to maintain the samples at  $27^{\circ}\text{C} \pm 0.1$ . Sealed quartz cuvettes were used for sample holders. All measurements were made in transmission mode using a path length of 20 mm.

After data collection the absorbance spectra were converted to second derivative spectra using a subroutine of the NIRSystems (NSAS) software. The segment gap was 20. Derivatization provided a convenient means to normalize the spectra, increase band resolution, and to achieve better correlations with octane.

#### RESULTS AND DISCUSSION

Figure 1 shows the absorbance spectra of the gasoline samples in the second overtone region of the NIR from 1100-1300 nm. Due to the absence of baseline resolution only two bands are readily apparent. The second overtone of the aromatic C-H stretch is centered at 1150 nm and the second overtone of the methyl C-H stretch is centered at 1192 nm (3).

Figure 2 shows the second derivative near infrared (SDNIR) spectra of the gasoline samples in the second overtone region. In contrast to the absorbance spectra five distinct features can be seen.

Because no band assignments had previously been reported in the SDNIR, band assignments were made by comparing the SDNIR spectra of the gasoline samples to the SDNIR spectra of model compounds.

Figure 3 shows the SDNIR spectra of n-hexane and n-butylbenzene. The second overtone of the aromatic stretch can be seen between 1130-1158 nm with a minima at 1144 nm. The position of the aromatic group can be deduced from the flatness of n-hexane's SDNIR spectrum in this region when contrasted to the band seen in the SDNIR spectrum of n-butylbenzene. Two other peaks, which can not be assigned at this time, are centered at 1202 and 1238 nm.

Figure 4 shows the SDNIR spectra of 2,3,4-trimethylpentane and cumene. These compounds were chosen as model compounds because, with the exception of the aromatic group of cumene, these two compounds are composed entirely of methyl and methyne functionalities. No methylene groups are present in either compound. The second overtone of the aromatic C-H stretch is

again centered at 1144 nm. By comparing Figures 3 and 4 one can deduce that the second overtone of the methyl C-H stretch is centered near 1195 nm. This functionality is common to each of the four spectra shown in Figures 3 and 4.

It is also possible to assign the second overtone of the methylene and methyne groups in the SDNIR by comparing Figures 3 and 4. The second overtone of the methylene C-H stretch is the band centered at 1238 nm in Figure 3. This can be inferred from its proximity to the second overtone of the methylene absorption band near 1220 nm and the presence of methylene groups in the two model compounds shown in Figure 3.

The second overtone of the methyne C-H stretch in the SDNIR can be deduced from Figure 4. It must be the band centered between 1212-1210 nm since cumene and 2,3,4-trimethylpentane do not contain methylene C-H groups.

Figure 5 shows the SDNIR spectra of MTBE and t-butylbenzene. The second overtone of the aromatic C-H stretch is centered at 1142 nm. The second overtone of the methyl group is centered near 1196 nm for these two compounds. The t-butyl group is assigned to the bands centered near 1214 nm because neither of the compounds contains methylene or methyne functionalities.

Figure 6 shows the band assignments for the SDNIR spectra of the gasoline samples. Based on the model compounds we assign the second overtone of the aromatic C-H stretch from 1138-1154 nm with a minima at 1146 nm. The second overtone of the methyl C-H stretch is from 1174-1214 nm with a minima at 1194 nm. The region from 1214-1228 nm is assigned as a combination band originating from the second overtone of the methyne and t-butyl C-H stretches centered at 1224 nm. The second overtone of the methylene C-H stretch is positioned between 1230-1264 nm with a maxima at 1236 nm.

Multiple linear regression was performed using the SDNIR spectra in the second overtone region. The second overtone of the methyne/t-butyl group at 1220 nm was picked first during the forward stepwise regression procedure. Later it was demonstrated that this wavelength showed the highest correlation with octane of any wavelength in the absorbance, baseline offset absorbance, first, second, third, or fourth derivative spectra over the wavelengths from 400-2500 nm. The regression model was completed using the second overtones of the methyl and methylene groups at 1196 and 1238 nm, respectively.

Tables 1 and 2 show the results of the multiple linear regression for these wavelengths. The standard error of the estimate was 0.310. Originally a value of 0.343 was obtained. Four data values were removed because of apparent discrepancies and the

regression procedure was repeated to arrive at the standard error of the estimate shown in Table 1. This was later demonstrated to be justified based on a comparison of standard errors of prediction for the two models. The standard error of prediction shown in Table 1 was determined using the jackknife procedure. Details of this procedure appear elsewhere (3).

The standard error of prediction of 0.326 pump octane units agrees nicely with the standard error of prediction of the knock engine laboratory we were calibrating against and ASTM guidelines. The knock engine lab had a standard error of performance of 0.323 pump octane units, and the inferred ASTM error over this octane range is 0.361 pump octane units.

Table 3 shows a blind prediction set of 12 gasoline samples which contained MTBE in concentrations from 1-11 volume %. Excellent results are seen. The utility of this model can be appreciated by realizing that only ~20% of the calibration samples contained any MTBE. This makes this model useful for all blends of gasoline currently being produced at Ashland Petroleum's refineries.

From a chemical standpoint the regression model is also quite satisfactory and can be explained on the basis of the potential stability of free radicals generated by the functionalities incorporated into the model. This is related to octane because combustion is a free radical process.

The methyne and t-butyl groups are capable of producing tertiary free radicals. This accounts for the large positive simple correlation of the second overtone of the methyne/t-butyl combination band with octane. This also accounts for the predicted increase in octane seen for increases in the 1220 nm band within the model. It was not possible to relate increases in the SDNIR spectra of the second overtone of the methyne/t-butyl absorption band, however. This appeared to stem from the transparent nature of this band in the absorbance spectra. Spectral subtraction of model compounds did show the band to be centered near 1240 nm, but generally the signal was too weak to be seen due to the relatively strong absorbance of the second overtone of the methylene and methyl C-H groups.

Increases in the magnitude of the second overtone of the methyl and methylene SDNIR spectra, however, were related to increases in the second overtone of the absorbance spectra. This was determined by comparing the mean absorbance values at 1196 and 1220 nm to the mean value at 1196 and 1238 nm in the SDNIR spectra for differing octane ranges. The data showed a 1:1 relationship between the average absorbance measurement and the magnitude of the corresponding SDNIR band.

Some question initially arises in interpreting the role of methyl and methylene groups in this model. As expected the second overtone of the methylene group at 1238 nm shows a negative simple correlation to pump octane and the methyl group at 1196 nm shows a positive correlation to pump octane. However, in terms of the model, increases in the methylene band add to the models estimate of pump octane and increases in the methyl band subtract from the overall prediction of octane.

While the latter results do go against preconceived notions of the methyl and methylene groups relationship to octane, they fit nicely into an octane model based on potential free radical stability.

To begin with it is important to realize that the relationship between the methyne, t-butyl, methylene, and methyl functionalities can only be interpreted in relationship to the model as a whole. For example, the variance in pump octane due to isoparaffins is frequently explained by the methyl and methylene groups. However, in this model all of the variance attributable to branching has already been explained by the methyne/t-butyl combination band. Even the presence of paraffins can be explained by the methyne/t-butyl band since the band will be proportionately lower as straight chain hydrocarbon content increases.

The assumption that the variance explained by the methyne/t-butyl band is different from the variance explained by the methyl and methylene bands is also supported by the statistics used to verify the validity of the model. Most importantly the regression data showed an absence of multicollinearity and autocorrelation. This would not be expected if the functionalities were explaining the same variance.

The other wavelengths used in this model are presumed to account for different types of variance in pump octane. For example, it is possible to explain the methylene group's positive relationship to pump octane in the model on the basis of its free radical stability. It can be seen from Figure 3 that n-butylbenzene shows a maxima near 1238. In terms of free radical stability this is significant because this is an indication that a benzylic carbon is present.

The negative relationship of the methyl band can readily be explained by its tendency to form primary free radicals.

In summary a pump octane model was developed and shown to be useful for gasolines containing 0-11 volume % MTBE. The wavelengths used in the model showed that functionalities that could give rise to benzylic, tertiary, or secondary free

radicals were positively related to pump octane whereas primary free radicals bore a negative relationship. The strong relationship between potential free radical stability and octane is believed to occur because combustion is a free radical process.

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Table 1. Multiple regression data for the pump octane model.

PARAMETER	VALUE
Coefficient of correlation	0.9939
Standard error of estimate	0.310
Standard error of prediction	0.326
Average absolute deviation	0.261

Table 2. The multiple regression coefficients and simple correlations for the regression wavelengths.

WAVELENGTH	REGRESSION COEFFICIENT	SIMPLE CORRELATION
Constant	85.79	-
1220 nm	73.66	0.988
1196 nm	18.40	0.362
1238 nm	33.04	-0.961

Table 3. A comparison of predicted pump octanes versus knock engine pump octanes for samples containing varying amounts of MTBE.

PERCENT MTBE	KNOCK ENGINE OCTANE	NIR PREDICTED OCTANE	DIFFERENCE IN PUMP OCTANE
4	89.2	88.900	-0.300
5	92.15	92.054	-0.096
6	92.55	92.195	-0.355
1	92.1	91.806	-0.294
1	92.05	92.000	-0.050
1	91.65	91.956	0.306
10	93.2	93.244	0.044
1	87.8	87.989	0.189
10	92.9	93.149	0.249
10	93.35	93.346	-0.004
10	93.55	93.357	-0.193
11	93.55	93.386	-0.164

Figure 1. The absorbance spectra of the gasoline samples in the second overtone region of the near infrared spectrum.

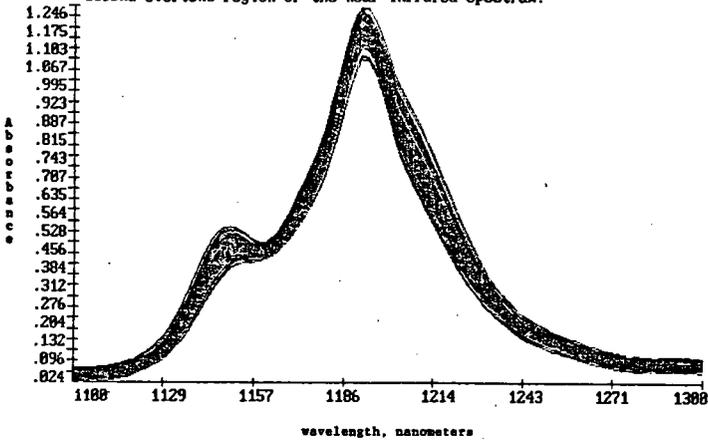


Figure 2. The second derivative of the near infrared spectra of the gasoline samples in the second overtone region of the spectrum.

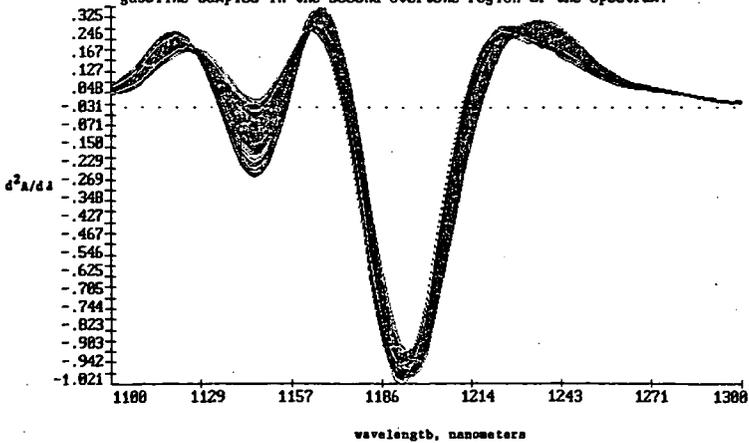


Figure 3. The second derivative of the near infrared spectra of n-hexane and n-butylbenzene.

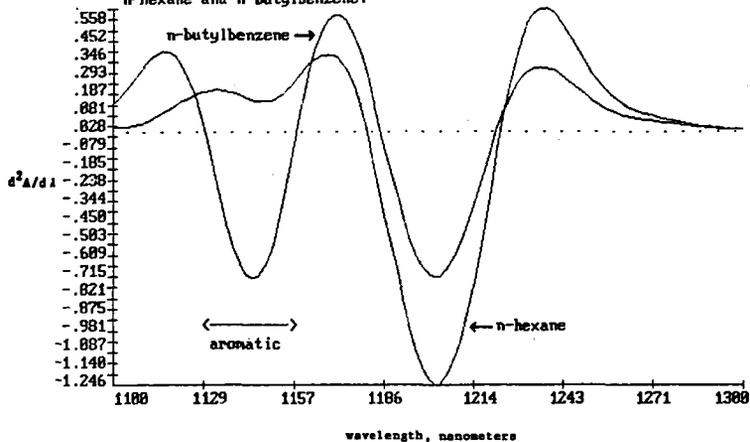


Figure 4. The second derivative of the near infrared spectra of cumene (isopropylbenzene) and 2,3,4-triethylpentane.

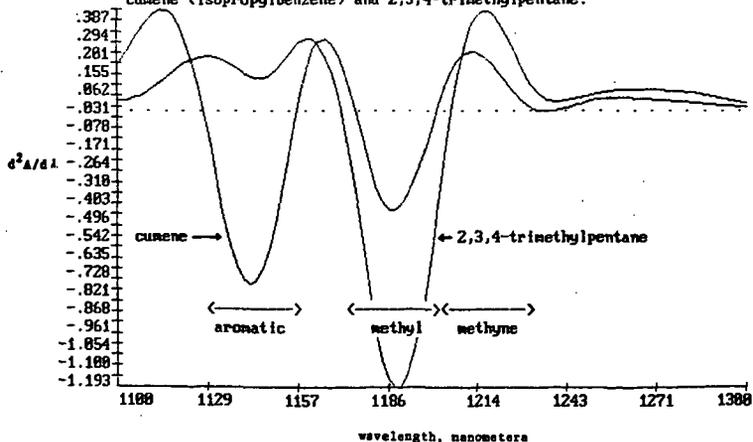


Figure 5. The second derivative of the near infrared spectra of t-butylbenzene and methyl t-butyl ether (MTBE).

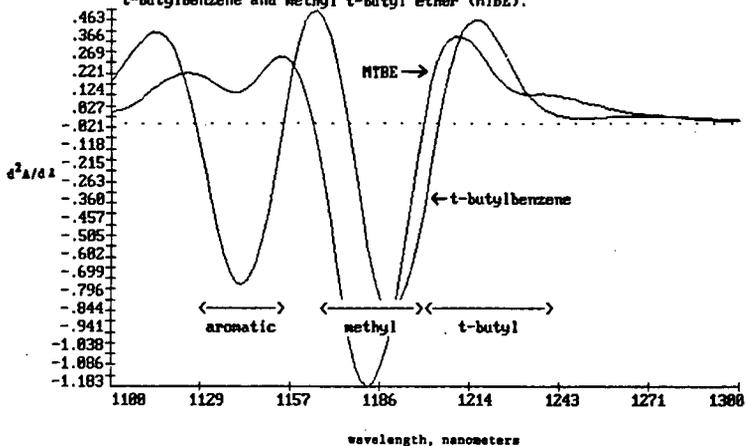
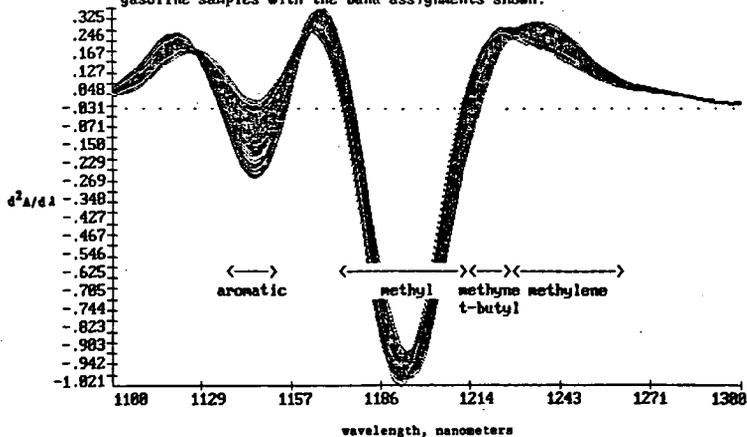


Figure 6. The second derivative of the near infrared spectra of the gasoline samples with the band assignments shown.



## WATER TOLERANCE OF GASOLINE-METHANOL BLENDS

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Keywords: water tolerance, phase separation, gasoline

### ABSTRACT

A new method based on laser attenuation was devised to accurately measure the phase separation and, in turn, the water tolerance of gasoline-methanol blends with and without cosolvents. Water tolerances were quantified for a variety of blends in model and actual gasolines, as well as in major refinery streams--alkylate, FCC gasoline, and reformat--which make up commercial gasoline pools. Regression analysis of the data shows that the water tolerance behavior of blends with each cosolvent well-described by a correlation which includes cosolvent concentration, temperature, and base fuel hydrocarbon type.

### INTRODUCTION

Refiners and marketers have been turning to oxygenates to meet increasing demands for gasoline pool octanes in light of more stringent volatility and fuel composition controls. Oxygenates which have become important as gasoline blending components include methanol (MeOH), ethanol (EtOH), isopropanol (IPA), t-butyl alcohol (TBA), and methyl t-butyl ether (MTBE). MeOH is generally the most attractive oxygenate from a strictly economic point of view, but its direct use as a blending component in current fuel systems can cause technical problems [1]. The most serious of these is the separation of blends into hydrocarbon and methanol phases when the water content exceed a critical level, i.e. the water tolerance. This problem is exacerbated at low ambient temperatures.

Water tolerance is defined as the volume % water that a blend can retain in solution--"tolerate"-- at a given temperature without phase separation. The water tolerance of gasoline-MeOH blends can be improved by the addition of a cosolvent, which is typically a higher alcohol such as IPA or TBA. TBA has been identified as the most attractive cosolvent for most commercial gasolines, and mixtures of MeOH and TBA have been marketed as an oxygenate blending component for gasoline for some time [2] although such mixtures are currently in very limited use in the U.S.

Previous studies on the water tolerance of gasoline-methanol (MeOH) blends have been both qualitative [3,4] and quantitative [5,2] in nature. One quantitative study has investigated the water tolerance of gasoline-MeOH blends to compare the relative effectiveness of IPA vs. TBA as cosolvents in a regular grade leaded gasoline [5]. Other quantitative work [2] has examined the relative effectiveness of other alcohols in gasoline, as well as the effect of changing aromatics and cosolvent levels on phase separation temperatures. One study has reported findings on the effect of boiling point and hydrocarbon type in gasoline-MeOH mixtures with no cosolvent [6]. However, the effect of base gasoline composition over a wide range on the water tolerance of gasoline-MeOH-cosolvent blends has remained largely unexplored.

In the current study, the water tolerance behavior of various gasoline-MeOH

blends using several cosolvents was investigated to determine and compare the efficacy of the cosolvents and the effect of fuel composition over a wide range. As part of this work, a useful, new technique based on laser attenuation was devised to rapidly and reliably measure phase separations.

## EXPERIMENTAL

### Preparation of Blends

Three unleaded gasolines--designated as Gasoline A, B, and C--representing both regular and premium grades, and three gasoline blending stocks taken directly from refinery streams--Light Alkylate, FCC Gasoline, and Reformate--were included for study as base fuels. Properties of these materials are given in Table 1.

Three classes of gasoline hydrocarbon types were simulated by model compounds, as follows: 1) Saturates - 85 vol% i-octane/15 vol% n-heptane; 2) Olefins - 50 vol% 1-hexene/25 vol% 1-heptene/25 vol% 1-octene; and 3) Aromatics - 33 vol% benzene/34 vol% toluene/33 vol% xylenes.

The following reagent grade oxygenates were dried over 3A molecular sieves before use in the blends: MeOH, EtOH, IPA, TBA, and MTBE.

Blends were prepared by mixing the base fuel with 5 vol% MeOH, and 0, 2.5, or 5 vol% cosolvent--EtOH, IPA, TBA, or MTBE. The water content of each MeOH/gasoline cosolvent blend was adjusted using a precise gravimetric method and was measured directly using a Brinkmann Model 652 Karl Fischer Coulometer.

### Measurement of Phase Separation

The method of determining the water tolerance of a blend was based on measuring the optical attenuation of a laser beam as it passes through a fuel sample which is undergoing cooling [7]. A photodiode equipped with a laser line filter is used to measure the intensity of the transmitted laser beam, while a thermocouple is used to simultaneously measure the temperature of the sample. The output voltages from the photodiode and thermocouple are continuously monitored and recorded via a calibrated dual-pen strip chart recorder. A schematic diagram of the apparatus is shown in Figure 1.

When the sample undergoes a phase separation, the transmitted laser beam intensity is attenuated due to scattering caused by small droplets of a second immiscible phase. The temperature which corresponds to the initial rapid loss of photodiode signal is recorded as the phase separation temperature. This is the temperature of phase separation for the given water level in a base fuel/MeOH blend. Accordingly, the water tolerance at this temperature is equal to the measured water content of this sample. Measurements were made over a temperature range of -116 to 44°C, depending on the fuel blend under consideration.

## RESULTS AND DISCUSSION

### Laser Attenuation Technique Improves Data Acquisition

Water tolerance data were obtained on over 50 gasoline-MeOH-cosolvent blends (~200 data points) in this study using the laser attenuation technique. The collective results (to be more extensively reported elsewhere) demonstrated

the utility of this electro-optic approach for routine and reliable laboratory measurement of phase transition temperatures in fuel blends. Previous techniques for such measurements, including ASTM methods, have generally relied on visual observation by an operator and manual recording of the temperature as read from a thermometer. These techniques are often time consuming and subject to inconsistent visual observation by one or more operators, and their accuracy can be influenced by ambient lighting conditions. The current technique significantly alleviated these problems.

#### Water Tolerance Improves With Increasing Temperature

The water tolerance of gasoline/MeOH blends increases with temperature. To illustrate this, water tolerances are plotted versus  $1/T$  for gasoline A/MeOH/EtOH blends (Figure 2), for FCC gasoline/MeOH blends with and without TBA as the cosolvent (Figure 3), for refinery streams containing MeOH alone (Figure 4), for reformat/MeOH blends with various cosolvents (Figure 5), and for alkylate/MeOH blends with various cosolvents (Figure 6).

The relationship between the water tolerance of a fuel blend and temperature is adequately described by equation (1):

$$\ln WT = m (1/T) + k \quad (1)$$

where

WT is water tolerance, vol%

m, k are constants depending on the nature of the base fuel and the nature and concentration of the cosolvent

T is temperature, °K

This linear relationship between log of water tolerance and the reciprocal of temperature was found to be valid for all fuels, cosolvents, and concentration levels investigated in this study.

In general, the higher the water tolerance of a given blend set, the less sensitive that fuel/MeOH/cosolvent combination tends to be with respect to temperature (Figures 3-6). Table 2 gives the constants m and k derived from linear least squares fits of the data from representative blend sets, as well as the corresponding water tolerances at 0 and 20°C calculated for these blends. The slope, m, represents the sensitivity of the water tolerance of the blend with respect to temperature.

For any given MeOH/cosolvent combination, the temperature sensitivities (slopes, m) tend to decrease in the order of alkylate, FCC gasoline, and reformat, and similarly decrease in the order of saturate, olefin, and aromatics. This decrease in temperature sensitivity correlates with increasing water tolerance as illustrated by the calculated water tolerances at 0 and 20°C for each blend set shown in Table 2. This sensitivity decreases as cosolvent is added (Figure 3) and as the efficacy of the cosolvent improves (Figures 5 and 6).

#### Water Tolerance Improves As Aromatics In Base Fuel Increase

The composition of the base gasoline has a significant effect on the water tolerance of blends containing MeOH. As indicated in Figure 4 and Table 2,

water tolerance increases in the following order for the refinery streams:

Reformate > FCC Gasoline >> Alkylate

For example, at 0°C the water tolerances are 0.0724, 0.0309, 0.0019 vol% for 5 vol% MeOH blends of reformat, FCC gasoline, and alkylate, respectively, based on the data shown in Table 2. This relative ordering of water tolerance among base fuel types is generally maintained even upon addition of cosolvents, as indicated by the data in Table 2. For example, at 0°C the water tolerances are 0.2152, 0.1649, and 0.0411 vol% for 5 vol% MeOH/5 vol% EtOH blends of reformat, FCC gasoline, and alkylate.

The relative water tolerance behavior observed for the refinery streams is coupled to the specific hydrocarbon types present in the stream, improving in the order of increasing concentrations of:

Aromatics >> Olefins >> Saturates.

This finding is confirmed by the model compound data shown in Figure 7 for MeOH blends with no cosolvent. Here, the water tolerance is 0.1575, 0.0431, and 0.0038 vol% for 100% aromatics, 100% olefins, and 100% saturates, respectively. As before, this relative ordering persists in the presence of cosolvents as well, and is consistent with the relative contributions of both polar and hydrogen bonding effects of each hydrocarbon type [8].

Use of an aromatics-rich gasoline not only improves the water tolerance for a given MeOH blend, but also minimizes the cosolvent volume required to attain a given water tolerance. For example, when TBA was used as the cosolvent to maintain a water tolerance of 0.1 vol% at 0°C, the TBA concentration required was 1.0, 2.2, and 4.8 vol% for 5 vol% MeOH blends of reformat, FCC gasoline and alkylate, respectively.

#### Effectiveness of Cosolvent Increases With Concentration

The water tolerance of gasoline/MeOH blends improves significantly by the addition of a cosolvent in increasing concentrations. For example, by adding 2.5 and 5 vol% of TBA to FCC gasoline/5 vol% MeOH blends, the water tolerances at 0°C were increased from 0.032 to 0.11 and 0.24 vol%, respectively (Figure 3). Similar effects were observed in the other base fuel blends. However, the effect of base fuel composition on water tolerance diminishes as the concentrations of cosolvent are increased.

#### Effectiveness of Cosolvent Depends on Its Structure

The collective results confirm that higher alcohols are effective cosolvents for improving the water tolerance of MeOH/gasoline blends. The cosolvent behavior of MTBE, although poorer than the alcohols, indicates that ethers also can improve water tolerance of gasoline/MeOH blends. To illustrate this finding, the water tolerances of FCC gasoline/MeOH blends at 0°C are plotted against cosolvent concentration in Figure 8. Between the dosages of 2.5 and 5 vol%, the cosolvent efficacies are 0.056, 0.056, 0.030, and 0.012 vol%/vol% for TBA, IPA, EtOH, and MTBE, respectively. Consistent with this finding, and as illustrated in Figures 5 and 6, cosolvent performance for other fuel blends also generally follows the order:

TBA ~ IPA > EtOH > MTBE

The relative cosolvent effectiveness shown above is consistent with trends

in solubility parameters [8] which show the balancing between contributions to nonpolar, polar, and hydrogen bonding for each of these oxygenate cosolvents as a function of structure.

As the temperature increases, the relative differences in efficacy of each cosolvent begin to diminish (Table 2). At 20°C, EtOH begins to approach the effectiveness of TBA and IPA in many blends. However, because wintertime transport, storage, and use of gasoline/MeOH blends is where phase separation problems are likely to occur, higher alcohols such as IPA or TBA would be preferred cosolvents.

#### Regression Analysis Provides Good Correlation for Water Tolerance Prediction

The water tolerance of a MeOH/cosolvent blend can be expressed in terms of the collective effects of temperature, base fuel hydrocarbon type, and cosolvent concentration as follows:

$$WT = c \text{ Conc}_{\text{cosolvent}} + t_1 T + t_2 T^2 + s \text{ Sat} + o \text{ Olef} + a \text{ Arom} \quad (2)$$

where

$\text{Conc}_{\text{cosolvent}}$  is in vol%  
 $T$  is temperature in °C  
 $\text{Sat}$ ,  $\text{Olef}$ ,  $\text{Arom}$  are in vol% and derived from FIA analysis of the base fuel

Equation 2 closely approximates the observed water tolerance behavior of all base fuel/MeOH/cosolvent blends examined in this study and is the result of a multiple linear regression analysis of all data obtained for all blends prepared in this study. The results of the analysis are summarized in Table 3, which gives the coefficients (at the 95% significance level) for each term in Equation 2 for each cosolvent. The correlation coefficient for each fit,  $r$ , is also given, as is the number of data points considered.

The correlation coefficients indicate that Equation 2 fits the observed data well, despite that the temperature dependence was linearized in terms of a quadratic instead of a log  $c$  vs.  $1/T$  relationship for convenience. Non-linearities evident in the cosolvent concentration dependence data (Figure 8) were not statistically strong enough over the whole range to warrant a non-linear concentration term.

The results shown in Table 3 tie together the main findings discussed separately above. For example, the relative ordering of cosolvent efficacy is reflected in the values of the relative coefficients  $c$  across a wide range of temperatures and compositions (TBA > IPA > EtOH >> MTBE). Similarly, the relative ordering of chemical type effects on water tolerance is reflected in the relative coefficients  $s$ ,  $o$ , and  $a$  across a wide range of temperatures and compositions (Aromatics >> Olefins >> Saturates). Although this correlation may not accurately predict water tolerances at the extremes of concentration, temperature, and composition (for example, 100% saturates at 0°C and no cosolvent), it offers the potential to be a useful tool for predictive evaluation of MeOH/cosolvent blend behavior in a variety of practical gasoline compositions.

#### ACKNOWLEDGEMENT

B. A. Jones is gratefully acknowledged for her significant contributions to the experimental portion of this work.

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Table 1  
Base Fuel Properties

	Light Alkylates	Reformats	FOG Gasoline	Gasoline A	Gasoline B	Gasoline C
Gravity, °API	72.7	46.5	56.1			
Research Octane Number	92.8	98.9	93.4	97.6		
Motor Octane Number	91.2	89.1	80.7	87.3		
Resid Vapor Pressure, psi	6.3	7.7	9.5	13.7		
Distillation, °F						
- 10%	165	141	116			
- 50%	215	247	223			
- 90%	232	330	382			
Composition (FIA), vol%						
- Aromatics	1	62	33	54	31	36
- Olefines	1	2	36	1	3	15
- Saturates	98	36	31	45	66	49

Table 2  
Effect of Temperature on Water Tolerance:  
Constants for Eq. (1)  $\ln C = m \cdot 1000/T + k$   
and calculated water tolerance at 0°C and 20°C

Fuel Blend <sup>a</sup>	m	k	W.T. @ 0°C	W.T. @ 20°C
Alkylate/MeOH	-7.082	19.54	.0019	.0109
+ MTBE	-4.729	12.99	.0133	.0432
+ EtOH	-3.386	9.205	.0411	.0958
+ IPA	-1.917	4.670	.0955	.1542
+ TBA	-1.726	4.178	.1173	.1805
FCC Gasoline/MeOH	-2.143	4.369	.0309	.0528
+ MTBE	-1.342	2.484	.0881	.1232
+ EtOH	-1.716	4.480	.1649	.2532
+ IPA	-1.425	3.734	.2270	.3240
+ TBA	-1.037	2.321	.2287	.2963
Reformate/MeOH	-1.781	3.822	.0724	.1125
+ MTBE	-0.835	0.907	.1275	.1570
+ EtOH	-0.814	1.444	.2152	.2638
+ IPA	-0.429	0.169	.2462	.2741
+ TBA	-0.451	0.313	.2623	.2938
100% Saturates/MeOH	-4.739	11.789	.0038	.0126
+ MTBE	-4.234	11.279	.0147	.0423
+ EtOH	-5.899	18.057	.0293	.1280
+ TBA	-1.948	4.998	.1193	.1939
100% Olefins/MeOH	-2.061	4.401	.0431	.0721
+ MTBE	-2.000	4.875	.0709	.1188
+ EtOH	-1.821	4.133	.1851	.2474
+ TBA	-1.142	2.671	.2209	.2939
100% Aromatics/MeOH	-1.852	4.932	.1575	.2502
+ MTBE	-0.737	1.116	.2055	.2471
+ EtOH	-0.755	1.920	.4300	.5192
+ TBA	-0.627	1.382	.4011	.4691

<sup>a</sup> Fuel blends contain 5 vol% MeOH and, for those containing a cosolvent, 5 vol% cosolvent.

Table 3  
Results of Regression Analysis  
of Collective Water Tolerance Data:

$$WT = c(\text{Conc})_{\text{cosolvent}} + t_1(T) + t_2(T^2) + s(\text{Sat}) + o(\text{Olef}) + a(\text{Arom})$$

C O E F F I C I E N T S

Cosolvent <sup>a</sup>	c	t <sub>1</sub>	t <sub>2</sub>	s	o	a	Number of Data Points	Correlation Coefficient, r
None	-	.00174	-.00001	-.00024	.00042	.00140	19	.8492
MTBE	.01089	.00189	.00001	-.00040	.00023	.00140	68	.9289
EtOH	.03136	.00304	.00001	-.00104	.00013	.00200	73	.9060
IPA	.03376	.00226	.00001	-.00055	.00030	.00150	46	.9182
TBA	.03975	.00263	.00001	-.00077	.00020	.00166	62	.9804

<sup>a</sup> In fuel blends containing 5 vol% MeOH

FIGURE 2

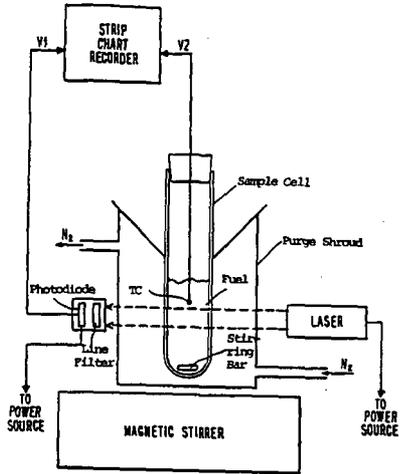


FIGURE 3

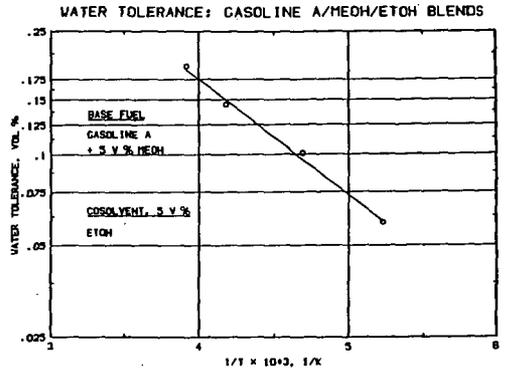


FIGURE 3

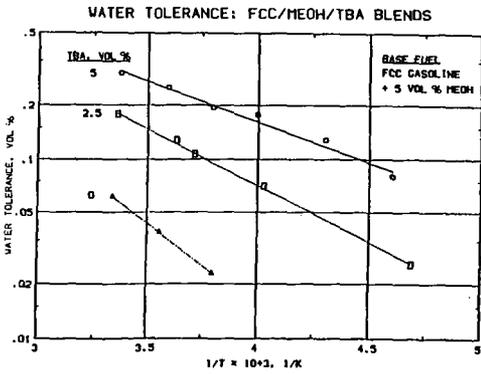


FIGURE 4

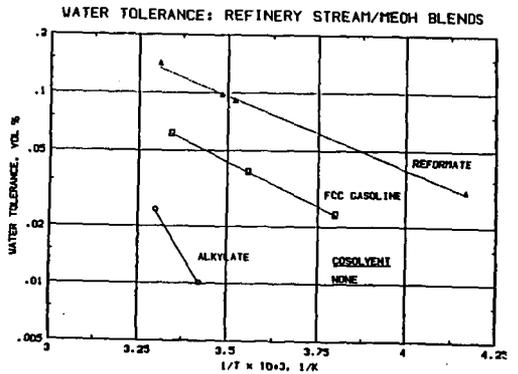


FIGURE 5

WATER TOLERANCE: REFORMAT/MEOH/COSOLVENT BLENDS

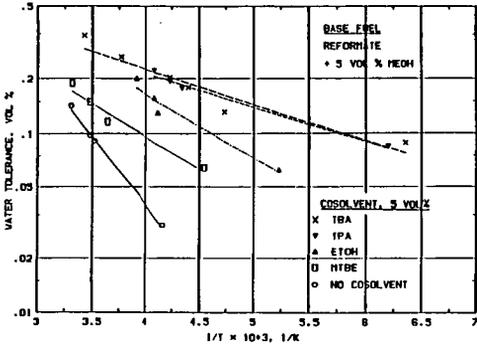


FIGURE 6

WATER TOLERANCE: ALKYLATE/MEOH/COSOLVENT BLENDS

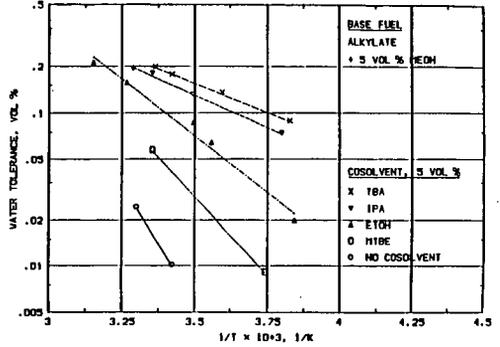


FIGURE 7

WATER TOLERANCE: MODEL FUEL/MEOH BLENDS

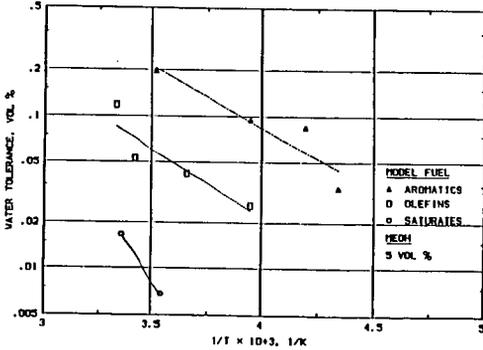
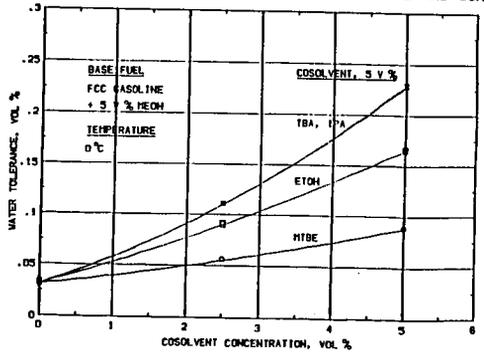


FIGURE 8

WATER TOLERANCE: EFFECT OF COSOLVENT TYPE AND CONC



## CHEMICAL RELATIONSHIPS IN ETHANOL AND NON-ETHANOL FUELS

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### INTRODUCTION

The U.S. national transportation fuel supply is changing significantly because of environmental pressure to reduce carbon monoxide, ozone, hydrocarbon, and lead emissions. The desire to replace petroleum fuels with alternative fuels because of world shortages and cost has abated but will reappear again as world demand for petroleum approaches supply. The variety of gasoline fuel blends is becoming and will be more varied in the future. The goal of this research is to track changes of the chemical composition of current and emerging transportation fuels by providing: 1) a survey of gasoline chemical composition at the pump from ten sites throughout the U.S., 2) data on seasonal chemical changes in gasoline in a "hot" and a "cold" community, (3) analytical data for tracing actual fuel-related engine problems to constituents in gasoline, and 4) foundational data for tracking changes in chemical composition. This paper deals with the analytical methods being used to "fingerprint" the over 180 fuel samples that will be analyzed in this study.

Gas chromatography (GC) analysis separates volatile organic mixtures into individual compounds depending on GC conditions. This can provide information on the identity of the compounds present as well as quantitative data. Quantitation is complicated by peak overlap and detector response to individual compounds. Whereas most hydrocarbons in petroleum derived fuel have similar response factors, ethanol has a significantly lower response factor and does not elute in the proper boiling point position relative to normal alkanes. These difficulties require a more involved GC method and calculations to analyze fuel blends and to relate them to distillation data.

Proton nuclear magnetic resonance spectroscopy (NMR) provides data on the hydrogen distribution in organic liquids and is relatively easy and fast to obtain on liquid samples. Minimal information is obtained for mixtures of compounds containing similar functional groups. For instance, a mixture of normal alkanes with only  $-CH_2-$  and  $-CH_3$  groups would give a simple spectrum and no single alkane could be quantified. However, when compounds are present in a bulk mixture that contain protons which resonate in a unique NMR region (such as ethanol or benzene in gasoline), rapid identification of these compounds and their quantitation is possible. Proton NMR, therefore, becomes much more useful for analyzing mixtures that contain a wider variety of functional groups.

### EXPERIMENTAL

#### Gas Chromatography

The gas chromatography (GC) work was done with a Hewlett-Packard Model 5890 GC connected to an HP 3396A integrator with data transfer to an IBM compatible PC.

Ethylcyclohexane (0.1 g) was mixed with 2 grams of the gasoline sample for use as an internal standard. The GC analysis conditions were as follows:

Column: Supelco Petrocol-DH, 100m x 0.25 mm I.D., 0.5 micron film  
Carrier: H<sub>2</sub>, linear velocity of 34 cm/s set at 320°C  
Injector: Injection split ratio: 100:1  
Detection: FID with 30 ml/min of N<sub>2</sub> make-up  
Oven Temp. Prgm: 30 to 35°C at 0.5°/min then 2°/min to 320°C  
Critical: The injector insert (unpacked mixing chamber) was deactivated with HMDS and DMDCS (1).

### Proton NMR Spectroscopy

All of the proton nuclear magnetic resonance spectra were determined on a Varian XL200 NMR Spectrometer. Its 47-KGauss magnet has a wide bore and superconducting solenoid that operated at liquid helium temperatures. The proton probe used 5-mm sample tubes and observed the protons at a frequency of 200 MHz while spinning the samples between 25 and 30 Hz. The gasoline samples were prepared for analysis by diluting 40 microliters of the sample with one milliliter of deuterated methylene chloride that contained 0.25% tetramethylsilane as an internal reference standard. The spectra were obtained using a 90 degree flip angle and 5-second delay between pulses for a total of 100 pulses. All spectra are stored on 5.25 inch floppy disks.

### **RESULTS AND DISCUSSION**

#### Base Gasoline Analysis by GC

The GC system was calibrated with a series of known compounds: methanol, ethanol, n-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, hexane, benzene, cyclohexane, iso-octane, heptane, toluene, n-octane, ethylbenzene, o-xylene, decane, and naphthalene. Retention index and response factor information was determined for these compounds. It was found that when ethanol content was over 3 wt%, its response factor was non-linear. However, if the sample was diluted, compounds present in small amounts were not detected. A possible solution to this paradox is to use GC to perform a base gasoline analysis (all compounds except ethanol) on a neat sample and to determine ethanol content on a diluted sample, or by using a different method (i.e., NMR spectroscopy).

Figure 1 depicts the computer generated GC profile and simulated distillation curve. Each peak is represented by a line equal to its area% plotted at its relative elution position to the boiling points of normal alkanes (the horizontal scale is 0 to 250°C). One sample (without ethanol) was analyzed five times and the area% standard deviations were calculated for each of 211 peaks. The results are depicted in Figure 2. For peaks under 0.2 area%, the standard deviation was up to 10%, with only a few points off scale above 10%. For peaks of over 0.2 area%, standard deviations of under 3% were obtained. Figure 3 depicts the five overlaid simulated distillation data for these analyses. Essentially one broadened line was obtained. The dotted line is ASTM D86 distillation data. The GC simulated distillation emphasizes the low boiling regions. This is due to a difference in response factors of early and later eluting alkanes for the GC conditions used in the analysis and to early hang-up of material during distillation. A factor, to correct for response factor differences and column influences on the elution position versus boiling point, is planned to enable GC data to better approximate distillation data.

### Determination of Ethanol in Gasoline by NMR

Proton NMR observes the hydrogen atoms in a compound. It differentiates them by the functionality they are in and adjacent functionalities. A typical NMR spectrum of gasoline is shown in Figure 4. Differentiation of specific compounds due to the presence of unique protons is evident; primarily ethanol, benzene, and MTBE. If methanol were present it would also be detected by this method.

The proton NMR spectra of a series of gasoline samples spiked with known amounts of ethanol were obtained using the normal proton pulsing sequences. Each spectrum was integrated over each of the integral regions normally used for gasoline samples. The data was reduced after eliminating the baseline regions from 10.00 to 8.15 ppm, 6.60 to 6.00 ppm, 4.60 to 3.75 ppm, and 0.40 to 0.06 ppm from the total area, along with the solvent peak area, 5.36 to 5.25 ppm. The data was then normalized to 100%. The integral region from 3.75 to 3.50 ppm is totally unique to the methylene protons of the ethanol in the gasoline samples, thus the normalized area of this integral should be directly proportional to the concentration of the ethanol. A summary of the ethanol spiked gasoline samples is presented in Table 1. The calculated vol% and calculated wt% data were determined by linear regression analysis of the NMR area% and corresponding ethanol concentration of the standards from 0 to 12 vol% ethanol. The volume % ethanol versus NMR area% gave a regression line described by the formula,  $y = 0.2822x + 0.02443$ , where  $y$  is the NMR area% and  $x$  is the ethanol vol%. The wt% data gave the line  $y = 0.26087x + 0.00475$ , where  $x$  is the wt% ethanol. The error is higher at ethanol concentrations over 13 wt%. Figure 5 shows the data graphically for the samples containing 0 to 13 wt% ethanol.

### Determination of Benzene in Gasoline by NMR

The proton NMR spectrum of gasoline gives a single resonance for benzene in the region between 7.31 and 7.42 ppm since benzene contains six equal protons. This region in the gasoline samples was nearly devoid of interfering resonances, which allows calculation of benzene concentrations in the gasoline samples. The standards used were spiked gasoline samples from 0 to 5% added benzene. The spectrum of each standard was integrated and normalized in the same manner as the ethanol standards. Since the base gasoline contained some benzene (the same gasoline was used for each standard), the area of its benzene peak had to be subtracted from the benzene peak areas of standards with added benzene. This added benzene area was then used in the linear regression analysis of the benzene standards presented in Table 2. Here the calculated vol% and wt% data are from the regression lines described by  $y = 0.50497x + 0.0437$  for the vol% and  $y = 0.4274x + 0.0284$  for the wt%, where  $y$  is the NMR area% and  $x$  is the vol% or wt%. From this data, the concentration of benzene in the base gasoline standard can also be calculated. The base gasoline has a benzene area% of 1.6583, which calculates to 3.20 vol% and 3.81 wt% benzene.

### Data Base Generation

A computer data base is presently being generated for a suite of samples using the previously described methods containing GC and NMR data. The initial use of the data base is to determine the range of various gasoline blends being used by consumers in the U.S., how gasoline blends vary with additives (BTX and ethanol), and how blends vary seasonally and over shorter time periods. Future work will involve closely integrating the data base to presently used gasoline specification data and to engine performance.

## CONCLUSIONS

The preferred method of gasoline analysis for this study is a combined GC and proton NMR analysis. This method will provide an analytical "fingerprint" of gasoline samples for use in determining unique characteristics affecting engine performance. The method encompasses a "neat" analysis of the gasoline sample by GC for identification and quantitation of components, completed by NMR analysis for the determination of functionalities present as well as ethanol and benzene quantitation. All samples in the study are being analyzed by this method and additional research data will be completed on select samples to further define CHN, S, water, lead and solids content, as well as specific gravity and density determinations. Detailed component analysis by GC/FTIR/MS will also be performed.

## REFERENCES

1. Jennings, W. "Gas Chromatography with Glass Capillary Columns", 2nd Edition, p. 69-70, Academic Press, NY, 1980.

## ACKNOWLEDGMENTS

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TABLE 1  
ETHANOL CONCENTRATION BY NMR

Concentration	NMR		Calculated	
	vol%	wt%	vol%	wt%
0	0.0	0.0736	0.17	0.26
2	2.35	0.5280	1.78	2.01
4	4.39	1.1752	4.08	4.49
4	4.39	1.1118	3.85	4.24
8	8.73	2.3361	8.19	8.94
10	10.92	2.8259	9.93	10.81
12	13.02	3.4089	11.99	13.05
50	52.67	16.3733	57.93	62.75
75	77.77	24.8332	87.91	95.17

TABLE 2  
BENZENE CONCENTRATION BY NMR

Concentration		NMR	Calculated	
vol%	wt%	area%	vol%	wt%
0.0	0.0	0.0	0.04	0.03
0.5	0.61	0.3734	0.65	0.81
1.0	1.23	0.5559	1.01	1.23
1.5	1.84	0.8151	1.53	1.84
2.0	2.39	1.0895	2.07	2.48
2.5	3.02	1.2479	2.38	2.85
3.0	3.62	1.5253	2.93	3.50
4.0	4.73	1.9622	3.80	4.52
5.0	5.92	2.6711	5.20	6.18

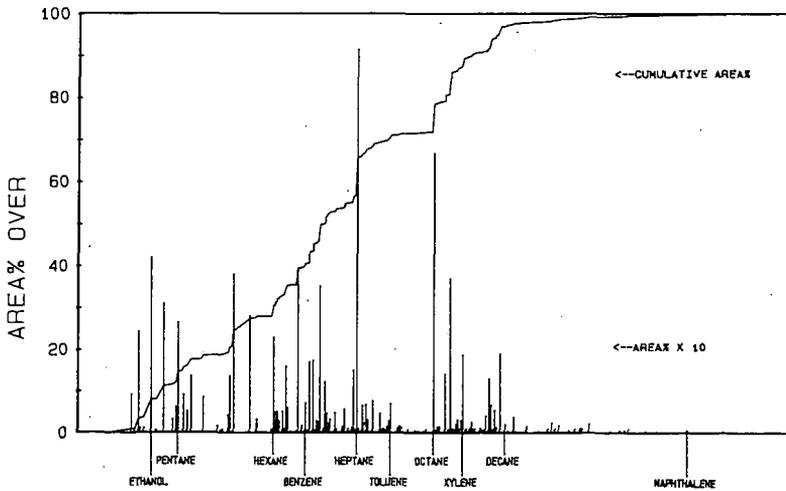


Figure 1. Computer generated GC profile and simulated distillation curve.

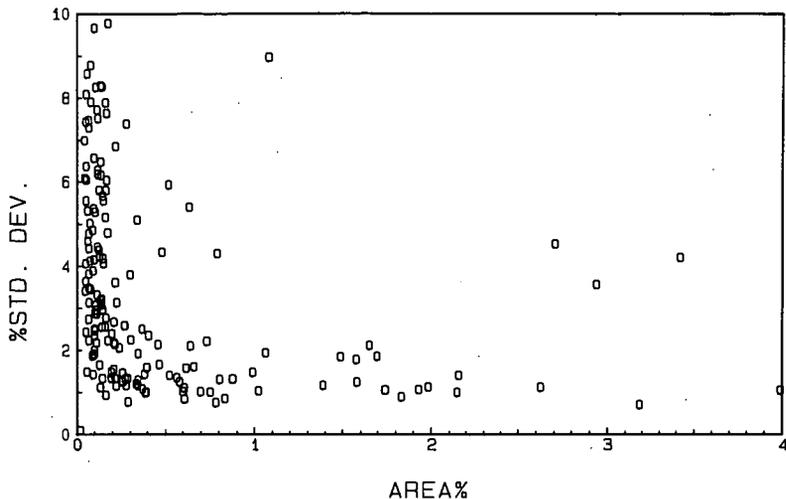


Figure 2. Area percent standard deviations for one gasoline sample analyzed five times by GC.

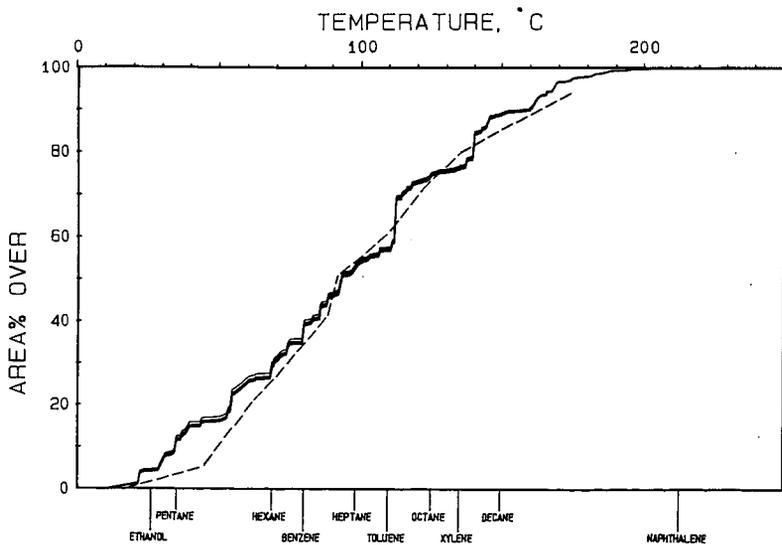


Figure 3. Overlay of five simulated distillation curves for one sample (—), with corresponding ASTM D86 distillation (----).

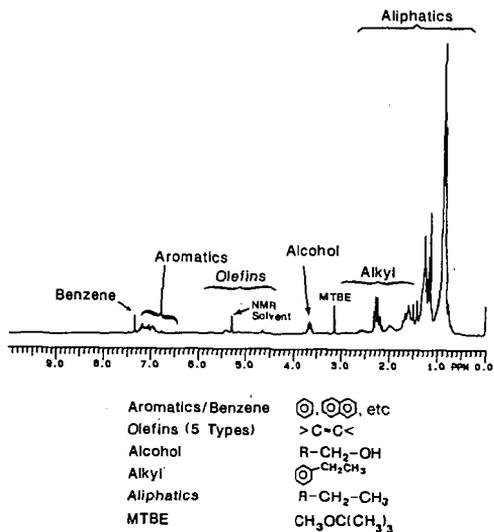


Figure 4. Typical NMR spectrum of gasoline depicting identified components and functional groups.

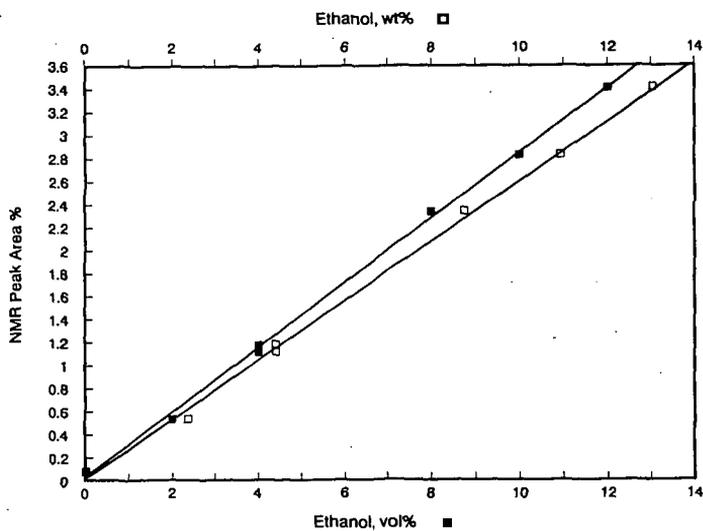


Figure 5. Ethanol content by NMR, vol% and wt%.