

OXYGENATED FUEL STRATEGIES TO COMBAT AIR POLLUTION  
A FEDERAL OVERVIEW

David J. Kortum and Meredith G. Miller  
Field Operations and Support Division 6406J  
U. S. Environmental Protection Agency  
Washington, DC 20460

Keywords: oxygenate, pollution, MTBE

INTRODUCTION:

The use of oxygenate fuel additives in gasoline as a strategy to decrease dangerous ambient air levels of pollutants, especially carbon monoxide (CO), has recently expanded dramatically. Two especially significant programs to combat air pollution were required under the 1990 amendments to the Clean Air Act: the carbon monoxide oxygenated fuels program and the reformulated gasoline program. This paper explores the legislative and statutory history of oxygenate use in gasoline and oxygenate-based pollution abatement programs, program implementation problems and public reaction, health research on oxygenates and the resulting changes in ambient air quality for cities which have instituted programs.

STATUTORY BACKGROUND

Section 211(m) of the Clean Air Act as amended in 1990 (the Act or CAA) requires states with areas experiencing dangerous levels of carbon monoxide pollution to implement winter oxygenated gasoline programs no later than November 1, 1992. This mandate is applicable to 39 areas throughout the country, although just 36 began the program on November 1, 1992.

The oxygenated gasoline program requires gasoline in the specified control areas to contain an average of 2.7% oxygen by weight during that portion of the year in which the areas are prone to high ambient concentrations of CO, typically during the core winter months. The lengths of these control periods have been established by the EPA Administrator. The Act requires that the winter oxygenated gasoline program apply to all gasoline sold or dispensed in the larger of the Consolidated Metropolitan Statistical Area (CMSA) or the Metropolitan Statistical Area (MSA) in which the nonattainment area is located. (See Table 1 below for a complete list of the CMSAs and MSAs affected by this requirement and their control periods.)

Just a few states opted to allow averaging programs, including Pennsylvania and Ohio. Other states, such as Oregon and Washington, have adopted limited averaging scenarios, allowing individual companies to average their oxygen contents over the course of the season, but not allowing companies to sell and trade credits among themselves. The majority of the states adopted programs which did not allow for averaging, thus requiring that each gallon of gasoline contain no less than the minimum 2.7% oxygen by weight.

---

**Table 1: Program Areas**

November 1 - February 29

Hartford-New Britain- Middletown, CT CMSA	Washington, DC-MD-VA MSA
Seattle-Tacoma, WA CMSA	Grant's Pass, OR
Philadelphia-Wilmington-Trenton, PA-NJ-DE-MD CMSA	Baltimore, MD MSA
Greensboro-Winston-Salem- High Point, NC MSA	Medford, OR MSA
Raleigh-Durham, NC MSA	Missoula, MT
El Paso, TX MSA	Klamath County, OR
Denver-Boulder, CO CMSA	Provo-Orem, UT MSA
San Diego, CA MSA	Albuquerque, NM MSA
	Colorado Springs, CO MSA
	Fort Collins-Loveland, CO MSA
	Portland-Vancouver, OR-WA CMSA

October 1 - April 30

New York-Northern New Jersey-Long  
Island, NY-NJ-CT CMSA

October 1 - January 31

Minneapolis-St. Paul, MN-WI MSA	Chico, CA MSA
Fresno, CA MSA	Modesto, CA MSA
Reno, NV MSA	Sacramento, CA MSA
San Francisco-Oakland-San Jose, CA CMSA	Stockton, CA MSA

October 1 - February 29

Las Vegas, NV MSA	Phoenix, AZ MSA
Los Angeles-Anaheim-Riverside, CA CMSA	

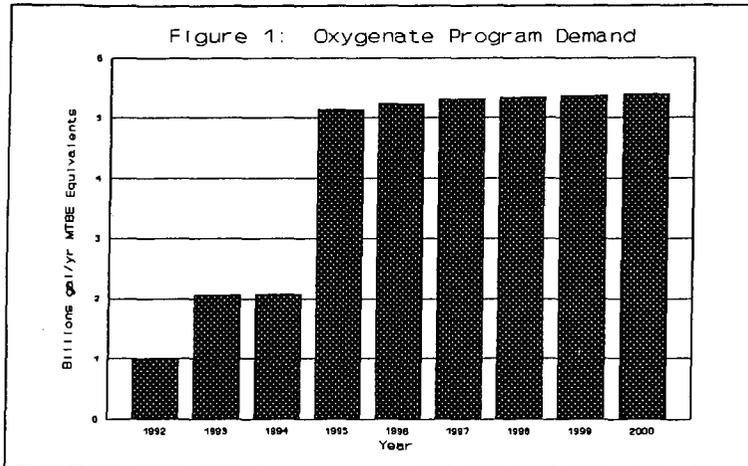
September 1 - February 29      Spokane, WA MSA

---

Under authority set forth in another part of the Act, the Administrator promulgated labeling regulations for the sale of gasoline at retail gasoline stations in oxygenated gasoline control areas. Under the Agency's regulation, the gasoline pumps at retail stations in each control area must be labeled during the applicable control period with conspicuous labels. The labels must be clearly readable in order to provide the public with information that oxygenated gasoline is being dispensed.

Under section 211(k) of the Act, "reformulated gasoline" is required in certain ozone nonattainment areas beginning in 1995. Among other things reformulated gasoline requires at least 2.0 percent oxygen by weight throughout the year. Reformulated gasoline could represent as much as half of the gasoline utilized in the U.S. depending upon the number of states that decide to adopt the program. (Although some areas are required to adopt the program, other less severe ozone nonattainment areas can "opt into" the program.)

The program-generated demand, on a yearly basis, for oxygenates can be seen in Figure 1.



#### ENVIRONMENTAL BENEFITS OF OXYGENATED FUELS

Carbon monoxide (CO) is a colorless, odorless gas which can cause central nervous system effects such as a reduction in visual perception and manual dexterity, decreased exercise performance, and among individuals with chronic heart disease, a marked decrease in physical capacity and increase in chest pain. Motor vehicles are significant contributors to carbon monoxide emissions nationwide, adding approximately 75 percent to the CO inventory in major metropolitan areas. Millions of U.S. citizens are exposed to dangerous levels of this pollutant especially during the winter months.

One important strategy which an area may utilize to reduce CO emissions is the implementation of a cleaner-burning oxygenated gasoline program. For any given set of conditions, there is an optimum ratio of fuel to oxygen or air which provides the most efficient combustion. In cold weather when combustion tends to be less efficient, extra oxygen enhances combustion by offsetting fuel-rich operating conditions, especially during vehicle starting. If oxygen is added to the fuel in the form of oxygenates, a second source of oxygen becomes available (in addition to the primary source from the air). A gasoline blend containing 2.7 percent oxygen, by weight, will result in a 15% to 20% reduction in CO emissions, on a mile-for-mile basis, when compared to gasoline not containing oxygenates.

Oxygenates also cause decreases in unburned hydrocarbon exhaust emissions including certain toxic air pollutants such as benzene and 1,3-butadiene. Although oxygenates do increase aldehyde emissions, total toxic emissions decrease through oxygenate use.

#### WHAT OXYGENATES ARE USED?

Alcohols and ethers have been added to gasoline in various forms for over fifteen years, sometimes to enhance octane, sometimes simply as a fuel extender, and, more recently, to decrease emissions. Typically, although other oxygenates could be utilized (and have been in the past), fuel oxygen is added to gasoline in the form of ethanol, an alcohol, or methyl tertiary butyl ether (MTBE).<sup>1</sup> These oxygenates are used because they are the most economically viable in today's fuel market. Ethanol has been traditionally added to gasoline at 10 percent by volume, which adds approximately 3.5 percent oxygen to the fuel. However, in oxyfuel program areas, ethanol is often added at about 7.7 percent by volume to meet the program requirement of 2.7 percent oxygen. To reach the same oxygen level, MTBE is added at a level of approximately 15 percent by volume.

#### PROGRAM RESULTS

The previously stated 15 to 20 percent reduction in CO emissions is evidenced by what occurred last year in the cities which implemented an oxygenated fuels program. A preliminary study of exceedances of the National Ambient Air Quality Standard for carbon monoxide in these cities covering the winter months in the 1992-93 season during which an oxygenated fuels program was in place reveals a very telling picture. (See Figure 2.) For 21 areas which had not previously implemented oxygenated fuels programs, CO exceedances dropped by 95 percent when compared to the previous winter (1991-92). In California, where a program was implemented requiring slightly less total oxygen (2.0 percent oxygen instead of 2.7 percent - equivalent to about 11 percent MTBE instead of 15 percent), exceedances dropped by 80 percent. In areas with pre-existing programs, most of which required oxygen levels around 2.0 percent but, under the new program, increased to 2.7 percent, exceedances dropped by about 50 percent. Although normal year-to-year variations in meteorological conditions or patterns of vehicle use might have contributed to the decline in CO exceedances in some nonattainment areas, these aggregate national data suggest strongly that MTBE is having the kind of positive effect overall that was intended.

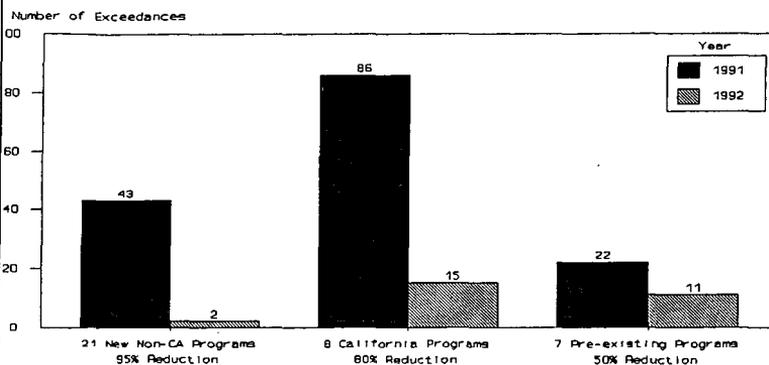
---

<sup>1</sup> Other oxygenates which can be used include tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE), both of which have been used to a very small extent during the past season in some isolated cases. In the past certain blends of methanol and other alcohols have been used but these blends are not viable in today's market.

Figure 2

### FIRST YEAR PROGRAM RESULTS

- \* Program compliance was excellent in first season.
- \* Comparison of data from this winter to data from last winter show an 80% reduction in CO exceedances.



Note: California had 2.0% oxygen by weight program.

### HEALTH ISSUES

Citizens in some areas of the country complained of acute health symptoms such as headache and nausea which they associated with use of MTBE in gasoline. There are a number of reasons why this reaction to MTBE-blended gasoline was unexpected. MTBE has been used in the U.S. as an octane enhancer since the late 1970's (at concentrations of 2-11%). Industry had tested many aspects of the fuel additive prior to 1992 and this research indicated no significant health concerns. Seven cities had, in fact, required wintertime use of oxygenated gasoline prior to 1992, most notably Denver which began its program in 1988, and experienced no problems similar to those in Alaska. Under the Clean Air Act oxygenated gasoline program, however, concentrations of MTBE must be generally higher than they were in Denver. (Denver required MTBE concentrations from 10-14.4%, while the Act requires 15%.)

The Environmental Protection Agency (EPA) took these concerns seriously and, in a very short time, organized a comprehensive strategy to investigate Alaska's complaints. In order to address the issue of health symptoms associated with acute exposures to

MTBE-blended gasoline, EPA outlined a six-month test program in January 1993. EPA coordinated almost \$2 million worth of studies, working with the Centers for Disease Control and Prevention (CDC), the State of Alaska, industry groups represented by the American Petroleum Institute (API) and the Oxygenated Fuels Association (OFA), as well as other EPA and state offices.

The testing effort included animal studies, human clinical studies, epidemiological studies, exposure studies and automobile emissions studies and air and fuel sampling. In addition, ORD accelerated its review of existing research on chronic effects of MTBE. The results from these studies were presented at a workshop, sponsored by ORD, API and OFA, on July 26-28, 1993. The workshop enabled EPA and others to assess these health concerns before the start of the oxygenated gasoline season in 1993 in Alaska and elsewhere. EPA's assessment of the potential health risks associated with MTBE-oxygenated gasoline has been completed and indicates that MTBE appears to have very little acute health risk to healthy people under relatively temperate conditions. Hence, in terms of short-term acute health effects, these results seem to provide no basis to question continuing the overall MTBE oxyfuels program. This conclusion does not reflect that there may be a particularly sensitive subpopulation which may react to MTBE differently. However, results to date provide no firm evidence that such sensitive individuals exist or, if they do, how they might be identified. Further research on exposure to MTBE and the health effects of MTBE continues.

**CONCLUSION:**

Available data indicate that oxygenated fuels program implemented for pollution abatement have successfully decreased exceedences of the National Ambient Air Quality Standards for carbon monoxide pollution. Health research appears to indicate little health risk to healthy people under relatively temperate conditions.

SYMPOSIUM ON OXYGENATES AS FUEL ADDITIVES  
AMERICAN CHEMICAL SOCIETY, FUEL DIVISION  
SAN DIEGO NATIONAL MEETING  
MARCH 13 -18, 1994

FUTURE FUEL DIVERSIFICATION WITH OXYGENATES

William J. Piel  
ARCO Chemical Company  
3801 West Chester Pike  
Newtown Square, Pa 19073

Keywords: Emissions, Oxygenates, Fuels

### INTRODUCTION

Fuel oxygenate blending in motor fuels first became commercialized in 1969 with the blending of t-butyl alcohol in gasoline. This first fuel alcohol was made by adding oxygen to isobutanes. Now most of this alcohol production is converted to isobutylene for methyl tertiary butyl ether (MTBE) production. MTBE blending was first commercialized in the U.S. in 1979 when the U.S. EPA granted a section 211F waiver request to blend it into unleaded gasoline. MTBE use grew during the 1980's as a high octane replacement for lead compounds in gasoline. Similarly, 10% ethanol blending was approved in 1978. With a government tax incentive for alcohols made from renewable sources, ethanol's use also grew as a non-petroleum gasoline extender in the mid-1980's.

Relative to mobile source emissions, the 1990 revision to the Clean Air Act (CAA) requires reductions of carbon monoxide (CO), volatile organic compounds (VOCs), and toxics from gasoline fueled vehicles. Reductions in nitrogen oxides (NOx) and greenhouse gases (such as carbon dioxide - CO<sub>2</sub>) were not required. The strategy in the CAA to decrease ground level ozone is by reducing VOC mass emissions by 15% in 1995 and 25% in 2000. The other attributing compound to ozone, NOx emissions, are only capped at the 1990 levels in the CAA. Based on the predictive models developed by the U.S. EPA and by the California Air Resource Board (CARB), it appears that the fuel reformulation will be able to achieve the year 2000 performance requirements targeted in the CAA.

Fuel oxygenates played a key role in both the Oxygenated Fuels and Reformulated Fuels outlined in the CAA. The next wave of environmental interest is to possibly modify motor fuels and/or motor vehicles for reductions in NOx emissions and greenhouse gases such as CO<sub>2</sub>. Fuel oxygenates can also play a significant role in such fuel modifications. To achieve the maximum emissions reduction potential, minor engine modifications may be required to take full advantage of the possible fuel property improvements.

### FUEL OXYGENATES

Though MTBE and ethanol are the most commonly used oxygenates, there are many other potential fuel oxygenates that are being developed or investigated such as TAME (tertiary amyl methyl ether) and ETBE (ethyl tertiary butyl ethers)(Ref 1). The properties of these oxygenates and others are listed in Table 1. The most useful property of the oxygenates is their high octane. Outside of metal compounds, oxygenates are generally the only high octane alternative to aromatics in gasoline. The potential octane contribution of oxygenates are shown in Figure 1 as a function of the their oxygen contribution in gasoline.

While mixtures of alcohols are allowed up to 3.7 weight percent oxygen in gasoline under various EPA approved waivers, ethers are currently limited to 2.7 weight percent oxygen in gasoline. Under these limits, ethers can potentially add 3 to 4 octane numbers to the gasoline pool. If the oxygen limit for mixed ethers were raised to 3.7 percent, ethers could contribute 4 to 5 octane numbers, and up to 20+ volume percent to gasoline. Their potentially large octane and volume contribution can play a significant role in replacing most of the aromatics in gasoline, and modifying future gasoline formulations for reductions in NOx and CO<sub>2</sub> emissions as will be discussed later.

Besides their octane, a major advantage of ethers over aromatics is their relatively lower boiling temperatures. Since lead phasedown in gasoline, the increased use of aromatics in premium gasolines have lead to poor mid-range volatility and a degradation of cold engine driveability and performance(Ref 2). The automakers have been making an effort to limit this performance degradation by proposing a cap on a Driveability Index (DI) that is calculated from distillation temperatures of gasoline. Using their individual boiling temperatures, then DI differences between ethers and aromatics are illustrated in Figure 2. Though both provide octanes higher than a 100 (r+M)/2, the DI of most ethers are favorably lower while the high boiling temperatures of the aromatics contributed to higher DI for gasoline, particularly premium gasolines. The DI benefits of using ethers for octane is best illustrated by comparing the DI changes between the 1992 and 1993 winter DI averages for the oxygenated and non-oxygenated cities in the AAMA (American Automobile Manufacturers Association) gasoline surveys.

<u>Gasoline Grade</u>	<u>DRIVEABILITY INDEX</u>		<u>DI</u>
	<u>1992</u>	<u>1993</u>	<u>CHANGE</u>
Regular - Oxygenated	1112	1061	-53
Non-oxygenated	1071	1092	+21
Premium - Oxygenated	1154	1087	-67
Non-oxygenated	1153	1147	- 6

Though the non-oxygenated cities showed very little change in DI, the oxygenated cities (with predominately MTBE) showed very favorable decreases greater than 50 DI. Therefore, the use of ethers appears to provide an effective means for improving the mid-range volatility of the gasolines which should also benefit the 1990 CAA Reformulated Gasoline program.

#### **EXHAUST NOx EMISSIONS**

The work completed by AUTO/OIL established sulfur in gasoline as a major influence on tailpipe NOx because of its effect on the activity or efficiency of the catalytic converters(Ref 3). However, the other fuel variables that effect NOx emissions were not quite as clear(Ref 4-5). Since NOx is a side reaction of combining oxygen and nitrogen during the combustion process, NOx in engine exhaust is expected to be a function of the peak temperatures during combustion. The dilemma is what fuel property changes have the most influence on the peak combustion temperatures. Earlier research by others had found the flame temperature and resulting NOx emissions of fuels to be most easily correlated with the hydrogen to carbon ratio (H/C) of the fuel (Ref 6-8) where high H/C has a lower flame temperature and therefore lower NOx thermal equilibriums.

This relationship can also be seen in some more recent work conducted with ARCO Chemical Europe in conjunction with BP Oil, and Volvo. ECE emission test were conducted with 11 different fuels of varying composition but relatively similar octanes in two 1991 non-cat cars with VOLVO engines (B-230 2.3 litres, 4 cylinders). The relative change in the NOx emissions compared to each fuel's hydrogen to fuel ratio in this study is shown in Figure 3. Also, three of the fuels contained oxygen, one from ethanol and two from MTBE. The data in Figure 3 suggest that the NOx emissions are strongly related to the fuels' hydrogen to carbon ratio independent of oxygen content in the fuel. This correlation to H/C ratio is consistent with the results reported in previously referenced studies.

However, in addition to the flame temperature of the fuel, the ultimate combustion temperature would also be expected to be a function of the octane of the fuel. Octane is a good indicator of the fuel's resistance to autoignite under the more severe operating conditions in the engine. Low octane fuel may autoignite early prior to optimum timing under severe engine conditions and thereby increase peak pressures and temperatures. Therefore, higher octane fuels would be expected to suppress autoignition and generate lower peak temperatures and lower NOx under severe engine operating conditions. The possible sensitivity of NOx to octane, particularly motor octane, of the fuel has been observed in some previous studies(Ref 9-10).

To test this theory that NOx production may be influenced by octane number independent of fuel composition, the octane of a reference fuel was artificially lowered by adding minute amounts of tertiary butyl hydro peroxide (TBHP), a very powerful pro-knock compound. FTP emission tests were conducted on two cars (1991 Dodge Spirit 2.5 liter/TBI and 1990 Ford Probe 2.2 liter/PFI) using the reference fuel (indolene) and the same fuel with two levels of peroxide. The average results for the two cars is as follows:

<u>TBHP</u> <u>(ppm)</u>	<u>Fuel Octane</u>		<u>% NOx</u> <u>Changes</u>
	<u>MON</u>	<u>(R+M)/2</u>	
0	88.7	93.0	Base
420	87.2	91.4	+ 15%
1100	86.5	90.5	+ 14%

These results support the theory that octane number, independent of fuel composition, can also effect NOx emissions in the engine exhaust. Evidence of this octane effect has also been seen in Ethyl Corporation's work with MMT (methylcyclopentadienyl manganese tricarbonyl), a metal based octane additive. In the emission work to support a MMT waiver request, fuels containing 0.03125 grams of MMT per gallon increased the fuel's octane by approximately 0.8 octane numbers, but more importantly decreased NOx emissions(Ref 11).

A review of the emission results for AUTO/OIL's older car fleet shows similar fuel effects on the NOx emissions. Figure 4A shows the average NOx emissions relative to the fuels' H/C ratio. The AUTO/OIL's fuel matrix essentially falls into two groups: low H/C fuels and high H/C fuels. The NOx emissions from the high H/C fuels are approximately 12% lower than that from the low H/C fuels. The data also shows no oxygen effects since the emissions for the oxygenated fuels appear to be evenly dispersed among the non-oxygenated fuels. As Figure 4A shows, there also is more variance in the low H/C fuel group than the high H/C group. Much of this variance seems to be explained by the motor octane which varies as much as 5 octanes for the low H/C fuels as shown in Figure 4B. Though motor octane seems to explain some of the variance in the high H/C fuels as well, it is not as clear since the range of motor octane is only 2.5 numbers for this group.

The review of these studies suggest that much of the fuel effects on NOx emissions from gasoline vehicles can be explained by three main factors: the H/C ratio and the motor octane of the fuel as it effects peak combustion temperatures, and the fuel's sulfur content for its effect on the catalyst activity in the catalytic convertor. One other fuel quality for investigation is the ability of the fuel to warm-up the engine quicker (with higher DI), and thereby increase total NOx over an emissions test cycle. However, this might offset by the catalytic convertor also warming up quicker.

#### CARBON DIOXIDES EMISSIONS

Carbon dioxide (CO<sub>2</sub>) from fuel combustion is considered to be a major source of greenhouse gases, and the current administration is dedicated to capping the year 2000 greenhouse gases at the same level as 1990. Though the stationary power sources may have the flexibility to switch from high fossil carbon fuels such as coal or heavy oils to low fossil carbon fuels such as natural gas or biomass fuels as a way to reduce CO<sub>2</sub>, transportation fuels are not quite as flexibility. However, the CO<sub>2</sub> emissions associated with gasoline energy content is still related to the H/C ratio of the fuel components as shown in Figure 5. Aromatics represent the highest carbon content fuels and therefore the gasoline components with the highest CO<sub>2</sub> per unit of energy. Ethers, like paraffins, are gasoline components with the lowest CO<sub>2</sub> per unit of energy. Therefore, using ethers in place of aromatics for octane in gasoline may be an effective way to reduce fossil carbon dioxide emissions from gasoline by 4 to 5 percent. This CO<sub>2</sub> relationship to fuel H/C is consistent with the analysis reported by the AUTO/OIL analysis (Ref 12).

Raising the octane of gasoline presents another opportunity to significantly reduce CO<sub>2</sub> emissions from transportation fuels by allowing the automakers to raise the compression ratios of the engines of their new car models. Increasing the compression ratio would reduce fuel consumption by increasing the thermal efficiency of the engine's operation. The optimum octane for gasoline was last debated in industry about two decades ago when unleaded gasoline was about to be widely distributed in the marketplace (Ref 13-21). The conclusion from most of these studies was that the optimum octane for unleaded gasoline was around 91 to 92 (R+M)/2 octane even though the industry went with 87 (R+M)/2 as the standard octane for gasoline. The economic basis used in these studies was generally limited to comparing the cost of fuel savings versus the cost of raising the octane of gasoline. The environmental benefit of reducing CO<sub>2</sub> emissions was not considered in these studies at the time. If it had been included, it would have further supported the higher octane fuel / higher compression engine combination.

Figure 6 shows typical relationships to engine compression ratio which is derived from one of these studies (Ref 15). In the range of interest, Figure 6 shows that increasing the compression ratio by two numbers would increase fuel efficiency by approximately 10 percent but would also increase engine's octane requirement by approximately 6 octane numbers. This study suggest that each octane is potentially worth 1.8 % increase in fuel efficiency or fuel economy. This ratio between efficiency and octane seems to be approximately the same in most of these studies.

Some of these studies also attempted to address the issue on whether there was any increase in other emissions such as NOx or hydrocarbons(Ref 18-21). Their results suggested that there was little change in these emissions after re-optimizing other engine operating parameters such as timing and air to fuel mixtures. However, these studies did not evaluate any possible emission reduction benefits associated with also raising the fuel's octane for the higher compression ratio operation.

What these prior studies did not review in their analysis is any possible loss in driveability performance associated with higher fuel octane, particularly if high boiling aromatics should be the main source of the octane increases. As mentioned earlier, this is now a major concern of the automakers. Therefore, the source of increased octane would likely have to be from ethers which can potentially add five octane numbers to the gasoline pool with out worsening the driveability index of the gasoline.

Another benefit of using ethers instead of aromatics for octane is their greater increase in combustion gas volumes. Higher H/C ratio fuels generate more moles or volumes of product gases per volume of combustion air that is consumed or drawn into the engine's cylinders. This higher volume of combustion gases increases combustion pressures even further for an added boost in engine efficiency and power. This comparison between ethers and aromatics is illustrated in Figure 7. In general, the ethers provide about 4 to 5 percent more gas volume than the aromatics during combustion.

Therefore, using oxygenates to further increase gasoline octane can potentially help reduce fossil based CO<sub>2</sub> emissions in two ways: one by reducing the carbon to energy ratio of the fuel, and second to allow the automakers to increase the fuel economy of cars by raising the engine compression ratio. Also, if oxygenates become a significant proportion of gasoline, it opens up an avenue to use more renewable carbon in gasoline since the alcohols in oxygenates can be made from renewable resources (Ref 22). This can further reduce the fossil based CO<sub>2</sub> emissions from transportation fuels.

## SUMMARY

A review of the available data suggest there is still potential to reduce NOx emissions and the fossil fuel based CO2 emissions from mobile sources. Based on the review presented here, both of these emission reductions can be accomplished by increasing the hydrogen / carbon ratio of gasoline and also raising its octane number, particularly the motor octane. This would have been difficult to accomplish if the high carbon content aromatics were the only source of high octanes for gasoline blending. However, with the development of oxygenates as an octane enhancer, particularly ethers, both of these changes in gasoline can be done simultaneously and are technically feasible. Based on the reviews of past studies, both these changes in the fuel are probably economically and environmentally justifiable. Therefore, fuel oxygenates are not only capable of adding oxygen to gasoline to improve combustion, but they are also tools for increasing fuel H/C ratios as well as adding more octane for potentially better engine efficiencies in the future.

## ABBREVIATIONS

DI	- Driveability Index (1.5xT10 + 3.0xT50 + T90) degrees fahrenheit
ETBE	- Ethyl tertiary butyl ether
IPTBE	- Isopropyl butyl ether
MTBE	- Methyl tertiary butyl ether
NOx	- Nitrogen oxide compounds
MON	- Motor octane number
RON	- Research octane number
(R+M)/2	Average of RON and MON
H/C	- Hydrogen to carbon atomic ratio
CO2	- Carbon dioxide

## REFERENCES

1. Piel,WJ, "Expanding refinery technology leads to new ether potential", FUEL REFORMULATION, Vol 2 No.6 , Pgs 34-40, Nov/Dec 1992
2. Benson, JD,et.al., "AUTO/OIL Air Quality Improvements Research Program An - Update of Research Results", presented at 1993 DEWITT Petrochemical Review Conference, March 1993
3. Benson, JD,et.al., "Effects of Gasoline Sulfur Level on Mass Exhaust Emissions", SAE 912323
4. Benson, JD,et.al., "Effects of Gasoline Composition and Properties on Vehicle Emissions: a Review of Prior Studies", SAE 912321
5. Benson, JD,et.al., "The effects of Aromatics, MTBE, Olefins and T90 on Mass Exhaust Emissions from Current and Older Vehicles", SAE 912322
6. Ninomiya, JJ & Golovoy, A, "Effects of Air-Fuel Ratio on Composition of Hydrocarbons Exhaust from Isooctane ,Diisobutylene, Toluene and Toluene-n-Heptane Mixtures", SAE 690504
7. Carr,RC, et.al., "The influence of fuel composition on emissions of carbon monoxide and oxides of nitrogen", SAE 700470
8. Harrington, JA & Shishu,RC, "A single cylinder engine study of the effects of fuel type, fuel stoichiometry, and hydrogen-to-carbon ratio on CO, NO and HC exhaust emissions", SAE 730476
9. **Present and Future Automotive Fuels**, by O. Hirao and R.F. Pefley, copywrit 1988 by John Wiley & Sons, Inc, pgs 101-106
10. Boekhaus, KL,et.al., "reformulated Gasoline for California: EC-Premium Emission Control Gasoline", SAE 911628
11. Holtrah, DP, & Burns, AM, "MMT increases octane while reducing emissions", Oil & Gas Journal, Mar 11, 1991, pgs 86-90
12. Benson, JD, et.al., "Fuel composition effects on automotive fuel economy", SAE 930138
13. Editorial, "Air-quality control takes on a major role", Oil & Gas J., June 15, 1973, pgs 97-113
14. Wagner, TO, & Russum, LW, "Optimum octane number for unleaded gasoline", SAE 730552
15. Corner, ES, & Cunningham,AP, "Value of high octane number unleaded gasoline", ACS Los Angeles meeting, Mar 28 - Apr 2, 1971, D77-87
16. Hakala, NV, et.al. "The impact of product quality requirements on gasoline composition: past present, future", ACS New York Meeting, Aug 27 - Sept 1, 1972, B131-145
17. Lawrence, DK, et.al., "Automotive fuels-refinery energy and economics", SAE 800225
18. Oberdorger, PE, "Compression ratio, emissions, octanes and fuel economy-an experimental study", 1972 API Proceedings, Div. of Refining, Vol 52, pg 936-953
19. Lee, RC, "Effects of composition ratio, mixture strength, spark timing, and coolant temperature upon exhaust emissions and power", SAE 710832
20. Felt, AE & Krause, SR, "Effects of compression ratio changes on exhaust emissions", SAE 710831
21. Baker, RE, et.al., "Selecting compression ratio for optimum fuel economy with emission constraints", SAE 770191
22. Piel, WJ, "Expanding Liquid Transportation Fuels Through Methanol, Higher Alcohols and Ethers", Proceedings of First Biomass Conference of the America's, Aug 30-Sept 2, 1993, Burlington, VT, Vol II, pgs 1116-1132

**TABLE 1****TYPICAL PROPERTIES OF FUEL ALCOHOLS IN GASOLINE :**

	Methanol & Co- Solvent	(1) Ethanol	Iso- Propanol	tert- Butanol	Iso- Butanol	tert- Amyl Alcohol
OCTANES: Blending (R&M)/2	108+	115	106	100	102	97
VAPOR PRESSURE: Neat RVP (100F)	4.6	2.3	1.8	1.7	0.6	0.7
Blending RVP (2)	31+	18	14	9	5	6
BOILING PT. (F)	148	173	180	181	226	216
DENSITY (LB/GAL)	6.63	6.61	6.57	6.59	6.71	6.79
ENERGY DENSITY: MBTU/Gal (LHV)	56.8	76.0	87.4	94.1	95.1	100.1
HEAT OF VAPOR.: MBTU/Gal @ NBP	3.14	2.39	1.90	1.55	1.67	1.58
OXYGEN CONTENT (WT.%)	50	34.8	26.7	21.6	21.6	18.2
SOLUBILITY IN WATER: (WT.%)	I	I	I	I	10.0	11.5

**TYPICAL PROPERTIES OF FUEL ETHERS IN GASOLINE :**

	<u>MTBE</u>	<u>ETBE</u>	<u>DIPE</u>	<u>TAME</u>	<u>IPTBE</u>	<u>TABE</u>
OCTANES: Blending (R&M)/2	110	112	105	105	113	100
VAPOR PRESSURE: Neat RVP (100F)	7.8	4.0	4.9	2.5	2.5	1.2
Blending RVP	8	4	5	2.5	2.5	1
BOILING PT. (F)	131	161	155	187	188	214
DENSITY (LB/GAL)	6.19	6.20	6.1	6.41	6.30	6.39
ENERGY DENSITY: MBTU/Gal (LHV)	93.5	96.9	100	100.6	NA	NA
HEAT OF VAPOR.: MBTU/Gal @ NBP	0.86	0.83	0.9	0.90	NA	NA
OXYGEN CONTENT (WT.%)	18.2	15.7	15.7	15.7	13.8	13.8
SOLUBILITY IN WATER: (WT.%)	4.3	2.6	2.0	2.0	NA	NA

I - Infinite Solubility  
 NA - Not Available

- (1) Typical for methanol waivered blends with cosolvents  
 (2) Blending RVP for 2.7% oxygen or higher in gasoline

FIGURE 1

Potential Octane Contribution of Oxygenates in Gasoline

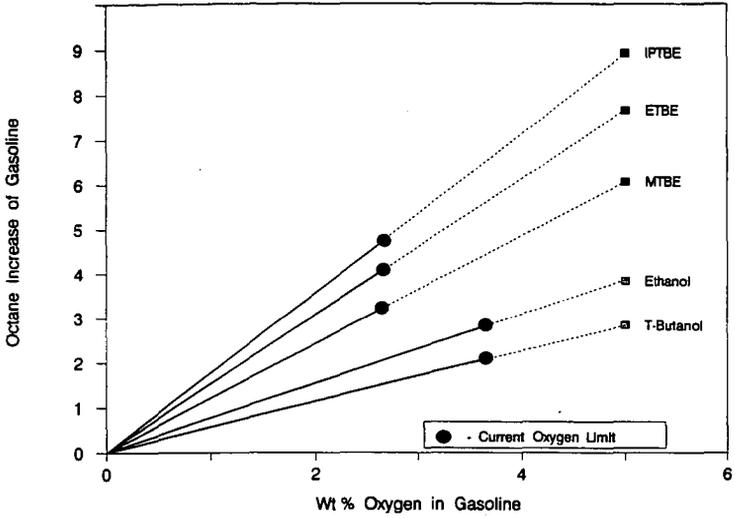
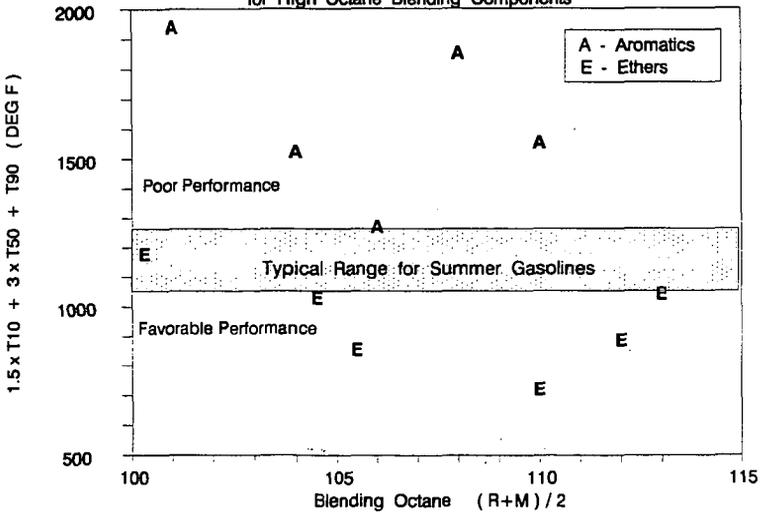


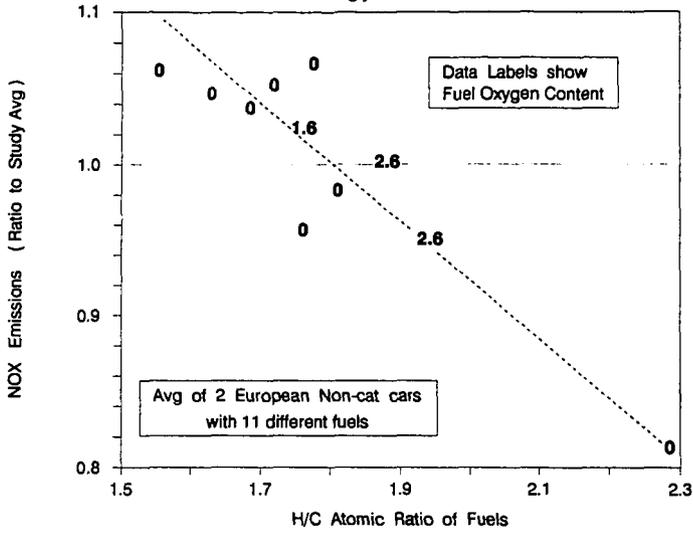
FIGURE 2

Driveability Index (DI) vs. Octane for High Octane Blending Components



**FIGURE 3**

NOx Emissions Strongly Related To Fuel H/C Ratio



**FIGURE 4A**

NOx Emissions vs H/C Ratio of Fuel

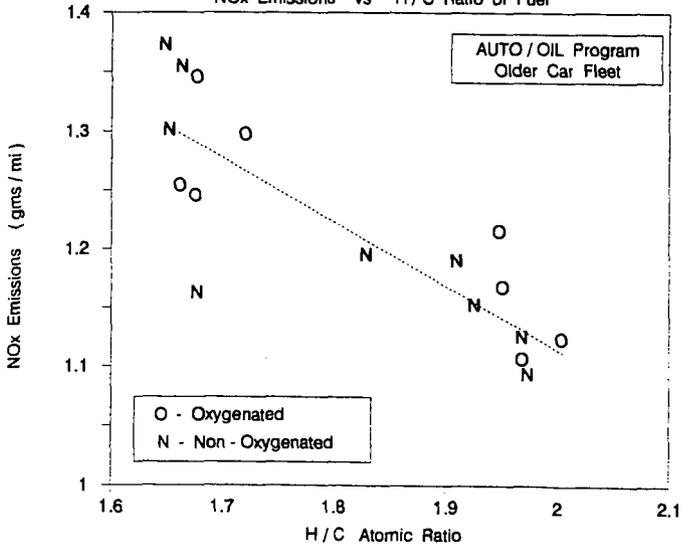


FIGURE 4B

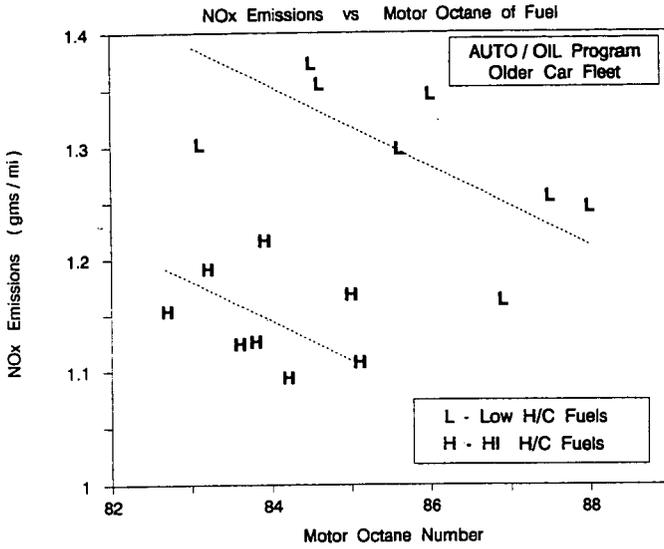


FIGURE 5

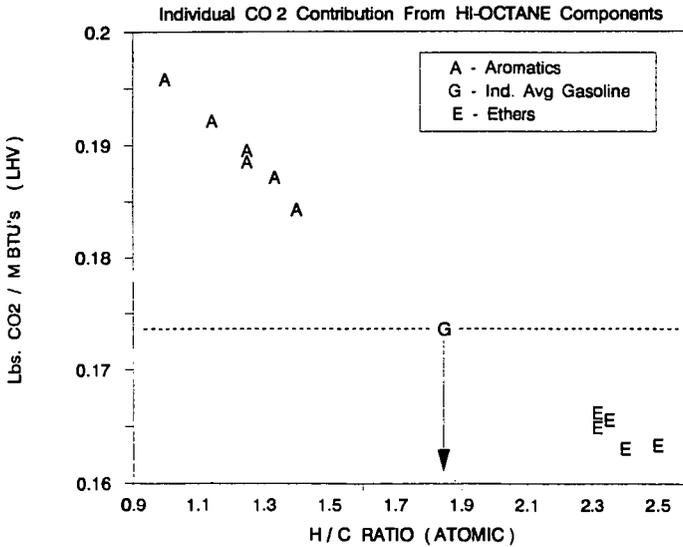


FIGURE 6

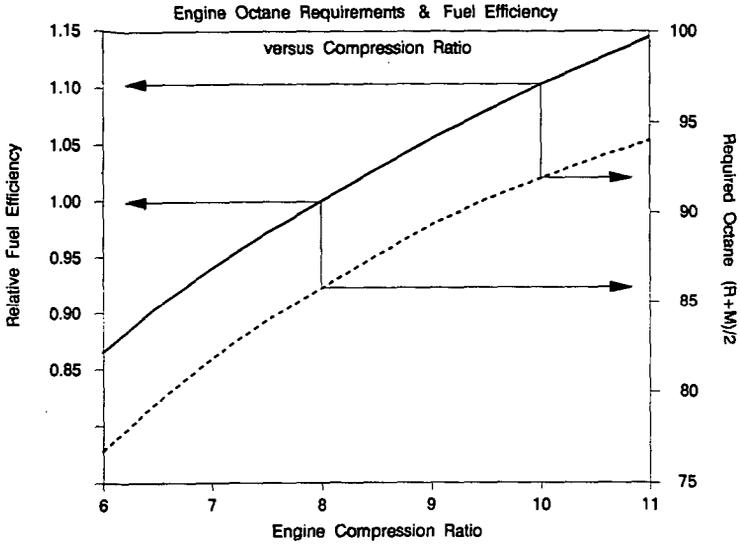
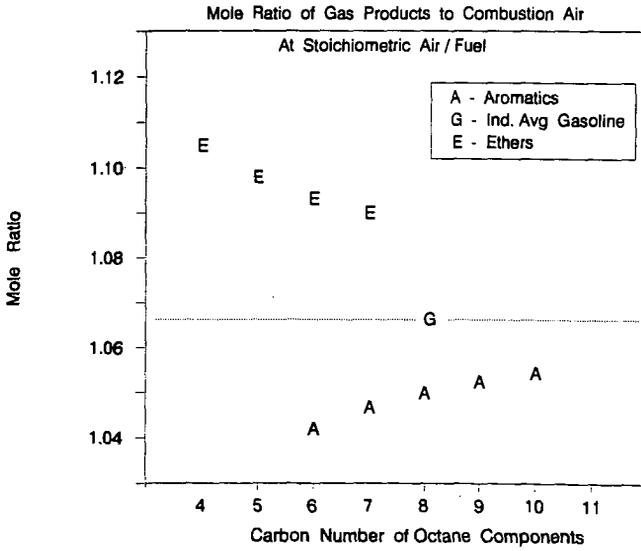


FIGURE 7



ALTERNATIVE FUEL USE  
IN COLORADO

Kim B. Livo  
Dr. Jerry Gallagher  
Martin W. Boyd  
Air Pollution Control Division  
Colorado Department of Health  
4300 Cherry Creek Drive South  
Denver, Colorado 80222

Abstract

The use of alternative fuels hold the promise of promoting energy diversity and reducing motor vehicle emissions. With the passage of the federal Clean Air Act Amendments of 1990, the National Energy Policy Act of 1992, and state initiatives such as from California, these fuels will have a far reaching influence on the fuels motor vehicle fleets operate on in the next century.

Many of the emission benefits of alternative fuels are dependent on the quality of the alternative fuel implementation, as well as the fuels themselves. To prevent degradation of motor vehicle emissions, the Colorado Department of Health has implemented alternative fuel retrofit system certification procedures. These, as well as EPA and California certification standards will allow present vehicles to have acceptable emissions, as well as future vehicles to meet required low emission standards.

Introduction

Transportation fuels have been at the heart of two major public policy issues facing the United States for the last several decades; pollution caused by motor vehicles, and the growing dependence on imported oil. Clean fuels, such as alternative fuels, are of increasing importance as a way to lower motor vehicle emissions. Diversification of transportation fuels is equally important, and will lessen or mediate future supply disruptions or price hikes which were saw in the oil shocks of the 1970s.

In Colorado, alternative fuel use has been growing dramatically since the start of the 1990s. Today there are more than 5000 vehicles capable of operating on alternative fuels. This growth is posing significant challenges to the fuels industry and fleet users. To support the expanding vehicle fleet, the fuels industry has been actively expanding the alternative fuel infrastructure. In turn, fleet users are being challenged to integrate and maintain new types of vehicles and fuels.

Background

Alternative fuel use in Colorado, and elsewhere, is been shaped largely by two significant pieces of federal legislation, the Clean Air Act Amendments of 1990 and the National Energy Policy Act of 1992. Developments in California are also effecting

alternative fueled motor vehicle use, as California "low emitting vehicle", "ultra low emitting vehicle" and "zero emitting vehicle" standards are driving the entire alternative fueled vehicle market

#### The Clean Fleet Fuels Program

The Clean Air Act Amendments of 1990 mandate the use of clean fuels for fleets, mainly as part of the Clean Fleet Fuels Program. This program is scheduled to begin in 1998 for public and private fleet of ten or more vehicles which are centrally refueled.

The Clean Fleets Fuels Program affects fleets in 21 ozone and one carbon monoxide non-attainment areas with populations of 250,000 or more based on the 1980 census. The program applies to automobiles and light and heavy duty trucks up to 26,000 pounds gross vehicle weight.

The Clean Fleet Fuels program is as the name suggests, a "clean" fuels program. It is a program which stresses air quality, rather than type of fuel, so is a performance, rather than alternative fueled, based program. To participate, a fuel/vehicle combination must meet the same standard as the California low emitting vehicle standard.

It is expected that alternative fuels will have an advantage in meeting the specific emission requirements of this program, but reformulated gasolines and clean diesel fuels may also participate. Any fuel, in combination with vehicle technology, which meets the standard is eligible for this program. This includes alternative fuels such as natural gas, propane, methanol, ethanol, and electricity, as well as clean gasolines and diesel fuels. Some types of vehicles will be exempted to this program. They include emergency and law enforcement vehicles, and vehicles which are garaged at home.

#### National Energy Policy Act of 1992

A second federal program expected to fuel the market for alternative fuels and fueled vehicles this decade and next, is the National Energy Policy Act of 1992. This act, unlike the Clean Fleet Fuels Program, is designed strictly to increase the use of alternative fuels and fueled vehicles. It mandates that certain fleets purchase alternative fueled vehicles.

The National Energy Policy starts in 1993 for the Federal fleet, and 1996 for State fleets and fuel provider fleets. Private and municipal fleets may have to participate also, as early as 1999, if the Secretary of Energy makes a determination that national alternative fuel usage goals require their inclusion to be met.

The National Energy Policy act affects all metropolitan areas in the United States with a population of over 250,000 people at the time of the 1980 census. It covers eligible fleets of fifty or more vehicles, with at least 20 or more in any one area. It affects vehicles with weights up to 8500 GVW. In addition, the covered vehicles must be capable of being centrally refueled.

Unlike the Clean Fleet Fuels Program, this program is an energy diversity program, so is not standards driven but rather alternative fuel driven. Alternative fuels which comply include, natural gas, propane, methanol, ethanol, and electricity.

Exempted vehicles for this program include, emergency and law enforcement vehicles, and vehicles garaged at home. At the discretion of the Secretary of Energy, the exemption for law enforcement vehicles may be waived.

#### State and Local Incentives

Colorado, because of air quality issues, as well as economic developmental reasons has encouraged the use of alternative fuels. In terms of air pollution, alternative fuels do hold the promise of reducing vehicle emissions which contribute to Colorado's winter-time carbon monoxide and PM-10 problems, and year round visibility concerns.

But showing promise does not necessarily lead to a solution. Mass emissions testing conducted by the Colorado Department of Health (CDH), has shown that not all alternative fueled vehicles are low emitting. As with traditional vehicles, good design and proper vehicle maintenance are needed to obtain and maintain appropriate vehicle emission levels. To assure that alternative fueled vehicles meet applicable emissions standards, the CDH regulates vehicle conversions through Air Quality Control Commission Regulation No. 14. Through this regulation, only CDH certified retrofit systems are allowed on vehicle conversions.

To encourage the use of alternative fueled vehicles, the state, and local municipalities, have adopted a number of incentive programs. One of the first programs established was a state fleet program which requires the state fleet manager to purchase or convert a number of vehicles to alternative fuels each year. Beginning in fiscal year 1991, the goal was 10% of all new vehicle purchases. This has been increased to 40% for the fiscal 1994 year.

The city of Denver has adopted a more pervasive ordinance, No. 330, administered by the City of Denver Health and Hospitals, requiring 10% of all fleet vehicles to be alternatively fueled for fleets of 30 or more vehicles. Diesel powered vehicles are excepted from conversion requirements, but are counted as part of that 30 or more vehicles.

#### Governor's Alternative Fuels Task Force

To encourage the use of alternative fuels, Colorado's governor, Governor Romer, established a Governor's Alternative Fuels Task Force. It was charged with the task of investigating ways of furthering the use of alternative fuels. This Task Force, composed of local state, county, and municipal officials, as well as citizens, met for over a year in determining the direction Colorado should take in meeting both clean air goals and economic development.

The principle recommendation of the Task Force was that Colorado implement a Clean Fleet Fuels Program as required by the Clean Air Act Amendments of 1990. Such a program should be implemented as soon as possible before the 1998 deadline. The task force also recommended an incentive program be developed to promote fuels such as CNG and propane which could reduce carbon monoxide emissions from appropriate vehicles. As a gas producing state, the use of fuels such as CNG and propane were also favored as a way of meet both clean air objectives, as well as economic development goals.

The recommendations of the Task force were given statutory authority through the passage of House Bill 1305. House Bill 1305 authorized the Colorado Clean Vehicle Fleet Program, which will conform with the federal Clean Fleet Fuels Program mandated by Clean Air Act Title I, Part D and Title II, Part C , 1990.

The Colorado program will affect fleets with 10 or more vehicles in the Denver-Boulder CO non-attainment area. Colorado is the only state participating in the Clean Fleet Fuels Program strictly due to having a carbon monoxide non attainment area. Other states which have areas required to implement this program, and are in nonattainment for carbon monoxide, are also nonattainment for ozone.

By House Bill 1305, the Colorado Air Quality Control Commission was given the authority to promulgate rules and regulations for the implementation of this program. At the present time, the AQCC is preparing a regulation which will implement the program.

House Bill 1305 also authorizes the establishment of a mechanic certification program for vehicle conversions, and authorizes the establishment, but does not fund, an alternative fuels rebate program authorized to rebate up to half the cost of a vehicle conversion, or the alternative fueled vehicle premium on new vehicles. Such vehicles must demonstrate that reductions in carbon monoxide emissions, as well as for fine particulate matter, visibility pollutants will be achieved.

#### Other Activities

As in other states, there is also much activity being conducted through federally funded pilot programs, such as the Regional Transportation District operation of five large over the road methanol fueled transit buses, as well as large and smaller CNG powered buses. The U.S. Government Accounting Office is also in the process of obtaining a fleet of methanol flexible fueled automobiles. Coors brewing is operating an ethanol powered semi-truck tractor and a fleet of propane powered vans. Many other private and governmental fleets are also now operating CNG or propane powered vehicles.

The National Renewable Energy Lab is in the process of developing ways of lowering ethanol production costs. The Colorado School of Mines has established a heavy duty emissions laboratory, and Colorado State University has established a light duty emissions laboratory which are both measuring motor vehicle emissions from alternative fueled vehicles.

#### Conclusion

Presently almost all transportation fuels used are derived from oil. Increasingly that oil is imported. In 1990 it is estimated that close to half of all oil consumed in the United States was imported. With consumption increasing and production decreasing, it is expected that by the year 2010, approximately 70% of all oil consumed in the United States will be imported, if the measures in the National Policy Act are not implemented.

New federal clean fuel requirements will pose a significant challenge to states in the future. New alternative fuel infrastructures will have to be created. New motor vehicle designs will also be needed to utilize those fuels for maximum air quality and vehicle performance benefit. The potential is there to take advantage of the different characteristics of the new clean fuels to lower vehicle emissions as well as develop secure supplies of North American produced fuel.

# OXYGENATED GASOLINE-THE CALIFORNIA EXPERIENCE

Dean C. Simeroth and Jose Gomez  
California Air Resources Board  
2020 L Street  
P.O. Box 2815  
Sacramento, CA 95812

**KEYWORDS:** Oxygenated Gasoline, California wintertime oxygenates regulations, gasoline oxygen content

## ABSTRACT

The Air Resources Board (ARB) adopted regulations in December 1991, which require that gasoline contain 1.8 to 2.2 weight percent oxygen during specified months. The regulations were adopted in response to the Federal Clean Air Act Amendments of 1990. California's wintertime oxygenates program was implemented November 1, 1992. The use of oxygenated gasoline reduced ambient carbon monoxide concentrations by six to ten percent during the first implementation season. The wintertime oxygenates regulations sunset February 29, 1996. At that time, the wintertime oxygen content requirement becomes part of the Phase 2 reformulated gasoline regulations.

## INTRODUCTION

This paper summarizes the California wintertime oxygenates regulations and discusses California's experience in implementing these regulations.

In response to the requirements of the federal Clean Air Act Amendments of 1990 (Act), the ARB adopted regulations in December 1991, which require that gasoline contain 1.8 to 2.2 weight percent oxygen during specified months. These regulations were implemented on November 1, 1992. Because California's regulations differ from the federal requirements, the ARB requested a partial waiver under section 211(m)(3) of the Act. The U.S. Environmental Protection Agency (U.S.EPA) is currently reviewing ARB's request for a waiver.

Based on our review of the program's first implementation season, the Board approved minor modifications to the regulations on September 9, 1993, which are intended to provide additional flexibility to those required to comply with the regulations, while not compromising the overall effectiveness of the program.

## BACKGROUND

### The Federal Requirements

The Act requires states with carbon monoxide (CO) nonattainment areas to implement oxygenated gasoline programs in these areas. In most cases, the states' programs must require that gasoline sold in the nonattainment areas have an oxygen content of at least 2.7 weight percent, during the specified months. The states are required to submit their oxygenated gasoline regulations as a revision to the State Implementation Plan (SIP). The U.S.EPA identified eight areas in California in which an oxygenated gasoline program is required, including: the Chico Metropolitan Statistical Area (MSA), the Sacramento MSA, the San Diego MSA, the Modesto MSA, the Fresno MSA, the Stockton MSA, the San Francisco-Oakland-San Jose Consolidated Metropolitan Statistical Area (CMSA), and the Los Angeles-Anaheim-Riverside CMSA. The EPA also specified the control period applicable in each of the affected areas'. The control periods are listed in Table 1.

### ARB's Actions to Comply with the Act

In response to the requirements of section 211(m), the ARB promulgated oxygenated gasoline regulations following a hearing on December 12, 1991. The regulations were submitted as a revision to the SIP in October 1992. The wintertime oxygenates regulations sunset February 29, 1996, after which the year-round oxygen content requirements in the ARB's Phase 2 reformulated gasoline regulations will go into effect. Because over 70 percent of the gasoline used statewide is consumed in the U.S.EPA-designated areas, the Board made the wintertime oxygenates regulations applicable statewide. Additionally, the Board concluded that a statewide program simplifies enforcement and maximizes the CO emission reductions achieved in the nonattainment areas.

In setting the standards, the Board determined that while requiring the 2.7 weight percent oxygen content mandated by the Act would result in greater CO reductions it would also result in increased emissions of NO<sub>x</sub>. An increase in NO<sub>x</sub> emissions would interfere with efforts to attain the ambient air quality standards for particulate matter (PM<sub>10</sub>), nitrogen dioxide (NO<sub>2</sub>) and ozone. Therefore, the Board established a minimum and maximum oxygen content requirement at 1.8 and 2.2 weight percent, respectively.

The Board has requested that the U.S.EPA partially waive the minimum oxygen content requirement of 2.7 weight percent specified in the Act. Section 211(m)(3)(A) of the Act directs the U.S.EPA to waive the requirement for any area where the state demonstrates that the use of oxygenated gasoline would prevent or interfere with the area's attainment of an ambient air quality standard for any pollutant other than CO.

## IMPACT OF OXYGENATED GASOLINE ON MOTOR VEHICLE EMISSIONS

Adding oxygen to gasoline affects the properties of gasoline in both performance and emissions. Generally, the oxygenates used today are ethanol and methyl tertiary butyl ether (MTBE). Over the past several years, there have been a number of test programs conducted to evaluate the impact of oxygen content on emissions. In the process of developing the wintertime oxygenates regulations, we evaluated all of the studies available to us at

the time and concluded that oxygen content in gasoline greater than 2.2 weight percent would increase NO<sub>x</sub> emissions from motor vehicles<sup>2,3,4</sup>. In general, NO<sub>x</sub> emissions increase as oxygen content increases.

Since the adoption of the wintertime oxygenates regulations and the Phase 2 reformulated gasoline regulations, we have been working to develop a predictive model to estimate emissions from alternative gasoline formulations that might be used in the vehicle fleet. As part of our waiver request to U.S. EPA, we used a draft version of the predictive model to evaluate the emissions characteristics of the most likely gasoline formulation that would be produced under the federal program<sup>5</sup>. This gasoline formulation was developed as part of an analysis conducted by Turner Mason and Company for the Western States Petroleum Association. It should be noted that variations in the gasoline formulations actually produced will influence the actual impact on NO<sub>x</sub> emissions. Figure 1 shows the estimated impact on NO<sub>x</sub> emissions for the different vehicle technology groups.

## **RATIONAL FOR LIMITING THE OXYGEN CONTENT OF GASOLINE**

### **Emissions Inventory**

Motor vehicle emissions are a major source of pollutant emissions, including CO, hydrocarbons (HC), and NO<sub>x</sub>. HC and NO<sub>x</sub> are precursors to ozone and PM<sub>10</sub>. Figure 2 shows that in 1987 emissions from on-road gasoline motor vehicles constituted about 57 percent of the total CO inventory, 35 percent of the VOC inventory, and 38 percent of the NO<sub>x</sub> inventory. Gasoline vehicles accounted for about 36 percent of the PM<sub>10</sub> precursors.

### **Air Quality in EPA-designated Areas**

Both the ozone and PM<sub>10</sub> standards are exceeded in all EPA-designated areas during some time in the control period. Figure 3 shows the average number of days the state ozone standard was exceeded during the period of 1987 through 1990 for five air basins (which contain all of the U.S. EPA designated areas). Figure 4 shows the average percent of PM<sub>10</sub> observations exceeding the state standard. Because violations of the standards for CO, NO<sub>x</sub>, ozone, and PM<sub>10</sub> can occur simultaneously, it is critical that the efforts to reduce CO emissions don't increase emissions of the other pollutants.

As noted earlier, use of gasoline with oxygen content greater than 2.2 weight percent would result in larger CO reductions of CO emissions, but it would also increase NO<sub>x</sub> emissions. Thus, it is critical to balance the need for CO reductions and the need to avoid NO<sub>x</sub> increases. California's oxygenated gasoline regulations were designed to balance these competing effects.

## **ARB'S EXPERIENCE IMPLEMENTING THE OXYGENATED GASOLINE PROGRAM**

### **Implementation Issues**

During the first implementation period of the wintertime oxygenated gasoline program, staff became aware of various concerns regarding the application of the wintertime oxygenates regulations. After evaluation of the program, staff proposed several minor modifications to the regulations which were adopted by the Board on September 9, 1993<sup>6</sup>. The modifications include changing the control period applicable in the San Luis Obispo County, allowing the distribution of gasoline containing greater than 2.2 weight percent oxygen during the transition period, providing a one pound per square inch Reid vapor pressure exemption for ethanol blended gasoline produced during the calibration of blending equipment, and providing an exemption for small gasoline retailers that obtain their gasoline from areas outside California, if they meet specified conditions. These changes are intended to provide industry with additional flexibility in complying with the regulations, while maintaining the effectiveness of the regulations.

### **Air Quality Improvements During the 1992/93 Winter**

Results of an analysis of CO, NO<sub>x</sub>, and HC ambient air quality data collected at nine monitoring stations during the November 15, 1992 through January 31, 1993 period indicates that concentrations of CO were significantly lower than past winters<sup>6</sup>. Although the 1992/93 winter had very favorable meteorology, we believe some of the reduction in CO concentrations are due to the use of oxygenated gasoline.

A linear regression analysis was done on the available data for the winter periods of 1985/86 through 1991/92 to characterize trends for the three periods 6 to 9 a.m., 6 to 9 p.m., and daily mean concentrations. The regression equations were used to compute the expected concentrations for CO, NO<sub>x</sub>, and HC for the 1992/93 winter. The actual values for 1992/93 winter were divided by the expected values derived from the regression analysis.

The ratio of the 1992/93 actual concentrations to the expected concentrations were 72 percent for CO and 78 percent for NO<sub>x</sub>, respectively. The ratios of the NO<sub>x</sub> concentrations were assumed to characterize the atmospheric dispersion during the winter 1992/93. Thus, the difference between the CO ratios and the NO<sub>x</sub> ratios was attributed to the use of the oxygenated gasoline. The analysis indicates that the use of oxygenated gasoline accounted for about a six to 10 percent reduction in CO concentrations. Figure 5 shows a summary of the ratios of actual to expected the concentrations of CO and NO<sub>x</sub>.

## **CONCLUSIONS**

California has successfully implemented its oxygenated gasoline regulations applicable in the winter months which has resulted in significant reductions of carbon monoxide emissions from motor vehicles. Although the regulations require a lower oxygen content than the minimum 2.7 weight percent specified in the Act, the regulations have been effective in reducing CO emissions. Minor modifications were made in September 1993 to address concerns raised during the first implementation season.

California's wintertime oxygenates regulations will help bring all CO nonattainment areas into compliance with the CO ambient air quality standards by the statutorily require deadlines. Additionally, the Phase 2 reformulated gasoline regulations which will become effective in March of 1996, will result in an additional CO reduction of about five percent.

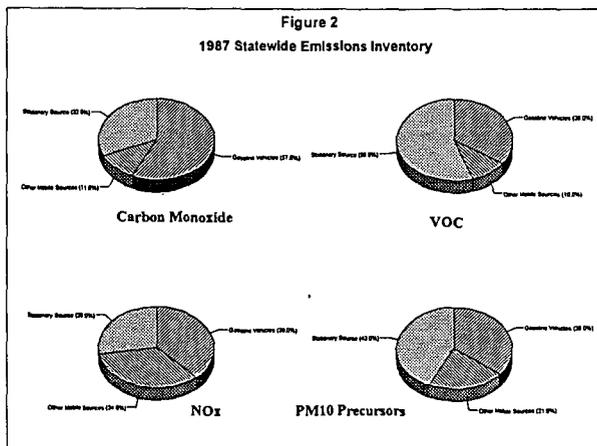
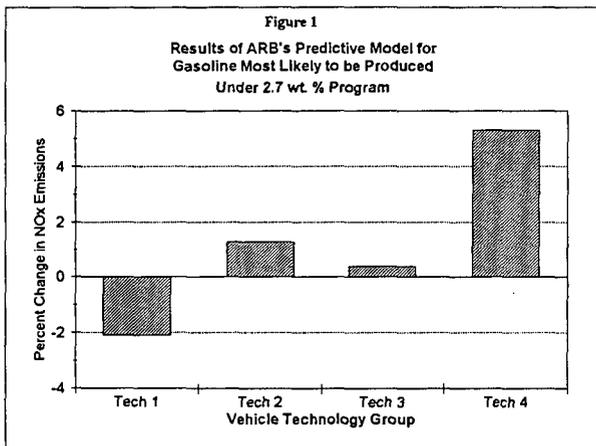
#### REFERENCES

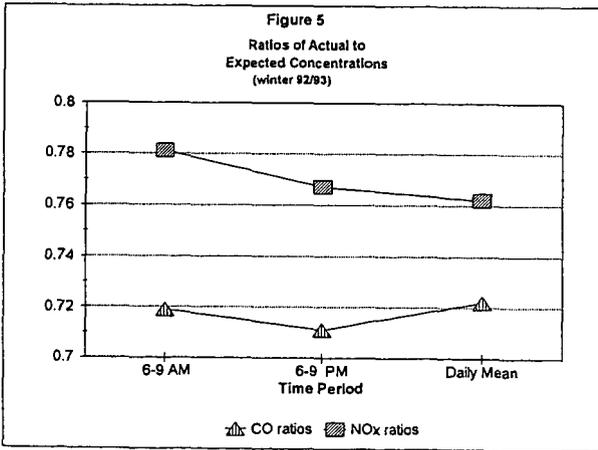
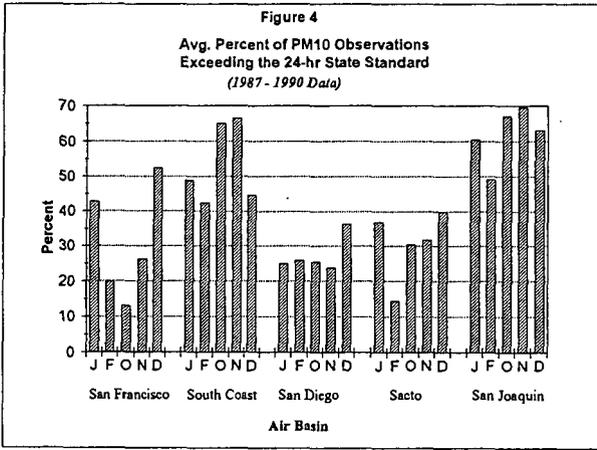
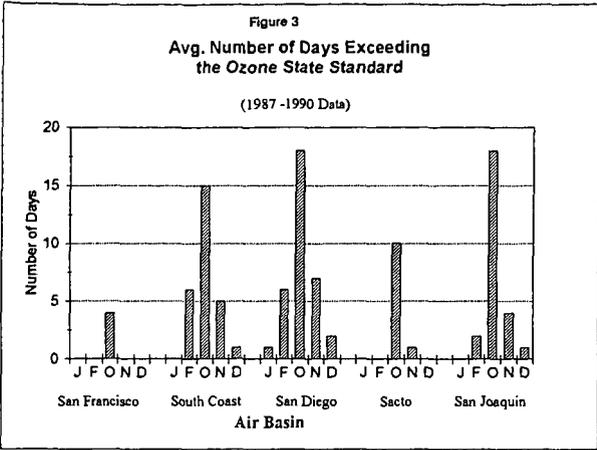
1. U.S. Environmental Protection Agency, Supplemental Notice of Proposed Guidance on Establishment of Control Periods Under Section 211(m) of the Clean Air Act as Amended, 57, FR 4408, February 5, 1992.
2. Air Resources Board, California Phase 2 Reformulated Gasoline Specifications, Volume 2 Proposed Regulation for California Wintertime Oxygenates Program, October 4, 1991.
3. Air Resources Board, California Wintertime Oxygenates Program, Technical Support Document, Request for a Waiver of the Minimum Oxygen Content Requirements for Wintertime Gasoline, Pursuant to Federal Clean Air Act Section 211(m)(3)(A), October 1992.
4. Air Resources Board, California Wintertime Oxygenates Program, Technical Support Document, Request for a Waiver of the Minimum Oxygen Content Requirements for Wintertime Gasoline, Pursuant to Federal Clean Air Act Section 211(m)(3)(A), Supplemental Submittal to U.S. EPA Docket No. A-93-13, June 17, 1993.
5. Air Resources Board, Proposed Amendments to Regulations Regarding the Oxygen Content of Gasoline, and Regarding Exemptions from Motor Vehicle Fuels Requirements for Fuels Used in Test Programs, July 23, 1993.
6. Dolislager, Leon J., Air Resources Board, Did the Wintertime Oxygenated Fuels Program Reduce Carbon Monoxide Concentration in California?, Presented at the Tenth International Symposium on Alcohol Fuels, November 7-10, 1993, Colorado Springs, CO.

Table 1		
EPA-Designated Areas	Control Period	
Chico MSA*	October 1	January 31
Sacramento MSA	October 1	January 31
San Diego MSA	November 1	February 29
Modesto MSA	October 1	January 31
Fresno MSA	October 1	January 31
Stockton MSA	October 1	January 31
San Francisco-Oakland-San Jose CMSA**	October 1	January 31
Los Angeles-Anaheim-Riverside CMSA	October 1	February 29

\* Metropolitan statistical area

\*\* Consolidated metropolitan statistical area





ENVIRONMENTAL AND ECONOMIC IMPLICATIONS  
OF OXYGENATED GASOLINE USE IN COLORADO:  
COLORADO'S OXYGENATED GASOLINE PROGRAM

Kim B. Livo  
Dr. Jerry Gallagher  
Air Pollution Control Division  
Colorado Department of Health  
4300 Cherry Creek Drive South  
Denver, Colorado 80222

Abstract

Starting in the winter of 1987-1988, Colorado instituted an oxygenated gasoline program to control winter-time carbon monoxide emissions from motor vehicles. As a result of this and other air quality programs, as well as fleet turn over, the number of days exceeding the federal carbon monoxide standard has been reduced from 32 days in 1986 to 5 days in 1992.

The Colorado Department of Health estimates that for the winter of 1992-1993, carbon monoxide emissions from motor vehicles were reduced by 25% on a fleet wide basis. This reduction is credited with preventing a possible four additional high pollution days from occurring. The use of these gasolines increased the cost of gasoline in the Denver area by 3.5 cents per gallon.

Introduction

The Front Range area of Colorado is subject to numerous carbon monoxide (CO) high pollution episodes each winter. These are produced by the interaction of cold temperatures, temperature inversions, and carbon monoxide emissions from gasoline powered automobiles and trucks, as well as from residential wood burning and other sources. Of the total CO emissions, mobile sources contribute approximately 85%.

Elevated carbon monoxide concentrations occur on calm winter days, when temperature inversions develop which inhibit the dispersion of carbon monoxide produced from motor vehicle traffic and residential wood burning. Exceedances of the federal eight hour CO standard may result, especially in low laying, high traffic volume areas, such as downtown Denver.

As one of several strategies aimed at reducing motor vehicle CO emissions, the Colorado Department of Health (CDH) instituted an oxygenated gasoline program beginning in the winter of 1987-1988. Implementation of this program resulted from a comprehensive vehicle mass emissions test program conducted by the CDH in the 1980s.

Vehicle Mass Emissions Testing

Beginning with vehicle mass emissions testing in the late 1970s by the U.S. EPA, and soon after, by the Colorado Department of Health, it was noted that gasolines blended with alcohols, such as

ethanol and methanol, produced lower carbon monoxide emissions than non-blended gasolines (1,2). Later testing involving methyl tert-butyl ether (MTBE) blends produced similar results (3).

The test method used in this program is a mass-emissions test called the Federal Test Procedure (FTP). It is used by the U.S. EPA to certify emissions for new model light duty cars and trucks. In this test, a vehicle is placed on a dynamometer and is driven over a simulated driving cycle lasting 1372 seconds. Vehicle emissions are collected during this period, and the mass of these emissions are determined. The driving cycle involves both cold and hot vehicle starts, accelerations, decelerations, and steady cruise conditions, designed to simulate a typical urban commute.

Analyzing mass emissions results from these tests indicated that fuel oxygen content, rather than the particular oxygenate, was the most important parameter in producing carbon monoxide changes. In determining this effect, the CDH examined both linear and logarithmic relationships to correlate the mass emissions database (4). For the logarithmic models, both positive as well as negative curves could be fitted to the data, depending on the individual study analyzed. Because of the differences in curvatures, as well as because the linear model fit equally as well as the logarithmic models, a linear model has been adopted in describing the CO effect of using oxygenated gasolines. Table 1 describes the CDH carbon monoxide FTP mass emissions results using the linear model, averaged for oxygen content, and differentiated by vehicle emissions control technology class.

The U.S. EPA and other organizations have also conducted mass emission test programs which have corroborated and expanded upon the CDH mass emissions testing. In the latest study, the Auto/Oil Air Quality Improvement Research Program, fuel composition parameters, including oxygen content, have been varied to study emissions effects (5). Again, directionally, increasing oxygen content was found to reduce carbon monoxide emissions.

#### CO Vehicle Emission Reductions

In analyzing the CO vehicle emission reduction of oxygenated gasolines, the CDH relies on the U.S. EPA MOBILE vehicle emissions model. Employing this computer model, vehicle emissions from an area's motor vehicle fleet can be averaged and estimated. This model takes the CO emission reductions seen in the FTP mass emissions testing, and applies it across the entire motor vehicle fleet, and under different driving conditions. Inputs to the model include: vehicle age and distribution, speed, road type, time of day, and area type.

Utilizing the present MOBILE 5a emissions model, the CDH estimates that in the winter of 1992-1993, carbon monoxide exhaust emissions from motor vehicles, in the Front Range area, were reduced by 26.6% in October and November, and by 24.9% in January and February (6). Reductions in ambient CO concentrations are less, since mobile sources are not the sole source of CO emissions, and concentrations are dependent on the rates of production and dispersion.

Contributing to the effectiveness of the 1992-1993 program was the increased percentage of ethanol blended gasoline sold along the Front Range area. Ethanol blends made up 45% of the total gasoline sales of this winter, compared to 20% the winter before. When blended at the 10% vol. level, ethanol blends have a higher oxygen content than 15% MTBE blends (3.5% vs. 2.7% wt.). A higher oxygen content produces a greater average CO reduction. 15% vol. MTBE blends constituted the balance of the oxygenated gasoline sold.

During the winter of 1992-1993, the average oxygen content of the Front Range gasoline pool was 3.0% percent in November and December, dropping to 2.8% for January and February, when a new I.R.S. ruling took effect, permitted the blending of ethanol at a reduced level (7.8% vs. 10% vol.).

#### Air Quality

In terms of ambient air quality, there were five exceedances of the 9ppm eight-hour average national ambient air quality standard (NAAQS) for CO in the winter of 1992-1993. An additional four possible exceedances were prevented because of the use of oxygenated gasolines (6). Figure 1 documents the daily 8-hour maximum reading for the winter of 1992-1993. The lower clear bar represents monitored values. The solid dark bars represent estimated concentrations, if oxygenated gasolines were not used.

For the calendar year 1992, there were five days exceeding the NAAQS 8-hour average CO standard, a decline from 32 days in the calendar year of 1986. The continuing reduction in CO exceedances as shown in Figure 2, is due to a continuing decline in CO emissions due to fleet turn over, the use of oxygenated gasolines, vehicle inspection and maintenance programs, and no woodburning on high pollution days, as well as favorable weather conditions.

#### Costs

The Colorado Department of Health analyzed the costs associated with the 1992-1993 oxygenated gasoline program. The costs of base gasoline, oxygenates, transportation costs, as well as octane and butane credit savings were examined to determine oxygenated gasoline costs. These were then compared to the differential costs observed between oxygenated and non-oxygenated gasolines Denver RACK prices received from the Oil Price Information Service. Retail prices were also observed.

For the winter of 1992-1993, the average cost of gasoline increased by three and a half cents per gallon because of the Oxygenated Gasoline Program (6), a similar amount as for previous season's program. This cost represents increased refiner and blender costs due to oxygenate blending and does not take into account any changes in vehicle fuel economy.

While the average cost associated with blending oxygenates remained the same as the previous winter, the cost of gasoline blended with ethanol rose slightly. Average program costs remained similar to the 1991-1992 season however, because the

market share for ethanol blends increased, and ethanol blended gasoline costs remained below MTBE blended gasoline costs (2.75 cents/gal. vs 3.75 cents/gal.).

#### Supplies

This year over 360 million gallons of oxygenated gasoline were sold along the Front Range during the oxygenated gasoline program period (November 1, 1992 through February 28, 1993). Statewide, over 500 million gallons of gasoline (much of it oxygenated) was sold during this period.

#### Fuel Economy

Oxygenated gasolines have a small affect on fuel economy at high altitude. CDH fuel economy testing conducted during vehicle mass emission FTP testing, has shown on average, fuel economy reductions of up to 1.5% for some vehicle classes to slight increases of less than 1.0% for other motor vehicle classes.

Oxygenated gasolines lean the air to fuel ratio of a vehicle, increasing the engine's efficiency and in some older vehicles slightly improving fuel economy. Oxygenated gasolines have a slightly lower heating value though, which may decrease fuel economy in some vehicles, especially vehicles equipped with the latest oxygen sensors and feedback fuel injection. Altitude and the partial pressure at Denver (5280 feet) may also lessen fuel economy impacts of oxygenated gasolines. Table (2) gives CDH high altitude fuel economy test results for three types of emission control technologies, using 11% and 15% MTBE blends, and 10% ethanol blends.

#### Conclusions

Based on mass emissions testing, using the Federal Test Procedure, oxygenated gasoline have been demonstrated to decrease carbon monoxide emissions from gasoline powered motor vehicles. This decrease is related to oxygen content, and varies according to vehicle emission control technology class and vehicle operating modes. For the FTP, based on a linear oxygen effect, oxygenated gasolines decrease exhaust CO emissions by 4.83% to 6.45% for each one percent oxygen content, by weight, the gasoline contains.

Using the U.S. EPA MOBILE 5a motor vehicle emissions model, the CDH estimates that carbon monoxide emissions were reduced by 24.9 to 26.6% in the winter of 1992-1993. As a result of this and other air quality programs, as well as fleet turn over, the number of days exceeding the federal carbon monoxide standard has been reduce from 30 days in 1986 to 5 days in 1992. The use of these gasolines increased the cost of gasoline in the Denver area by 3.5 cents per gallon.

REFERENCES

1. Richardson, David, "Exhaust Emissions and Fuel Economy from Automobiles using Alcohol/Gasoline Blends under High Altitude Conditions", U.S. EPA, Office of Air, Noise, and Radiation, Oct. 1978.
2. Hollman, Ted, William Miron, "Effects of Ethanol-Blended Fuel on Motor Vehicles at High Altitude", Colorado Department of Health, Air Pollution Control Division, Mobile Sources Program, Sept. 1983.
3. Ragazzi, Ron, "The Effects of Two Different Oxygenated Fuels on Exhaust Emissions at High Altitude", Colorado Department of Health, Air Pollution Control Division, Mobile Sources Program, Jan. 1987.
4. Nelson, Ken, "The Effects of Fuel Oxygen on CO Emissions at High Altitudes", Colorado Department of Health, Air Pollution Control Division, Mobile Sources Program, May 1990.
5. Auto/Oil Air Quality Improvement Research Program (SP-920), Society of Automotive Engineers, Feb. 1992.
6. Livo, Kim, William Miron, "1993 Oxygenated Gasoline Program, Air Pollution Control Division Report to the Colorado Air Quality Control Commission", Colorado Department of Health, Air Pollution Control Division, Mobile Sources Program, April 15, 1993.

TABLE 1 CDH MASS EMISSIONS RESULTS AVERAGE PERCENT CARBON MONOXIDE REDUCTION BY VEHICLE EMISSION CONTROL TECHNOLOGY CLASS AND OXYGEN CONCENTRATION				
Vehicle Emissions Control Technology Group	2.0% Oxygen by wt. (11% MTBE)	2.7% Oxygen by wt. (15% MTBE, 7.8% ethanol)	3.5% Oxygen by wt. (10% ethanol 5% methanol)	1.0% Oxygen by wt.
Pre-Catalytic Converter	12.84%	17.33%	22.47%	6.42%
Two-way Oxidation Catalytic Converter Equipped	12.90%	17.4%	22.58%	6.45%
Three-way, Closed-loop, Catalytic Converter Equipped	9.66%	13.04%	16.91%	4.83%

Figure 1  
 Winter-time CO Concentrations  
 With and Without Oxygenated Gasoline  
 (8-HR DAILY MAX)

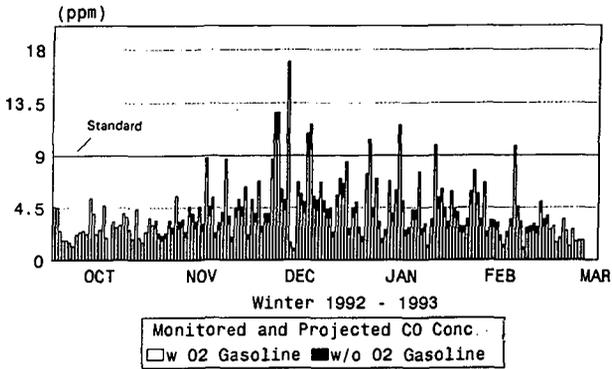


Figure 2  
 Colorado CO Exceedances

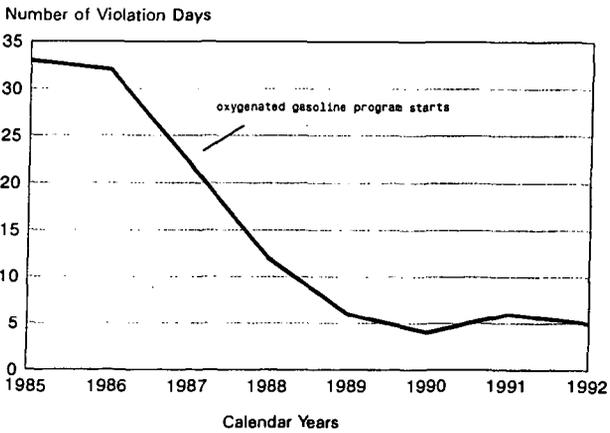


TABLE (2)  
FUEL ECONOMY EFFECTS

VEHICLE TECHNOLOGY	CDR FTP Measured Fuel Economy Change		
	11% MTBE	15% MTBE	10% ethanol
Non-Catalyst	+0.82%	+0.21%	+0.11%
Catalyst	+0.84%	+0.18%	+0.33%
Closed Loop	+0.7%	-1.13%	-1.41%

## WHY ARE ALCOHOL FUELS STILL ALTERNATE FUELS?

Reda M. Bata  
Department of Mechanical and Aerospace Engineering  
West Virginia University  
Morgantown, WV 26506

**Key Words:** alternate, oxygenated, methanol, CNG

### Abstract

The enthusiasm for using alcohols as alternate fuels in internal combustion engines (ICE) has been accelerating since the middle of 1970 and reached its peak by the middle of 1980. This was due to the serious effect of the exhaust emissions from automotive engines powered with oil-derived fuels coupled with a market rise in the cost of oil-derived fuels. Since then, the cost of oil has been decreasing and the need for alternate fuels has begun to slow down due to this economical reason. Alcohols are excellent fuels since they can be produced from renewable resources and their impact on health and the environment is limited. They are favorable for IC engines because of their high octane rating, burning velocities, and wider flammability limits. Experimental research and in-use applications showed drastic reduction in carbon monoxide (CO), particulate matter (PM), and moderate reduction in hydrocarbon (HC). Adverse effects on nitrogen (NO<sub>x</sub>) and aldehyde (CHO) were also noticed.

### Introduction

It is worth all of our efforts and dedications in order to become an energy-environment conscious nation. The attitude of increasing the stringent restrictions on pollutant emissions from automotive engines, the urgency for fuels derived from renewable sources, and the awareness of the expected rise in the price of oil-derived fuels in the future, have been the main motives of the 1990 Clean Air Act Amendments (CAAA) and the Energy Policy Act of 1992 (EPACT), Appendix A. Both acts are mandating the procurement of alternative fuel vehicles (AFV's) as well as imposing stringent exhaust gas emissions standards.

In the United States, the consumption of petroleum products exceeds the production rate of this strategic material. Meanwhile, the relaxation of the domestic companies to discover new oil fields because of the cheap surplus oil that is available in the international market, and the opposition from some environmentalists to explore new oil fields in the costal areas has been one of the major factors in creating the United States' negative balance of trade with other countries. Since new, revolutionary, non-traditional power plants are unexpected, and increasing demand is unavoidable as well, in the next few decades, the traditional IC engines will remain the prime power mover in our society. It took almost a century to develop the existing ICE, the oil refineries, and the distribution infrastructure. Huge investments have been dedicated for this business and they should be protected.

Alcohol fuels such as methanol (CH<sub>3</sub>OH), ethanol (C<sub>2</sub>H<sub>5</sub>OH), iso-butanol (C<sub>4</sub>H<sub>9</sub>OH), methyl-tertiary-butyle-ether (MTBE), ethyle-tertiary-butyle-ether (ETBE), have proven to be excellent octane booster and blend with the traditional fuels, gasoline and diesel, and require minor engine modifications.

As stated in the National Energy Strategy in February, 1992, "The U.S. fleet of more than 185 million cars, buses, and trucks consume two-thirds of the oil used by the United States." In 1991, almost 50% of the oil consumed in our country was imported and it is expected that this percentage will increase up to 61% by the year 2010. The transportation system is consuming 63% of total U.S. oil consumption. The cost of damage to the environment caused by the exhaust gas emissions ranges from \$11 billion to as high as \$187 billion, (1). The

forementioned scary statistics have led the U.S. Department of Energy's (DOE) Office of Transportation Technologies (OTT), through its Office of Alternative Fuels, to support innovative-cost-effective methods to produce and implement alternative fuels and achieve greater penetration into the marketplace. Details of the production plan is explained in Appendix B. Among the alternate fuels are reformulated gasoline (RFG) additives such as ethers (oxygenated fuel additives), methanol, and ethanol. Higher alcohols, such as iso-butanol, were not mentioned because of their higher cost of production and lack of political support when compared to methanol and ethanol.

### The Rationale for Alternate Fuels

Two main reasons justify the use of alternate fuels; the finite unrenewable supply of crude oil, and protection of the environment from the increasing ozone (photochemical smog) as well as the greenhouse effect. Since crude oil is cheap and available, demand for the use of alternate fuels will be realized in the long-term strategy. Protecting the environment is the short-term demand as was proven by the debate associated with the Clean Air Act Amendment in 1990. Use of alternate fuels in association with the new engine technology has the potential to reduce the harmful pollutants that cause damage to the environment.

### Why Alcohol Fuels

There is no miraculous, super fuel that will satisfy all the requirements of cost effectiveness, maximum thermal efficiency, and engine performance, and still remain clean enough to protect the environment. Every fuel has advantages and disadvantages, and selection of a particular fuel is a function of different parameters including the physical properties of the fuel as shown in Table 1 (3). If we start with the disadvantages of the alcohol fuels, they might be summarized as follows:

1. The economics of production. Unless the cost of alcohol production from renewable resources is made cost-effective, there will be no demand for it. These alcohols could be produced from biomass, coal, and natural gas.
2. Flame visibility of alcohol is difficult to be detected, which might be hazardous. The lack of visibility is due to the small number of carbon atoms present in the alcohol. Since there is very little carbon, there is no soot formation to give the flame color.
3. Cold startability problems. Due to their low vapor pressure, high latent heat of vaporization, and single boiling point, alcohols, especially ethanol, have difficulty meeting industry standards for starting in cold weather.

The last two of these disadvantages, however, can easily be solved. By the addition of a small amount of gasoline to the alcohol mixture, a more visible flame will be produced and the effect of cold weather on engine startability can be brought well within the industry standards.

Although there are a few minor disadvantages to the use of alcohol fuels, the advantages more than outweigh its easily solvable problems. The advantages are as follows:

1. Methanol can be made out of organic material such as biomass and municipal waste. In the long-term, it could even be made out of coal. The United States has 25% of the world's supply of coal, which will be abundant for years to come.
2. Alcohol combustion produces higher combustion pressures inside the combustion chamber of the ICE due to the higher molal products to reactants ratio, compared to gasoline, which improves power output and thermal efficiency (2).
3. Alcohols have a higher average octane rating  $\{(RON + MON)/2 = 104\}$  compared to gasoline. Increasing the compression ratio of the engine to 12:1 or higher increases power and fuel efficiency by 20% and 15% respectively (3&4).
4. Alcohols have better combustion characteristics and performance due to the increased volumetric efficiency of alcohol fuels, which is why methanol is a preferred racing fuel. Acceleration time decreases with power increase.
5. In case of fire, alcohols have higher visibility for escape-rescue, low asphyxiation, produce cool flame and low heat output which causes low burns, low smoke damage,

residue is easily washed away, and are extinguishable with water and more readily by powders and foams.

6. In case of leaks and spillages, alcohols are miscible in water and could be washed out with water for quick and easy removal. They are easily metabolized if absorbed by the ground.
7. Alcohol fuels have a lower evaporative emission. Not as many harmful by-products will be released into the atmosphere by using alcohol fuels.
8. Since the carbon content in alcohol fuels is very small, a negligible amount of soot is formed and released to the atmosphere when burned in the ICE.
9. Alcohol fuels are liquids, which make them accessible using the same means of transportation and handling infrastructure of the conventional fuels with minor modifications.

### **Alternate Fuels and Environment**

Deterioration in air quality is a vital issue that needs to be seriously monitored and limited. The transportation system is a major air pollution contributor due to the exhaust emissions such as carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO<sub>x</sub>), carbon dioxide (CO<sub>2</sub>), and particulate matter (PM). The transportation system is estimated, by the U. S. Environmental Protection Agency (EPA), to produce up to 44% of the total hydrocarbons emissions inventory in the U.S. The evaporative emissions share 31%, and the balance of 13% is from exhaust gas emissions. Production rate of exhaust gases differ from one place to another based on different parameters such as the geographic locations, altitude, weather conditions, traffic congestion, population, maintenance availability, etc. The greenhouse effect, which is caused by the production of carbon dioxide, has been suspected to cause the global warming and its adverse effect on the biological system. Ozone production is due to the chemical reaction between nitrogen oxides, hydrocarbons, and sunlight, which is known as photochemical smog. Los Angeles' polluted environment with photochemical smog is a good example, and is considered as one of the most non-attainment areas in the nation.

Implimentation of alternate fuels, in many pilot project over the nation, with dedicated and converted IC engines, has a positive effect on carbon monoxide and particulate matter reduction. Hydrocarbons emission, which is mainly "evaporative emission" is reduce when alcohol fuels are used. This trend is obvious in Table 2, which shows in-use emission measurements of regulated pollutants from jet A and neat methanol fuels, for similar vehicles and similar engines under transient test conditions. Hydrocarbons data do count the evaporative emissions which make up approximately 65% of the hydrocarbons emissions. In another study of carbon monoxide under steady-state conditions, wide open throttle (WOT), no load (NL), intermediate load (IL), and full load (FL) are shown in Table 3. Four different fuels-20% by volume iso-butanol-gasoline blend (B20), 20% ethanol-gasoline blend (E20), ethanol-gasoline blend (20M), and base line gasoline (GAS)-were used. Carbon monoxide emissions from alcohol-gasoline blends were lower than that from gasoline, and M20 was the lowest.

### **Conclusions**

Why are alcohol fuels still alternate fuels? Apparently, since production and use cost of conventional fuels (gasoline and diesel) are very cost-effective, nobody will use alcohol fuels except the Federal and State Governments because of the CAAA and EFACT through the AFV's programs. What about special fleets of companies, private sectors, and individuals? We are not yet environment-conscious users!

### **References**

1. The National Renewable Energy Laboratory report prepared for the U.S. Department of Energy, DOE/CH 10093-157, DE 92016412, May 1993.
2. Nichols, R. J., "Applications of Alternative Fuels", SAE Paper 821573, 1982.
3. Sriram Popuri and Reda Bata, "A Performance Study of Iso-Butanol-, Methanol-, and Ethanol-Gasoline Blends Using A Single Cylinder Engine".
4. Nichols, R. J., et al, "Ford's Development of a Methanol fueled Escort", Proceedings of the International Alcohol Fuel Technology Symposium, Auckland, 1982, II, pp. 109-116.
5. Bata, R. M., Elrod, A. C., and Rice, R. W., "Emissions from I.C. Engines Fueled with

Alcohol-Gasoline Blends: A Literature Review", Published in the Engine Emissions Technology for lthe 1990's, ICE Division of the ASME, Vol. 4, October 1988, pp. 141-151.

## Appendix A

*Clean Air Act Amendments of 1990 (CAAA)* -- The CAAA requires fleets in 22 urban regions to begin operating clean fuel vehicles (CFV's) by the end of the decade.. Beginning in 1998, 30 percent of new vehicle purchases by many fleets must be CFV's. This increases to 50 percent by 1999 and 70 percent by 2001. Stringent future emission standards are also established for cars, light-suty and heavy-duty trucks, and buses.

*Energy Policy Act of 1992 (EPACT)* -- EPACT establishes requirements for the purchase of AFV's in both public and private fleets. These requirements begin in 1993 for frdral fleets, 1996 for state and fuel supplier flets,and if necessary, in 1999 for private and municipal fleets. EPACT also provides economic and other incentives for fuel suppliers, original equipment manufactureres, and fleet owners.

## Appendix B

Production of alcohol fuels on developing cost-effective biomass-to-fuel processes. The following strategy has been adopted by the DOE.

1. Establishing cost-effective techniques for growing the biomass resource.
2. Developing high-yield, low cost systems for converting biomass to fuels.
3. Demonstrating alternative fuels(including methanol, ethanol, and natural gas) in vehicle fleets across the United States.
4. Acquiring data on the performance of alternative-fueled vehicles from fleets across the U.S.

Selection and production of energy crops that have high-yield biomass feedstocks is a primary step in the biomass-to-fuel process. Energy crops that can be grown in short-rotation such as trees (2-8 years), grasses that can thrive in marginal conditions, and aquatic plants such as algae with high oil (lipid) content. Researchers and scientists are genetically manipulating trees and grasses to increase yield which would produce more alcohol in less time.

**Table 1: Properties of Fuels**

Characteristic	Gasoline	NO.1 Diesel fuel	Methanol	Ethanol	Iso-butanol	Gasohol
Chemistry	Mixture of Hydrocarbons	Mixture of Hydrocarbons				90% Unleaded Gasoline 10% Ethanol
Specific Gravity @ 60 F	0.72 - 0.75 *	0.82	0.79	0.79	0.81	0.73 - 0.76
Boiling Point o F o C	85 - 437 30 - 225	360 - 530 190 - 280	149 65	173 78.3	227 108.1	77 - 410 25 - 210
Net Heating Value (Mass) BTU/lb MJ/kg	18,700 43.5	18,500 43	8,600 20.1	11,600 27	14,000 33	18,000 41.9
Net Heating Value (Volume) BTU/gal MJ/l	117,000 32	126,000 35.3	57,000 15.9	76,000 21.3	93,000 26	112,900 30.9
Heat of Vaporization BTU/lb kJ/kg	170 400	250 600	500 1,110	390 900	250 578.4	200 465
Vapor Pressure @ 100 F psi kpa	9 - 13 62 - 90	0.05 0.34	4.6 32	2.5 17	0.33 2.3	8 - 16 55 - 110
Octane Number Research Motor	91 - 100 82 - 92	Not applicable	112 91	111 92	113 94	Note 1
Cetane Number	Below 15	40 - 60	Below 15	Below 15	Below 15	Not applicable
Stoich. Air/Fuel Ratio	14.6	14.6	6.4	9	11.1	14
Vapor Flammability Limits	0.6 - 8	0.6 - 6.5	5.5 - 26	3.5 - 15	Note 2	Note 3
Appearance	Colorless to light amber color	Colorless to light amber color	Colorless	Colorless	Colorless, viscous	Colorless to light amber color
Vapor Toxicity	Moderate irritant	Moderate irritant	Toxic even in small doses	Toxic in only large doses	Moderate irritant	Moderate irritant

\* For premium gasoline the range is 0.73 - 0.78 (0.75 is used in this study)

Note 1: May be the same as gasoline, or add 1.5 or 2 numbers depending on blending practice

Note 2: Values not available

Note 3: Values not published

Sources: SAE 820261, SAE 890434, Bosch Automotive Handbook

Table 2. Exhaust Gas Emissions For Jet A and Methanol 100

Vehicle	Fuel	CO	NO <sub>x</sub>	HC	PM
1	Jet A	37.8	32.3	2.41	0.72
2	M100	22.2	86.5	5.77	0.22
3	M100	18	19.5	6.95	0.1
4	M100	25	20.8	7.5	0.17

Table 3. Carbon Monoxide Emissions  
from Different Fuels

Fuels	1250 RPM (NL)	2200 RPM (IL)	2500 RPM ( FL)
Gas	4.21	0.135	2.51
B 20	2.4	0.13	1.38
E 20	1.5	0.125	0.69
M 20	1.45	0.124	0.61

# DECREASED BENZENE EVAPORATIVE EMISSIONS FROM AN OXYGENATED FUEL

C. H. Bobro, L. J. Karas, C. D. Leaseburge, and D. J. Skahan

ARCO Chemical Company  
Research and Development  
3801 West Chester Pike  
Newtown Square, PA 19073-2387

**Key Words:** Ether Oxygenate, Oxygenated Gasoline, Benzene Emissions

## ABSTRACT

A chromatographic head-space analysis was developed to determine the vapor phase concentrations of non-oxygenated and oxygenated fuels. The effect of ether oxygenates on benzene evaporative emissions was evaluated. A base fuel and three oxygenated fuels were prepared to contain 1 volume percent benzene at matched volatility levels. Head-space composition for each blend was measured, as a function of temperature, to determine the effects of oxygenates on benzene volatility. Results indicate MTBE (methyl *tert*-butyl ether), ETBE (ethyl *tert*-butyl ether), and TAME (*tert*-amyl methyl ether) each reduce benzene vapor phase concentrations. Benzene reductions averaged approximately 14 percent for fuels containing 2.7 weight percent oxygen. Reductions were temperature dependent, but not generally dependent upon type of ether oxygenate. Significant environmental benefits result from reducing benzene volatility and the resulting decrease in evaporative emissions. Benzene is classified by the EPA as a known human carcinogen. The 1990 Clean Air Act Amendments require reductions in gasoline benzene levels to reduce toxic emissions.

## INTRODUCTION

The 1990 Clean Air Act Amendments require that gasoline sold in nine of the nation's most polluted cities be reformulated to produce less pollutant emissions. Beginning in 1995, reformulated gasoline will produce 15% less hydrocarbon emissions and regulated toxins. Hydrocarbon emissions are a key component to urban smog problems. Gasoline toxins reductions are an effective means of reducing human exposure risk to known and potential carcinogens. Benzene, a known human carcinogen contributes a significant fraction of the regulated emissions of toxins.

This paper examines the potential of ether oxygenates to reduce benzene evaporative emissions. The ether oxygenates under study include: MTBE (methyl-*tert*-butyl ether), ETBE (ethyl-*tert*-butyl ether), and TAME (*tert*-amyl methyl ether). An experimental program was developed to measure vapor phase hydrocarbon concentrations for both oxygenated and non-oxygenated synthetic fuels. Although a synthetic gasoline blend is used in this work, we believe conclusions based on the experimental data will successfully carry-over to actual reformulated gasoline(RFG).

## EXPERIMENTAL

### Fuel Composition

High purity oxygenates were used in all fuel compositions to minimize any impact that volatile impurities may have on altering head-space composition. Each ether oxygenate was freshly distilled immediately prior to use. Test hydrocarbons were purchased from Aldrich Chemical Company and were used without additional purification. The reported purity of our test oxygenates were > 99.99 % MTBE, 99.9% ETBE (without anti-oxidant), and 98% TAME.

Each batch of test fuel, typically 25 - 50 ml, was carefully blended so that the overall blending vapor pressure would be approximately 6.0 psi, assuming ideality. Total aromatic concentration in the blend is fixed at 20% toluene and 1% benzene to

simulate the RFG requirement of 1995. The three oxygenated fuels outlined in Table No. 1 were blended to contain 2.7 wt.% oxygen from the addition of either MTBE, ETBE, or TAME.

**Table No. 1 Liquid Fuel Compositions**

Fuel Oxygenate	Components	Composition (Vol.%)	Blending Vapor Pressure (Psi @ 100°F)
Base	Toluene	20.0	5.87
	Benzene	1.0	
	2,3-DMB	79.0	
MTBE	Toluene	20.0	5.98
	Benzene	1.0	
	2,3-DMB	64.0	
	MTBE	15.0	
ETBE	Toluene	20.0	5.88
	Benzene	1.0	
	2,3-DMB	37.0	
	2,2-DMB	25.0	
	ETBE	17.0	
TAME	Toluene	20.0	5.91
	Benzene	1.0	
	2,3-DMB	27.0	
	2,2-DMB	35.0	
	TAME	17.0	

DMB = Dimethylbutane

### Vapor Generation

A schematic diagram of the Micro Head-Space vapor generating apparatus is shown in Figure No. 1. Approximately 25 ml of fuel to be tested is placed in a clean and dry 100 mL volumetric flask. The flask and contents are submerged in a temperature regulated water bath to insure accurate and uniform heat transfer. The volumetric flask is then fitted with a rubber septum through which is inserted a 1/8 inch stainless steel aerator line. This aerator is then attached to a metered ultra high purity helium delivery system. A metered amount of helium can be introduced into the head-space cavity, if necessary, to charge the sample loop. A thermocouple is inserted into the liquid through a second 1/8 inch Teflon® tube. Equilibrium head-space sample is carried through the sample port via diffusion. This fills the 0.3 mL sample loop contained in the Valco valve system. The entire system is placed in a constant temperature oven to reach equilibrium. After the desired temperature has been reached in the liquid fuel sample, one hour is allowed to reach equilibrium before a head-space sample is taken for gas chromatographic analysis.

### Vapor Analysis

Effluent head-space sample is helium flushed from the sample loop through a pre-heated (120°F) 1/16 inch stainless steel line to the injector port of a Varian 3700 Gas Chromatograph. Hydrocarbon and oxygenate analysis is performed on a Hewlett Packard PONA 50 meter x 0.2 mm x 0.5 micron fused silica capillary column. Typical vapor analysis is carried out under isothermal conditions at 140°F. All data is collected and integrated for analysis on a Fisons Multichrom data acquisition system. The GC analysis was done a minimum of three times at each temperature. An average of the area percents was then calculated for each component present in the vapor sample.

A gas sample calibration standard was prepared and analyzed in the following manner. A precisely weighted liquid sample of all components was transferred to an evacuated one-liter round bottom flask, fitted with a Teflon® lined serum cap. We have experimentally determined that a Teflon® lined serum cap is required to prevent the

irreversible absorption of aromatic components into rubber septum. The flask contents are allowed to equilibrate at atmospheric pressure with ambient air to give a vapor sample of known concentration. The mass at atmospheric pressure was well below the components dew point. An aliquot of this vapor sample is then charged directly to the sample loop which had been thermally equilibrated to the temperature of the initial head-space experiment and then analyzed. Area percents determined in each temperature study were then converted to vapor mole percent.

## DISCUSSION

Head-space concentrations were predicted at 80, 100, and 120°F using UNIFAC-Flash Simulations<sup>1</sup> on all four test fuels with an ASPEN PLUS™ computer software package. These results are shown in Graph No. 1.

An examination of the computer generated data reveals that all three oxygenates suppress the volatility of benzene in the 80 - 120°F temperature range. A linear suppression is predicted over the 40°F range for each oxygenate. Overall benzene evaporative emissions are reduced an average of approximately 15% over the temperature range with MTBE. TAME yields a benzene reduction of approximately 13%. ETBE yields the lowest benzene suppression of approximately 10%. This data from the model strongly suggests that the amount of benzene suppression is **dependent** upon the type of ether oxygenate used with minor temperature effects.

An examination of the experimental benzene head-space concentration measurements obtained in our Micro head-space apparatus is outlined in Graph No. 2. These experimental results reveal that benzene suppression is **independent** of the type of ether oxygenate used and **dependent** upon the test temperature. This data supports the contention that reduced benzene evaporative emissions is a generic trait characteristic of all ether oxygenates. At a constant 2.7 wt.% oxygen content, benzene evaporative emissions were reduced an average of 14%, independent of the ether oxygenate structure. In general, there is a linear increase (approximately 8%) in the amount of benzene found in the head-space during a 40°F temperature increase. This trend is in line with our simplistic model of colligative polar solution interactions between ether oxygenates with aromatics which is manifested in lower benzene evaporative emissions. As the temperature is increased, solution molecules acquire sufficient kinetic energy which in turn increases volatility by weakening the colligative interaction.

## CONCLUSIONS

Benzene evaporative emission reduction averaged approximately 14% for fuels containing 2.7 wt.% oxygen in the 80 - 120°F range

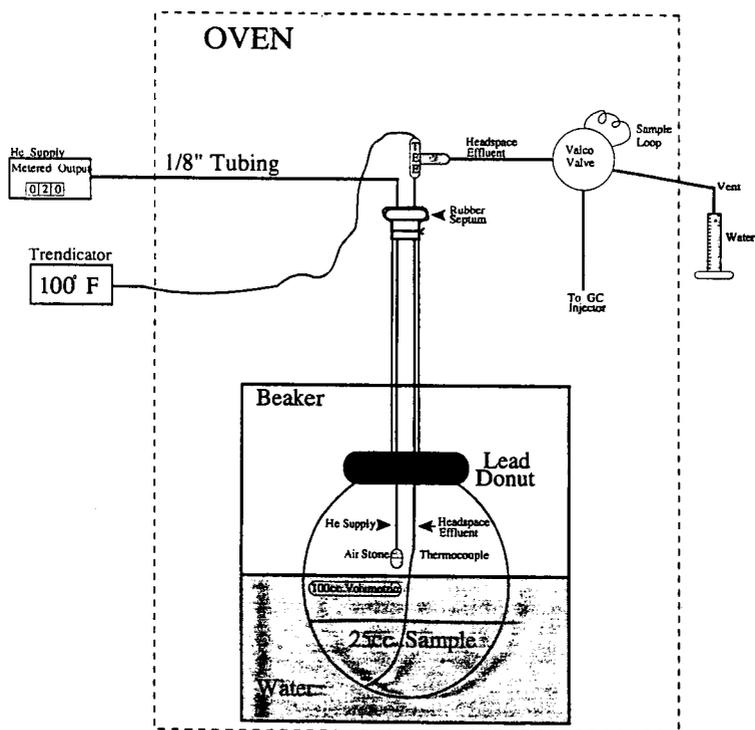
Reduced benzene evaporative emissions from an oxygenated fuel appear to be independent of the ether oxygenate molecular structure

## LITERATURE CITED

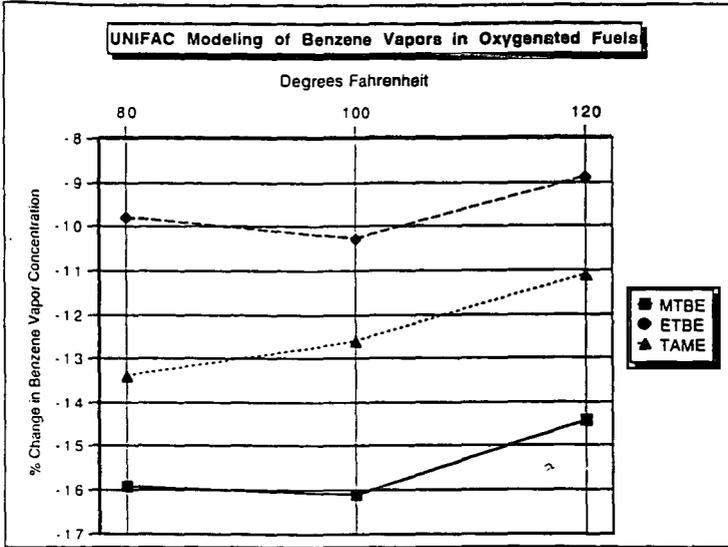
1. A. Fredenslund, J. Gmehling, and P. Rasmussen, **Vapor-Liquid Equilibria Using UNIFAC, A Group Contribution Method**, Elsevier, Amsterdam, 1977.

# Figure No. 1

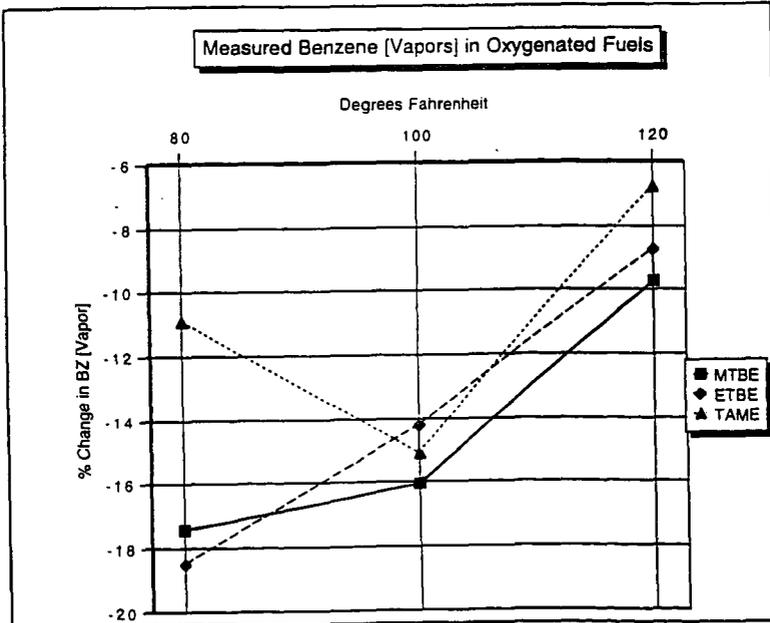
## Micro Head-Space Testing Apparatus



GRAPH No. 1



GRAPH No. 2



## VAPOR PRESSURE INTERACTIONS OF ETHANOL WITH BUTANE AND PENTANE IN GASOLINE

Jimell Erwin  
Southwest Research Institute  
P.O. Drawer 28510  
San Antonio, TX 78228

Keywords: Gasoline RVP, Ethanol Vapor Pressure Blending, Reformulated Gasoline

### ABSTRACT

The utility of ethanol as a fuel component is hampered by the greater than linear contribution it makes to the vapor pressure of resulting fuel blends. Careful measurements were made to see whether RVP control via addition of pentane resulted in the same nonlinear vapor pressure effect as observed for the usual component used to control moreover vapor pressure, butane. Within the resolution of the pressure measurements, no difference was detected. The result was the same for RVP control with a mixture of butane and pentane.

### INTRODUCTION

The Clean Air Act Amendments of 1990 require the production of reformulated gasoline (RFG) for ozone non-attainment areas starting in 1995. Volatility of RFG is a concern because of two requirements of the law and associated regulations:

- RFG must contain at least 2.0 weight percent oxygen from alcohol or ether.
- Performance standards include reduction in both volatile organic compounds (VOC) and toxic emissions and must not increase nitrogen oxides.

These requirements attempt to drive alcohol concentration in opposite directions under some circumstances. Some oxygenates, including ethanol, increase volatility and in turn cause an increase in evaporative VOC emissions. The contribution of ethanol to volatility of gasoline blends is higher than would be expected based on the pure component vapor pressure of ethanol. Diluted in a predominantly hydrocarbon mixture as in gasoline, the ethanol loses the hydrogen bonding enjoyed by the OH- groups in the neat liquid and exhibits a nonlinear or excess vapor pressure.

In the last year, casual observations in various places refocused attention on the factors which affect vapor pressure of ethanol in gasoline blends. Specifically the differential of butane versus pentane RVP control in gasoline mixtures was of interest. The current work used careful measurements of RVP interactions of butane with ethanol or pentane with ethanol in unleaded gasoline to demonstrate ethanol's vapor pressure behavior.

### PROCEDURES

A commercial gasoline (regular, summergrade purchased in San Antonio, Texas) was de-pentanized for use as the base stock in a test of RVP for several ethanol/gasoline mixtures. Depentanized gasoline was selected as the starting material to provide a full range of hydrocarbon types with which ethanol might interact to lower or raise the RVP of the blend. The experimental mixtures of base stock were made with butane alone, with pentane alone, or with butane and pentane to target RVP's (at standard 100°F) of 7 PSI and 8 PSI. These blends and the base gasoline were mixed with ethanol at 10 V%. This matrix is described in Table 1.

The work was done in a laboratory cold room (ambient temperature 35°F) with USP ethanol, reagent pentane, and commercial grade, normal butane. The cold lab was inherently dry, but no special precautions were taken to measure or control water content of the blends. The 8 RVP blends were made first and RVP was measured manually by ASTM D323. Later when the 7 RVP blends were made, both 7 and 8 RVP blends were measured by ASTM D5191 which is an automatic, instrumental method for RVP measurements using a Petrolab Grabner vapor pressure tester.

## RESULTS

The results are conclusive, showing the differences in RVP highlighted in Figure 1. The bars represent RVP with and without ethanol, and for 8 RVP samples, the D323 and D5191 results were averaged. For every case studied, the ethanol produced an increase at 100°F (standard RVP temperature) around the average 1.13 PSI.

The behavior shown by the flat RVP difference line in the butane and pentane plots Figures 2 and 3, indicates that identity or concentration of the high volatility component(s) does not affect RVP (within the repeatability of the method,  $\pm 0.16$  PSI). For measurements at 70°F and 130°F, the differences in vapor pressure are proportionately scaled as shown in Figures 4 and 5. The RVP differences cluster around 1.13 to 1.25 PSI at 100°F, the temperature at which the target blend compositions were calculated.

## SUMMARY

No trend arising from identity of pressurizing agent (butane, pentane, or their blends) was observed in the vapor pressure increase arising from the 10 V% ethanol addition in the gasoline samples tested. The results for RVP difference with and without ethanol are as follows:

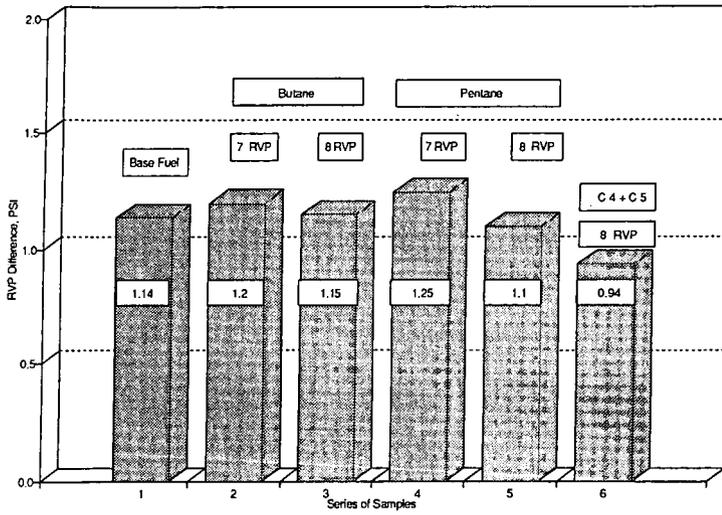
AVERAGE RVP INCREASE, PSI					
Base Gasoline	Butane Blends		Pentane Blends		C <sub>4</sub> + C <sub>5</sub> 8 RVP
	7 RVP	8 RVP	7 RVP	8 RVP	
1.14	1.20	1.15	1.25	1.10	0.94

## ACKNOWLEDGEMENTS

The concept and funding for this work are from the U.S. Department of Energy, Alternative Fuels Utilization Program through the National Renewable Energy Laboratory, B.K. Bailey, Project Manager. The careful blending and vapor pressure measurements were made by R.M. Rainwater of the Fuels Technology Department at Southwest Research Institute.

TABLE 1. RVP Measurements: Ethanol + Base Gasoline With or Without Butane or Pentane RVP Estimates by ASTM D 5191 (Mini-Method gives RVPE $\pm 0.12$ PSI)									
Description	Composition				Sample ID	Temperature			
	Basestock	Butane	Pentane	EtOH		70°F	100°F	130°F	
Depentanized Gasoline 1	100	--	--	--	Base 1	(1.28) *	(3.57) *	--	
Simulated 8 RVP Gasoline	$\left. \begin{array}{l} C_4 + C_5 \\ C_5 \\ C_4 \end{array} \right\}$	74.65	4.79	20.55	0	Blend 2	4.99	8.82	14.39
		8.82	--	41.18	0	Blend 3	4.63	8.51	14.30
		90.74	9.26	--	0	Blend 4	5.03	8.67	13.58
8 RVP Samples + 10 V% ethanol	$\left. \begin{array}{l} \text{with base} \\ \text{gasoline} \\ \text{Blend 2} \\ \text{Blend 3} \\ \text{Blend 4} \end{array} \right\}$	90	--	--	10	Blend 5 Base + EtOH	2.04	4.57	8.85
		Blend 2 90V%			10	Blend 6	5.38	9.95	17.11
		Blend 3 90V%			10	Blend 7	5.29	10.11	17.84
		Blend 4 90V%			10	Blend 8	5.55	9.89	16.46
Depentanized Gasoline 2	100	--	--	--	Base 2	2.23	4.34	7.63	
with 10 V% Ethanol	90	--	--	10	Base 2 + EtOH	2.65	5.62	10.37	
Simulated 7 RVP	$\left. \begin{array}{l} C_4 \\ C_5 \end{array} \right\}$	94.83 V%	5.17 V%	--	0	Blend 9	4.03	7.00	11.38
		68.55 V%	--	31.45	0	Blend 10	3.78	7.00	11.82
7 RVP Samples + 10 V% Ethanol	$\left. \begin{array}{l} \text{Blend 9} \\ \text{Blend 10} \end{array} \right\}$	Blend 9 90.0 V%		--	10.0	Blend 11	4.33	8.18	14.11
		Blend 10 90.0 V%		--	10.0	Blend 12	4.22	8.25	14.67

\* Calculated from Manual ASTM D 323



Plot 8

**FIGURE I. RVP DIFFERENCES**  
Neat vs. Ethanol Blends

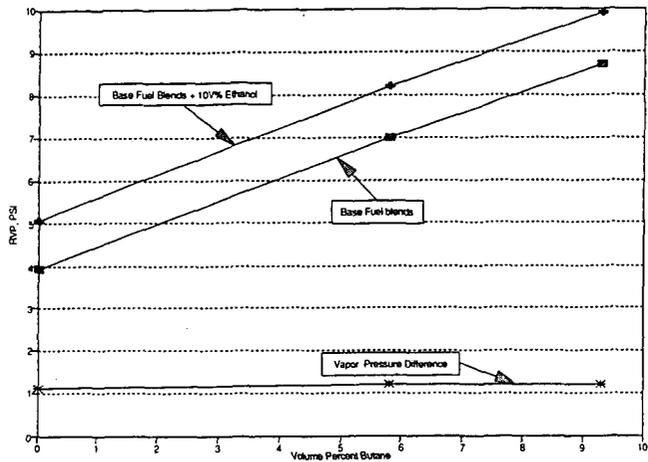


FIGURE 2. RVP VS. PERCENT BUTANE (100)

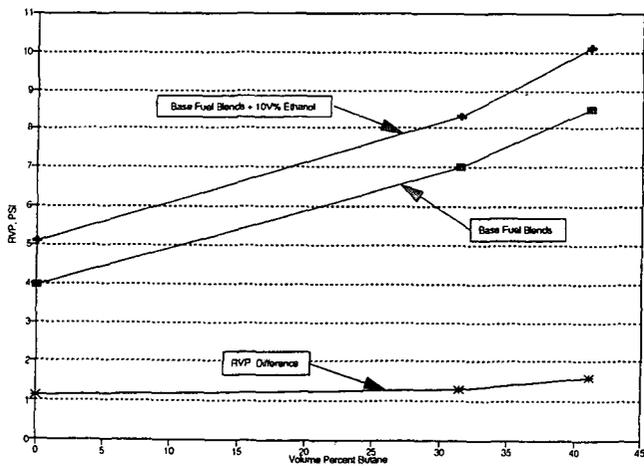


FIGURE 3. RVP VS. PERCENT PENTANE (100)

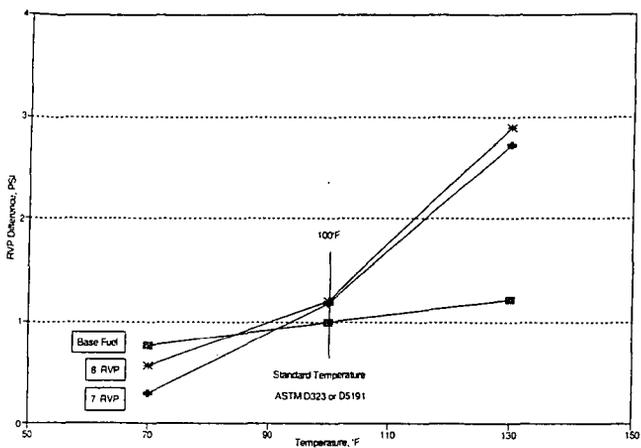


FIGURE 4. RVP DIFFERENCE VS. TEMPERATURE  
Blends made with Butane

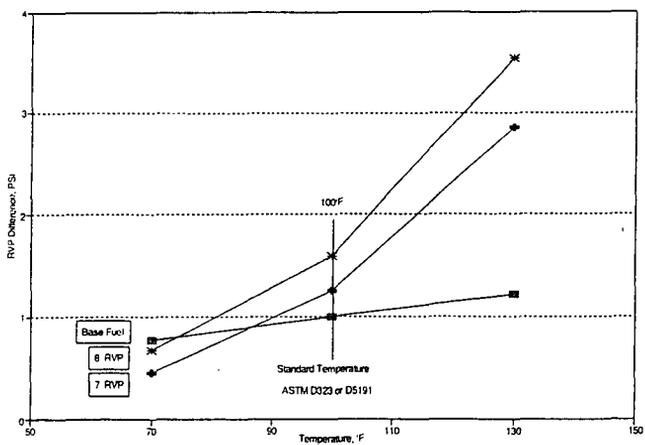


FIGURE 5. RVP DIFFERENCE VS. TEMPERATURE  
Blends made with Pentane

## LOW EMISSION OXYGENATED DIESEL FUEL

L. J. Karas, H. S. Kesling, Jr., F. J. Liotta, Jr., and M. K. Nandi,  
ARCO Chemical Company, Research and Development,  
3801 West Chester Pike  
Newtown Square, PA 19073-2387

**Keywords:** Oxygenate, Diesel, Fuel, Emission Reduction

### ABSTRACT

New diesel engines and fuels are required to meet stricter world-wide emission standards. Challenges include both lower particulate and NO<sub>x</sub> emissions. MTBE, ETBE, and TAME utilization in gasoline results in emissions reductions. Similarly, oxygen containing additive use in diesel fuel applications gives substantial particulate emission reduction. In combination with diesel ignition improvement additives, a typical "on-road" 30% aromatic content oxygenated diesel fuel can give an emission profile similar to a 10% aromatic California reference diesel fuel. Oxygenate selection criterion and emission reductions in heavy duty engines are detailed for several commercial P-series glycol ethers and for a new ether oxygenate, di-t-butyl glycerol. A di-t-butyl glycerol product mixture is prepared by etherification of glycerol available as a by-product from commercial biodiesel manufacture. Various strategies for oxygenate use to enhance diesel fuel performance are discussed.

### INTRODUCTION

The trend toward low emission diesel fuels is growing worldwide. In the United States, **Clean Air Act** legislation will mandate reduced particulates in 1994 and lower NO<sub>x</sub> emissions in 1998. Emission reductions beyond these targets will require a combination of new engine technology, additives, and reformulated diesel fuels (1). The production of economically viable low emission diesel fuels will remain a substantial challenge into the years to come. Oxygenated diesel fuel may offer one possible solution.

Oxygenate utilization to produce "cleaner burning" diesel fuels has been known for over fifty years. Oxygenates are well known to reduce particulate emissions. Low molecular weight alcohols, such as methanol, ethanol, and t-butyl alcohol, have been reported to reduce emissions (2). Higher alcohols (3), carbonates (4), diethers (5), such as diglyme, and various glycol ethers (6) have also been reported. Particularly attractive are P-series glycol ethers which contain both an ether and a propylene glycol end-group.

This paper deals with oxygenate selection criterion and emission reductions in modern diesel engines. Various application strategies to reduce emissions and enhance diesel fuel performance are discussed.

### OXYGENATE SELECTION

Key oxygen selection criterion include: cost, toxicity, environmental impact, fuel blending properties, and engine performance. Critical fuel blending properties, which were used to screen and identify viable oxygenate candidates, included: high oxygen content, diesel fuel solubility, flashpoint, viscosity, water solubility in the resultant fuel blend, oxygenate extractability from the fuel, and minimal impact on the natural diesel fuel cetane number.

The oxygenate should be soluble in diesel fuel from 1.0 to 5.0% to achieve maximum emissions reduction and improved engine performance. Above 5.0%, oxygenate cost per gallon of fuel treated is prohibitive. A number of high oxygen containing materials, such as ethylene and propylene carbonate, and most E-series glycol ethers, which

are based on ethylene glycol, were eliminated from consideration due to poor diesel fuel solubility. As aromatic content in future reformulated diesel fuels is reduced from 35% to 10 - 20%, oxygenate solubility in the less polar hydrocarbon fuels will become acute.

The oxygenated diesel fuel flashpoint needs to be over 52°C, as specified by ASTM D975, to reduce the transportation flammability risk. Many inexpensive ethers with high oxygen content, including MTBE, ETBE, TAME, and DIPE, were eliminated from consideration due to the low flashpoints of the resulting 1.0% oxygenated fuel blends. Fuel blends containing 1.0% or more of inexpensive dimethyl carbonate and diethyl carbonate, were also eliminated because the resulting blends had flashpoints lower than the target.

A key issue is how the additive behaves if the oxygenated blend becomes exposed to water. Both high degree of water solubility in the fuel blend and high degree of water extractability of the oxygenated additive from the fuel are unacceptable. Dimethyl and diethyl carbonate both have high water extractability from the fuel. Similarly, most fuel soluble E - series glycol ethers are easily extracted and are thus eliminated from consideration. P - series glycol ethers, generally, have acceptable partitioning characteristics.

Many intermediate molecular weight aliphatic, cycloaliphatic, and aryl alkyl alcohols meet the fuel blending selection criteria. Poly(ether) polyols based on propylene oxide or butylene oxide are viable oxygenate candidates. Methyl soyate, which is a form of biodiesel, meets selection criterion and was evaluated. Several commercial P - series glycol ethers and a new glycol ether oxygenate, di-*t*-butyl glycerol, are potentially inexpensive, and meet all the other selection criterion. Diglyme, which is associated with health risks, and too expensive to be economically viable, was also included in the test program so that benchmark comparisons can be made with previous studies. Various emission reduction strategies which utilize oxygenated diesel fuel are outlined in this paper.

## OXYGENATED DIESEL APPLICATIONS

There are many opportunities to use an oxygenated diesel fuel for emission reduction. A standard 1993 E.P.A. certification D2 diesel fuel reformulated with oxygenate has the potential to reduce emissions from both pre-1991 engines, which are required to meet a 0.60 gram / brake horsepower - hour particulate target, and post-1991 heavy-duty diesel engines which must meet a 0.25 gram / brake horsepower - hour Clean Air Act particulate emissions target. In addition, oxygenated diesel fuel could have the potential to benefit 1994 and 1998 heavy-duty diesel engine emission performance.

To demonstrate operability in older engines, an E.P.A 13-mode emission test was conducted in a 1990 Cummins L-10 heavy-duty diesel engine. Results show a 39 cetane number diesel fuel containing 43% aromatics and 0.25% sulfur, when blended with 5.0% GE-C (commercial P - series glycol ether), have the potential to reduce particulates emission with little impact on NO<sub>x</sub>. Similar results are expected in other older engines.

Most of the results reported in this paper focus on oxygenated diesel fuel performance in modern heavy-duty diesel engines. Emission testing was conducted in the prototype 1991 Detroit Diesel Series 60 CARB certification engine at Southwest Research Institute. Hot-start transient emissions, including hydrocarbons, carbon monoxide, NO<sub>x</sub>, and particulate matter, were measured using the standard E.P.A. transient test cycle and are shown in Table 1. The reference fuel is a E.P.A. certification D2 diesel fuel with a 43 cetane number, 0.037 Wt.% sulfur, and a 31% aromatic content. Various oxygenates were blended into this reference fuel at concentrations from 1.0 to 5.0%. The cetane number of the oxygenated fuel blends were adjusted to 43 using ethyl hexyl nitrate.

Oxygenates significantly reduce hydrocarbon, carbon monoxide, and particulate

emissions, but give a slight increase in NO<sub>x</sub> emissions. There is little or no increase in fuel consumption when an oxygenated diesel fuel is utilized. Results clearly demonstrate that reduced particulate matter emissions is a key benefit achieved through oxygenated diesel fuel use. In addition, 5.0% GE-C reduces unregulated aldehyde and ketone emissions by around 25%.

Not all oxygen containing additives are effective in reducing particulate emissions. 1-Phenyl ethanol and 1-cyclohexyl ethanol, for example, do not significantly reduce particulate emissions and methyl soyate is only marginally effective. Diethers, such as diglyme, and P-series glycol ethers; however, are very effective in reducing particulates. Based on a large amount of data, most of which could not be presented in a short paper, it can be concluded that particulate reduction is directly proportional to the ether oxygen content of the blended fuel. Results show GE-C at 1.0 wt.% oxygen gives around a 15% particulate emission reduction.

**Table 1 Oxygenate Additive Effect On Hot-Start Transient Emissions**  
(Grams/Brake Horsepower - Hour)\*

Additive; Conc. (Vol.%)	Oxygen Content (wt.%)	HC Ref. Fuel Cand Fuel	CO Ref. / Cand.	NO <sub>x</sub> Ref. / Cand.	PM Ref. / Cand.
MBA; 5	0.78	0.425 (.029) 0.468 (.059)	1.852 (.043) 1.867 (.045)	4.155 (.032) 4.327 (.087)	0.180 (.006) 0.174 (.002)
Cyclohexyl Ethanol; 5	0.68	0.388 (.029) 0.466 (.017)	1.933 (.088) 1.994 (.015)	4.091 (.027) 4.181 (.063)	0.180 (.005) 0.177 (.008)
Methyl Soyate; 5	0.59	0.392 (.011) 0.319 (.066)	2.004 (.029) 1.843 (.127)	4.303 (.056) 4.331 (.097)	0.182 (.007) 0.174 (.006)
Diglyme; 5	2.05	0.421 (.036) 0.307 (.021)	1.939 (.082) 1.634 (.033)	4.231 (.086) 4.340 (.065)	0.174 (.007) 0.146 (.007)
Poly(ether) Polyol; 1	0.34	0.385 (.012) 0.305 (.037)	1.919 (.030) 1.676 (.009)	4.175 (.029) 4.213 (.065)	0.176 (.005) 0.166 (.003)
GE-C, 1	0.37	0.424 (.037) 0.395 (.025)	1.990 (.086) 1.920 (.116)	4.242 (.102) 4.239 (.034)	0.171 (.002) 0.163 (.008)
GE-C, 2	0.74	0.433 (.040) 0.407 (.035)	1.946 (.081) 1.866 (.020)	4.159 (.070) 4.166 (.103)	0.183 (.003) 0.159 (.010)
GE-C, 5	1.82	0.384 (.019) 0.291 (.008)	1.872 (.034) 1.568 (.021)	4.159 (.045) 4.235 (.042)	0.183 (.004) 0.154 (.003)

\* Emission testing was conducted in the prototype 1991 Detroit Diesel Series 60 CARB Certification engine at Southwest Research Institute. Hot-start transient emissions (hydrocarbons, carbon monoxide, NO<sub>x</sub>, and particulate matter) were measured using the standard EPA transient test cycle and sampling techniques were based on 1992 Federal Test Procedures (FTP). The reference fuel is a standard EPA certification D2 diesel fuel with a 43 cetane number, 0.037 Wt.% sulfur, and 31% aromatic content. Oxygenates were blended into this reference diesel at the volume % indicated. Emissions are reported in Grams / Brake Horsepower - Hour. ( ) is one standard deviation. MBA is 1-phenyl ethanol. GE-C is a typical commercial P-series (propylene glycol based) glycol ether.

Emission regulations are directed at reducing both particulate matter and NO<sub>x</sub> emissions. Table 1 show ether oxygenates reduce particulates, but this particulate reduction is typically accompanied by a small increase in NO<sub>x</sub> emissions. Increasing the oxygenated diesel fuel cetane number using chemical cetane improvers, such as ethylhexyl nitrate or di-t-butyl peroxide, has been shown to reduce NO<sub>x</sub> emissions. Thus, the oxygenate / chemical cetane improver combination gives a diesel fuel with both lower particulate and NO<sub>x</sub> emissions. Results outlined in Table 2 suggest this combination strategy provides an opportunity to prepare an oxygenated diesel fuel which will meet current California emission standards.

**Table 2 Oxygenated California Diesel Fuel\***  
(Grams / Brake Horsepower - Hour)

Fuel Type	Cetane No / Arom.(%)	HC	CO	NO <sub>x</sub>	PM
EPA Base	43	0.433	1.979	4.17	0.174
Ref.	31				
Low Arom.	51	0.143	1.303	3.99	0.153
Ref.	15			(3.98)	(0.159)
GE-C & Peroxide	53	0.153	1.225	4.04	0.160
	31				

\* Transient protocol and data analysis are identical to those described in Table 1. The glycol ether, GE-C, blend concentration is 2.0% and enough di-t-butyl peroxide was used to increase the diesel fuel cetane number of the GE-C & peroxide experiment by 10.0 units. Since a 10% aromatic CARB reference fuel could not be purchased, a 15% containing aromatic fuel was used as the CARB low aromatic reference fuel. The Coordinating Research Council's (CRC) VE-1 Model (7) was used to correct emissions from the 15% aromatic fuel to CARB certification fuel properties on cetane, aromatic content, and sulfur. The number in ( ) is the adjusted emissions value. Considerable CRC data suggests the VE-1 Model is valid for this type of adjustment.

Effective October 1, 1993 all diesel fuel used in California must have an emission footprint which is equivalent to a low sulfur - 10% aromatic containing CARB reference fuel. Southwest Research Institute's prototype 1991 Detroit Diesel Series 60 engine, which is utilized for the oxygenate study, is the CARB certification engine. The emissions from an oxygenated diesel fuel, which contains 2.0% glycol ether (GE-C) and enough di-t-butyl peroxide ignition improver to increase the cetane number by 10.0 units, are nearly identical to the "pseudo-CARB" low aromatic reference diesel fuel used in this study. These results predicts that a combination of an oxygenated diesel fuel and chemical cetane improver provides an opportunity to produce a California "alternative" oxygenated diesel fuel with a 31% aromatic content Which has an emission performance equivalent to a low sulfur - 10% aromatic CARB reference fuel.

Cost is a significant issue in the preparation of a California diesel fuel. Clearly, a 30% aromatic containing oxygenated diesel fuel, which uses commercially available, p-series glycol ethers, is more cost effective than using a low sulfur - 10% aromatic fuel. Refinery hydrogenation to reduce diesel fuel aromatic content to 10% is an expensive option. The strategy used by most refiners is to reformulate with a 20% aromatic base fuel using high levels of chemical cetane improver. The California Air Resources Board (CARB) indicate costs for qualified fuels of this type will increase the diesel fuel costs by five to eight cents per fuel gallon. The oxygenated diesel fuel cost currently fits into the upper part of this cost range. Less expensive oxygenates are needed to make an oxygenated California diesel fuel a viable option.

One "non-commercial" oxygenate, which has the potential for reduced cost, is di-t-butyl glycerol. A di-t-butyl glycerol product mixture is prepared by etherification of glycerol which is available as a by-product from commercial biodiesel manufacture. The envisioned strategy is to blend 5% of an 80:20 methyl soyate / di-t-butyl glycerol oxygenate mixture with conventional low sulfur D2 diesel to create an inexpensive oxygenated diesel fuel. The cost and availability of by-product glycerol is leveraging. Biodiesel is a commercial reality in Europe and would provide the best opportunity for implementation.

Coupled with new heavy-duty diesel direct injection engine technology, reformulated oxygenated diesel fuels offers a potential option for achieving the 1998 Clean Air Act target which mandates a NO<sub>x</sub> reduction from 5.0 to 4.0 grams / brake horsepower - hour. The engine strategy for 1994 is to modify the engine design to give the 0.10 gram particulate target. Fortunately, NO<sub>x</sub>, carbon monoxide, and hydrocarbon emissions are acceptable. In 1998 engines, an oxygenated diesel fuel, which reduced particulates by 15%, would allow the OEM's to tune less rigorously for particulates, thus providing more flexibility on the NO<sub>x</sub> tuning.

There are numerous other opportunities to use oxygenates in specialty fuel applications where reduced emissions are of interest. For example, transit authority buses will use high quality low sulfur D1 or kerosene, particulate traps, and post-combustion catalysts to achieve a 0.07 gram particulate target for 1994. The downside for these specialty fuels is less power and higher fuel consumption. An oxygenated D2 diesel fuel has the potential to provide the same low emissions without increased fuel consumption. Other specialty fuel opportunities for an oxygenated fuel include: stationary powerplants, underground mining, marine diesel, locomotive diesel, and fuels for many smaller volume "off-road" applications.

## CONCLUSIONS

Cleaner burning diesel fuels can be produced through the use of oxygenated additives. Carefully selected "commercially" available *P*-series glycol ethers, which have the desired characteristics, are effective in reducing hydrocarbon, carbon monoxide, and particulate matter emissions. The magnitude of the particulate emissions reduction is directly proportional to the "oxygen" content of the ether oxygenate containing fuel. A combination of a glycol ether oxygenate with a cetane improver results in further emission reductions, especially NO<sub>x</sub>. One application strategy for the combination oxygenate / ignition improver diesel fuel formulation is a 30% aromatic containing oxygenated fuel which has the same emissions performance profile as the mandated low sulfur - 10% aromatic California diesel fuels.

## ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Mr. Dan M. Montalvo, Terry L. Ullman, Ms. Cynthia Chaffin, and Mr. Kent Spreen at Southwest Research Institute (SwRI) for their help with the emissions testing program. The authors also wish to thank Mr. Richard Englebach and Mr. Chris Green at ARCO Chemical Company for conducting the laboratory work on the oxygenated products associated with this paper.

## LITERATURE CITED

- (1) McCarthy, C. L., et. al, "Diesel Fuel Property Effects On Exhaust Emissions from Heavy Duty Diesel Engine That Meets 1994 Emission Requirements", SAE Paper 922267, October 1992.  
  
McCarthy, C. L., et. al, Fuel Reformulation, March 1993, p. 34.  
  
Cowley, L. T., et. al, "The Effect of Fuel Composition On Emissions From a Range of Heavy-Duty Diesel Engines", Coordinating European Council Paper CEC/93/EF03, May 1993.
- (2) Ecklund, E. E., "State of-the-Art Report On the Use of Alcohols In Diesel Engines", SAE Paper 840118, 1984.
- (3) Clerici, M. G., et. al., "Oxygenated Diesel Fuels Part - I", Presented At IX ISAF Meeting, Firenze (Italy), April 9 - 12, 1991.  
  
Pecci, G. C., et. al, "Oxygenated Diesel Fuels Part - II", Presented At IX ISAF Meeting, Firenze (Italy), April 9 - 12, 1991.
- (4) U.S. Patents 2,331,386; 4,378,973; 4,891,049; 4,904,279; and 5,004,480.
- (5) Bennethum, J. E. ; Winsor, R. E.; "Toward Improved Diesel Fuel", SAE Paper 912325, 1991.
- (6) Nikanjam, M., "Development of The First CARB Certified California Alternative Diesel Fuel", SAE Paper 930728, March 1993.  
  
Liotta, F. J.; Montalvo, D. M., "The Effect of Oxygenated Fuels On Emissions

From a Modern Heavy-Duty Diesel Engine", SAE Paper 932734, October 1993.

- (7) Ullman, T. L., et. al., "Study of Fuel Cetane Number and Aromatic Content Effects on Regulated Emissions From a Heavy-Duty Diesel Engine", CRC VE-1 Project Study, Southwest Research Institute, September 1990.

## OXYGENATED MICROEMULSION DIESEL FUEL

H. S. Kesling, Jr., F. J. Liotta, Jr., and J. M. McFarland  
ARCO Chemical Company, Research and Development  
3801 West Chester Pike  
Newtown Square, PA 19073-2387

**Keywords:** Oxygenate, Microemulsion, Diesel, Fuel

### ABSTRACT

New low emission fuel technology is needed to meet stricter world-wide particulate and NO<sub>x</sub> emission standards for both "on-road" and "off-road" fuel applications. The **Energy Policy Act of 1992** and the **1993 Executive Order 12844** establish clear national goals for the year 2000 and beyond which will reduce petroleum derived fuel use and provide greater utilization of alternate fuel vehicles. Technologies under evaluation include M85, E85, CNG/LPG, biodiesel esters, and electric vehicles. Microemulsion diesel fuel technology, which utilizes oxygenates to help compatibilize a biomass derived or hydrocarbon petroleum phase and water phase, offers strong potential as an alternate fuel option. Oxygenate selection criterion, microemulsion fuel formulation, and performance issues are discussed. Fuel formulations based on alcohol, glycol, ether, and glycol ether microemulsifying agents, which are readily available from world-scale propylene oxide / oxygenated coproduct technology, are described. Evaluation results suggest oxygenated microemulsion fuels are viable alternate fuel candidates.

### INTRODUCTION

The trend toward low emission diesel fuels is growing worldwide. In the United States, **Clean Air Act** legislation will mandate reduced diesel particulates in 1994 and lower diesel NO<sub>x</sub> emissions in 1998 (1). A combination of new engine technology, additives, and new low emission fuels will be required to achieve these targets. The **National Energy Policy Act of 1992** and **Executive Order 12844** of 1993 establish clear national goals for the year 2000 and beyond which will both reduce petroleum derived fuel use and ozone forming emissions. The **Clean Cities** program provides the framework for implementation which includes greater utilization of alternate fuel vehicles. In addition to "on-road" applications, there is considerable recent focus on "off-road" applications as a major source of particulate and NO<sub>x</sub> emissions. A comprehensive E.P.A. report (2) describes our national problem. A NO<sub>x</sub> emission inventory shows the magnitude of this problem in ozone nonattainment areas. Emissions from construction, agriculture, railroads, mining, marine, industrial stationary powerplants, airport services, and lawn and garden services all contribute to the global NO<sub>x</sub> problem. New alternative fuel technologies under evaluation include: M85, E85, CNG, LPG, and biodiesel esters (3). Microemulsion diesel fuel technology also offers great potential for reducing emissions and dependency on oil (4).

### DISCUSSION

#### Oxygenate Selection

Microemulsions are clear, stable, two-phase nanodispersions which readily form upon mixing water with an oil phase. Water-in-oil (w/o) microemulsions are comprised of a continuous non-polar hydrocarbon phase and a discontinuous aqueous phase. Because of the small droplet size (2 to 200 nanometers) of the discontinuous phase, these microemulsions appear to be clear, one-phase systems. Microemulsion diesel fuel technology uses a microemulsifier to compatibilize a diesel or biodiesel fuel and a water phase. The microemulsifier typically contains a surfactant and a compatibilizing agent (an oxygenate). The resulting microemulsion fuel, when utilized in conventional diesel engines, is "clean-burning", gives no power loss or increase in fuel consumption, and is thermal and shear stable in the fuel handling system.

The purpose of the oxygenate is to help solubilize the surfactant in the fuel, adjust the properties (i.e. viscosity) of the fuel, and possibly contribute to improving the ignition properties of the water-containing microemulsion fuel. Oxygenates in the microemulsifiers are also required to achieve inorganic salt tolerance, thermal and shear stability, and good shelf life. Oxygenates used as microemulsifying agents include C<sub>1-6</sub> alcohols (5), benzyl alcohols (6), and glycols (7). Key issues are oxygenate cost, flammability, and impact on stability of the microemulsion fuel.

The oxygenates must be inexpensive to achieve economics which are competitive with specialty diesel fuels. Alcohols, such as methanol, ethanol, and *t*-butyl alcohol, are inexpensive and readily available. Although they all are effective in microemulsion fuel preparation, these alcohol microemulsifiers are flammable. Less volatile alcohols, such as 1-phenyl alcohol (MBA), eliminate the flash point issue, but the resulting microemulsions are more difficult to prepare and have narrower stability windows. Clearly, new candidates, which provide stability and less flammable microemulsion fuels, are desirable.

World-scale propylene oxide technology as practiced by ARCO Chemical Company produces *t*-butyl alcohol (TBA) and 1-phenylethanol (MBA) as primary coproducts. TBA is the precursor to isobutylene, MTBE, and ETBE and MBA is a styrene monomer precursor. Using these coproducts as building-blocks, several new oxygenates were developed which have application as microemulsifying agents.

### **Preparation**

The microemulsions which have been formulated are water-in-oil microemulsions made up of four basic components: diesel fuel, surfactant, oxygenates, and water. The diesel fuel is a D-2 low sulfur fuel (< 0.5 wt% sulfur, 31% aromatics, 43 cetane number) which is commercially available. The surfactant for these formulations is the anionic long chain fatty acid Emersol 315. This linoleic/oleic/linolenic acid mixture has been neutralized (40% unless noted otherwise in Table I) with monoethanol amine (MEA). Oxygenates may be used alone or as combinations of several oxygenated compatibilizing agents. The microemulsifiers are formed by mixing the Emersol 315, MEA, and oxygenates.

The microemulsion fuels are mixed in the following order: diesel fuel, microemulsifier, water. After mixing the three components, the fuel mixture is shaken and allowed to settle. Any sign of phase separation, solid formation, or cloudy appearance over several weeks is a negative result. If a clear, single phase system is observed, the microemulsion is considered to have formed. Some of the microemulsion fuels prepared are listed in Table I.

### **Performance**

As shown in Table I, the choice of oxygenate in the microemulsifier has a major influence on the stable formation of a microemulsion diesel fuel. Combinations of oxygenates can also improve the ability of the fuel to form stable microemulsions. Optimization of the fuels for surfactant concentration will also improve the formation potential. Although not specifically shown in these examples, it is expected that the character of the different oxygenated compatibilizing agents will change the surfactant requirement of the overall microemulsion fuel. This will allow optimization of the fuels for cost, water loading and performance. Among the performance issues of importance to microemulsion fuels are thermal stability, shear stability, flash point, storage stability, engine performance, and emissions.

**TABLE I**  
Microemulsion Fuel Formulations†

Fuel #	ME‡	Wt% Oxygenate	Wt% Surfactant*	Stable Formation
1	A	34.1	65.9	+
2	B	34.1	65.9	+
3	C	34.1	65.9	+
4a	D1	34.1	65.9	+
4b	D2	34.1	65.9 (100%)	-
4c	D3	10.0	90.0 (27%)	-
5	E	34.1	65.9	+
6	F	33.9	66.1	-
7	G	33.9	66.1	+
10	J	34.0	66.0	+
11	K	33.8	66.2	-
12	L	34.2	65.8	-
13	M1	34.0	66.0	-
14	M2	33.8	66.2	+
15	N	34.0	66.0	-
16	O1	34.1	65.9	-
17	O2	34.6	65.4	+
18	P	34.6	65.4	-
19	R	34.4	65.6	+
20	E	34.1	65.9	+

† 71 / 19 / 10 vol% D-2 / ME / H<sub>2</sub>O formulation except: Fuel 2: 75.5 / 14.5 / 10 vol% D-2 / ME / H<sub>2</sub>O and Fuel 20: D-2 phase is 95% D-2, 5% of a 80/20 wt% mixture of biodiesel / Di-*t*-butyl glycerol (DTBG).

‡ ME is microemulsifier used in the particular formulation. Each letter designates a different oxygenate composition. Components of the various microemulsifiers will be discussed in the presentation.

\*surfactant weight is total of fatty acid and MEA. MEA is added at 40 mol% (40% neutralization) unless noted differently by the number in parentheses

A microemulsion diesel fuel is generally expected to remain stable for several weeks in a temperature range between -10°C and 70°C. This range covers most extremes a fuel would face either in storage and delivery or in the heat of a modern diesel engine fuel delivery system. The fuel must also be stable to the shear forces present in the fuel delivery system within a diesel engine. Preliminary results show microemulsion diesel fuels containing oxygenates in the microemulsifier phase are thermally and shear stable. If the fuel can withstand these conditions in the engine and fuel system, the fuels can be used in current engine technology without major modifications. This makes microemulsion diesel fuel an immediate possibility as an alternative fuel.

Fuel flammability is a major concern. The flash point of the fuel must be above 52°C (126°F) in order to be transported via pipeline in the U.S. As well, the international flammability standard is 140°F. Depending on the oxygenates chosen, the flash point of the microemulsion fuel may be widely adjusted. This is best represented by the data shown in Table II. By using combinations of oxygenates, it is possible to optimize the microemulsion fuel for stability while providing a fuel that meets flammability standards. As an example, fuels 4a and 5 contain the same oxygenate, except in fuel 5 the oxygenate is in combination with another oxygenate. Fuel 5 is a more stable microemulsion fuel formulation compared to fuel 4a, yet still shows an acceptable flash point. Another benefit of microemulsion fuels containing a dispersed water phase is fire resistance. Studies have shown that a microemulsion diesel fuel can be self-extinguishing or will not burn in the presence of an open flame (6). The choice of oxygenate will have an influence of this property of a microemulsion diesel fuel.

**TABLE II**  
**MICROEMULSION FUEL FLASH POINTS**

Fuel #	ME	Seta Flash Point (°F)
2	B	116
4a	D1	204
5	E	128
7	G	126
10	J	58
20	E	138

Long term stability is necessary to allow for tank storage of the fuel for extended periods of time, especially in some stationary applications. Several of the formulations have shown excellent long term stability, including some which are stable for over one year. Some of the stability data is shown in Table III.

**TABLE III**  
**LONG TERM STORAGE STABILITY**  
**OF MICROEMULSION DIESEL FUELS**

Fuel #	ME	Storage Stability
1	A	> 1 year
2	B	> 1 year
3	C	> 1 year
4a	D1	> 1 year
5	E	> 1 year
7	G	> 3 months
10	J	> 1 month
20	E	> 1 month

As previously mentioned, microemulsion diesel fuels can be used in current engine technology without major modifications to the engine. However, because of the water and surfactant concentrations in a microemulsion diesel fuel, some loss of ignition properties may be possible (4). The proper choice of oxygenate can reduce or eliminate this problem. As well, the aqueous phase of a microemulsion diesel fuel offers a way for the ignition properties of the fuel to be augmented with inexpensive cetane enhancers.

Regardless of these other performance issues, microemulsion fuels must reduce engine emissions to be a viable option as an alternative fuel. Microemulsion diesel fuels are known to reduce both NO<sub>x</sub> and particulates significantly over standard diesel fuels (5). The NO<sub>x</sub> reduction is believed to occur through the lowering of combustion temperatures. This is a result of the higher specific heat of the water and oxygenates in the microemulsion fuel. The microexplosion of the water in the discontinuous phase, more effectively vaporizing the fuel in the combustion chamber, is believed to lower the particulate emissions. Surfactant and oxygenate choice and concentrations have an effect on the size of the water micelles in the microemulsion fuel. Therefore, the selection of the proper oxygenated compatibilizer can improve the performance of the engine toward particulate emissions.

With these lower emissions, several new options are available as a result of the use of microemulsion fuels. First, in stationary applications, the lower NO<sub>x</sub> emissions from microemulsion fueled sources may help offset other more costly and difficult NO<sub>x</sub> emission reduction options. This will be especially beneficial when regional

attainment targets are enforced in the near future. Second, a decrease in NO<sub>x</sub> and particulate emissions from a microemulsion fueled engine may allow flexibility to tune the engine to reduce other emissions as well.

## CONCLUSIONS

With new emissions goals mandated by the Clean Air Act and other legislative mandates, alternatives to petroleum based fuels must be sought. Microemulsion diesel fuels are a cost-effective alternative fuel for both "on-road" and "off-road" applications. These fuels offer significantly reduced NO<sub>x</sub> and particulate emissions compared to normal diesel fuel. Microemulsion fuels which contain low cost oxygenated compatibilizing agents offer a range of possible formulations for these fuels. These new formulations have widely tunable stabilities, flash points, and engine performance, depending on the oxygenates chosen. Microemulsion diesel fuels also work with the existing engine technology and do not require any changes to the engines or the fuel infrastructure.

Microemulsifier E offers strong possibilities as a component for microemulsion diesel fuels. This microemulsifier phase contains a combination of oxygenates that gives a fuel which meets many of the requirements for an acceptable alternative microemulsion diesel fuel.

## ACKNOWLEDGEMENTS

The authors wish to thank Mr. Richard Englebach for conducting some of the laboratory work presented in this paper.

## LITERATURE CITED

- (1) McCarthy, C. L., et. al., "Diesel Fuel Property Effects On Exhaust Emissions From Heavy-Duty Diesel Engines That Meet 1994 Emission Requirements", SAE Paper 922267, October 1992.  
  
McCarthy, C. L., et. al., Fuel Reformulation, March 1993, p. 34.  
  
Cowley, L. T., et. al., "The Effect of Fuel Composition On Emissions From a Range of Heavy-Duty Diesel Engines", Coordinating European Council Paper, CEC/93/EF03, May 1993.
- (2) E.P.A. 460/3-91-02, "Nonroad Engine and Vehicle Emission Study - Report", November 1991.
- (3) SAE Publication SP-995, "Advanced Alternative Fuels Technology", October 1993.
- (4) Griffith, W. L.; Compere, A. L., Oak Ridge National Laboratory Report, ORNL/TM-11248, "Correlating Microemulsion Fuel Composition, Structure, and Combustion Properties", 1989.  
  
Griffith, W. L.; et. al., "High Alcohol Microemulsion Fuel Performance in a Diesel Engine", SAE Paper 902101, 1990.
- (5) U.S. Patents 4,58,354; 4,568,355; 4,568,356; 4,744,796; and 5,104,418.
- (6) U.S. Patent 4,770,670.
- (7) European Patent Application, EP441002-B1, 1993

# REFINERY FUEL OXYGENATES IN VIEW OF THE COMPLEX MODEL FOR REFORMULATED GASOLINE

by  
C. D. Crawford and C. P. Haelsig  
Fluor Daniel  
3333 Michelson Drive  
Irvine, California 92730

KEYWORDS: MTBE, TAME, ETBE

The final version of the Complex Model for reformulated gasoline (RFG) has now been issued with some surprising features that will significantly affect refinery fuel oxygenates planning. These include the following:

- The only oxygenates included in the model are MTBE, ETBE, TAME, and Ethanol.
- The Complex Model calculates that MTBE and TAME are significantly more effective for reduction of air toxics emissions than Ethanol and ETBE.
- The Complex Model calculates that MTBE and TAME typically produce about equal reduction in air toxics emissions at the same RFG oxygen content.

Although gasoline certification by the Complex Model is optional prior to 1998, after 1998 it will be mandatory for both reformulated and conventional gasolines. This paper considers refinery oxygenates production in view of these features of the Complex Model for RFG, basing the discussion on 2.0 weight percent oxygen content for RFG.

The Complex Model calculates that MTBE and TAME will be more effective in reducing calculated air toxics emissions than ETBE and Ethanol. Although MTBE can be purchased on the open market, MTBE production from the isobutylene contained in the FCC/Coker C4's cut is well-established practice, and can provide as much as 15 to 20 percent of the 2.0 weight percent reformulated gasoline oxygen content requirement for ozone non-attainment areas. Emerging high-olefin FCC catalyst technology can increase this contribution to approximately 25 percent or more.

TAME production from the isoamylenes contained in the FCC/Coker C5's cut is now commercial technology, with a number of plants onstream. Recently announced low-cost upstream C5 selective hydrogenation technology can reduce TAME production costs, making TAME a more economically attractive oxygenate than previously. Applying catalytic distillation for TAME production provides yield advantages, and can provide as much as 15 to 20 percent of the reformulated gasoline oxygen content requirement. Unreacted amylenes can flow to alkylation, or other uses. Developmental skeletal isomerization technology has been announced for C5 olefins, which could increase TAME yields to provide as much as 30 percent or more of the reformulated gasoline oxygen content requirement.

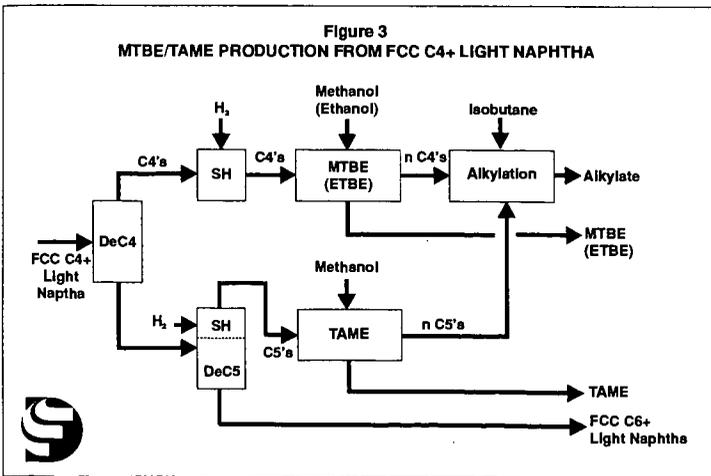
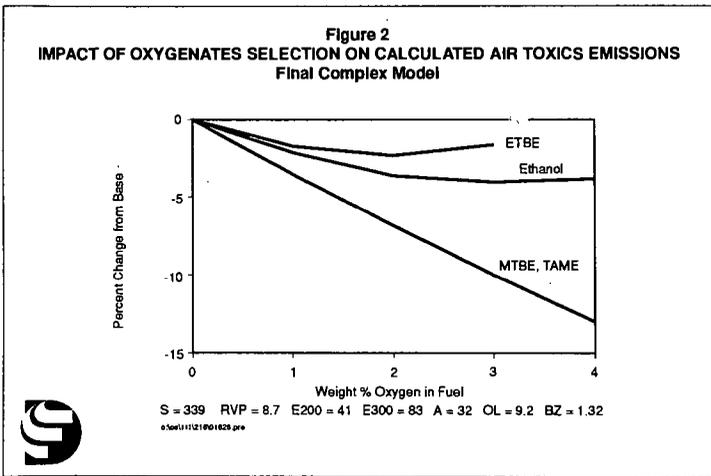
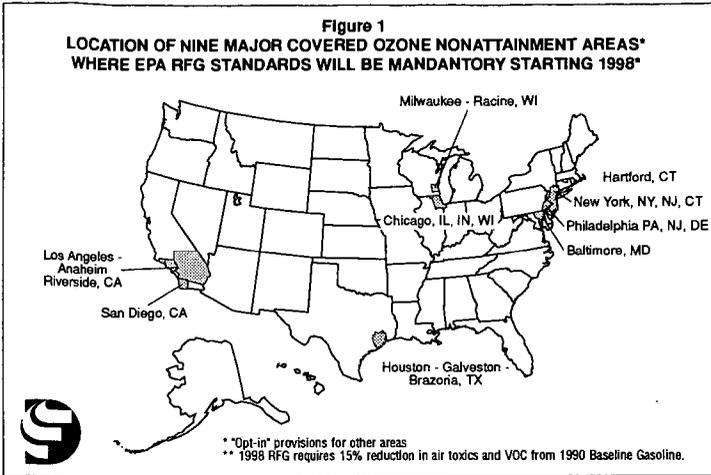
Overall, use of commercially proven technology for MTBE and TAME captive production currently can economically provide about 35 to 40 percent of refinery oxygenates blending requirements, based on FCC/Coker olefins sources. Since both MTBE and TAME are low-pressure processes conducted in mild steel equipment, existing equipment can be advantageously retrofitted to minimize plant investment.

Although the Complex Model shows less air toxics emissions reduction at a given RFG oxygen content, ETBE and Ethanol can play a role in certain RFG blends. It is possible with certain refinery configurations to meet mandated reductions in air toxics reduction using ETBE or Ethanol to furnish the 2.0 weight percent oxygen content requirement. For these refinery configurations, the primary driving force for oxygenates selection will be economics, since emissions targets can be met whichever oxygenate is used, provided the proper configuration is chosen.

High molecular weight developmental oxygenates such as DIPE, IPTBE, and TAEF offer potential advantages of high octane and low vapor pressure, plus extended captive production from propylene in the case of DIPE. However, these oxygenates are not

included in the current version of the Complex Model and special permits to blend them into fuels may be required where advantages for their use are anticipated.

Details of this paper, including Complex Model parametric studies and refinery configurations, will be presented at the national meeting. The attached figures are typical of those which will be included.



## WHICH OXYGENATE IS RIGHT FOR YOU?

Elaine J. Chang  
Petrochemicals, Polymers, and Energy Center  
SRI International  
Menlo Park, California 94025

Keywords: oxygenates; reformulated gasoline; oxygenate economics

### INTRODUCTION

Recent announcements of additional sources of oxygenates have generated considerable interest. Increasing demand for methyl tert-butyl ether (MTBE) worldwide, especially in the United States for oxygenated fuel and reformulated gasoline (RFG), provides the primary incentive for technologies that produce additional raw material (namely isobutene) and/or alternative oxygenate compounds. Normal butene isomerization and diisopropyl ether (DIPE) are two new processes introduced in 1992 to meet the oxygenate demand.

The U.S. Clean Air Act Amendments of 1990 (CAAA) have created a huge demand for capital. Between 1991 and 2000, the U.S. refining industry will need to make capital expenditures of about \$37 billion (1990 dollars) to meet refinery regulatory requirements, and to manufacture reformulated gasoline and ultra-low sulfur diesel fuel.<sup>(1)</sup> To obtain financing, whether internally or from external sources, projects must provide sound economics and pose minimal technological risks. These concerns have prevented several large MTBE projects, involving both established and new technologies, from going forward.<sup>(2)</sup>

The introduction of normal butene isomerization and DIPE processes has generated a great deal of enthusiasm, but neither process had been licensed by the third quarter of 1993. Technology risk is a major barrier to obtaining financing inasmuch as lenders are unlikely to finance the first commercial application of any technology. Currently, Texas Olefins/Phillips Petroleum and Lyondell have demonstrated normal butene isomerization on a commercial scale in their plants. However, Mobil has not demonstrated the DIPE process beyond the pilot plant stage.

In this paper, we assess the technological aspects of normal butene isomerization and DIPE processes, and compare their economics with existing etherification processes.

### DRIVING FORCES FOR USE OF OXYGENATES IN GASOLINE

Additives and improved refining processes have long been used to improve gasoline quality. Figure 1 shows how gasoline octane has been improved historically. To achieve widespread use, a new additive or process improvement must prove its economic worth. The addition of lead to increase gasoline octane was one of the most cost-effective methods, and its use was nearly universal until the detrimental environmental effects of lead became apparent.

The reasons for using oxygenates in gasoline have varied over time. Alcohols were added to commercial gasoline on an experimental basis as early as 1924. In response to the shortage of crude oil during the oil crises of 1973 and 1979, alcohols were promoted for use either as a substitute or a partial replacement for gasoline. Brazil developed the most significant program, which called for ethanol to be substituted for a large percentage of the gasoline consumed in that country. In the United States, a federally subsidized program was established to encourage the use of ethanol in gasoline nationwide. Although both the Brazilian and the U.S. ethanol programs are still active, the high cost associated with the use of ethanol constitutes a major disadvantage. Consequently, some form of monetary subsidy is required for acceptance of ethanol fuel.

During the mid-1980s, some U.S. gasoline marketers tried to introduce methanol into their gasoline. Both direct blending and cosolvent blending (methanol with tert butyl alcohol [TBA] to minimize phase separation) were tried. These blends were economically attractive because the cost of methanol was considerably lower than that of gasoline. However, compatibility and mechanical problems, together with limited availability of the cosolvent, prevented widespread acceptance of the use of methanol in gasoline.

Ethers, principally MTBE, became widely available in the early 1980s. They have gradually gained acceptance as gasoline blending agents because they offer high octane and excellent gasoline compatibility, and because they can be partially made from refinery by-product isobutene at a cost similar to the cost of producing toluene, whose octane quality is similar to MTBE in gasoline. Refiners originally began to

investigate the use of MTBE as an octane enhancer blended into gasoline at levels of 7 to 10%. Other ethers, such as ethyl tert-butyl ether (ETBE) and tert-amyl methyl ether (TAME), are newer products with gasoline blending properties somewhat similar to those of MTBE.

In the 1980s, the improved burning characteristics (more complete combustion) of MTBE-gasoline blends and their potential for reducing carbon monoxide and smog formation became recognized. Consequently, oxygenated fuel was adopted in the 1990 CAAA.

The CAAA requires the use of oxygenates in gasoline for environmental reasons. Most other countries will probably use oxygenates only for octane enhancement until the full environmental consequences of oxygenated and reformulated fuels are better understood.

#### EXISTING ROUTES FOR PRODUCING OXYGENATES

MTBE, produced by reacting isobutene with methanol, is the most widely used oxygenate. Isobutene, which is the critical raw material in meeting the demand for MTBE, is available from three commercial sources. By-product sources include mixed C<sub>4</sub> streams available from (1) catalytic cracking in refinery gasoline production, (2) steam cracking for ethylene production, and (3) TBA and propylene oxide (PO) production (dehydration of TBA, a coproduct with propylene oxide via the hydroperoxidation of isobutane). The rapid depletion of these traditional isobutene sources has led to the development of on-purpose isobutene production from field or mixed butanes. The dehydrogenation route to MTBE is a rapidly growing source of isobutene.

Figure 2 shows the world distribution of MTBE production by isobutene source. In the United States, dehydrogenation is now the major source for MTBE (40%), with fluidized catalytic cracking (FCC) and TBA/PO isobutene sources contributing about equal amounts (24% and 25%, respectively), and the remainder from steam cracking (11%). Dehydrogenation is also the major source of isobutene for regions rich in natural gas (e.g., Latin America, the Middle East). In contrast, ethylene cracking is a major source of isobutene in Europe and the Asia-Pacific region for MTBE productions. In these two regions, naphtha is the predominant feedstock in ethylene cracking with relatively high amounts of C<sub>4</sub> by-product, and FCC units are not as prevalent as in the United States.

Other ethers, such as TAME and ETBE, are based on similar technology as MTBE production. Potentially, TAME could be a large source of oxygenate in the United States. The use of ETBE faces two obstacles: (1) it competes with MTBE for isobutene, and (2) its economics depend in large part on government subsidies.

#### NEW ROUTES TO PRODUCE OXYGENATES

As we approach 1995, when reformulated gasoline regulations take effect in the United States, oxygenated gasoline and RFG will both become required by law, and MTBE supplies will tighten. Refiners may have no choice but to pay a premium above MTBE's octane value to obtain sufficient MTBE. As a result, many refiners are rushing to install their own oxygenate production capacity.

Isobutene is produced in refineries mainly in FCC units. In the United States, a shortage of refinery captive isobutene had kept MTBE plants' utilization rate low (i.e., 60% to 67% for 1988 through 1990).<sup>(3)</sup> To increase FCC isobutene production, higher FCC riser temperature or isobutene-selective catalysts can be used to raise the isobutene yield by 50-200%. Two drawbacks are the additional investment needed to debottleneck the FCC unit and reduced gasoline yield.

An alternative route is the isomerization of normal butene to isobutene. In addition, other oxygenates, which do not require isobutene as raw material, such as DIPE, can be considered.

#### Normal Butene Isomerization

Since March 1992, six companies—Lyondell, Phillips/Texas Olefins, Mobil, IFP, UOP, and Snamprogetti—have announced the development of one-step processes to isomerize normal butenes to isobutene. The 4-carbon monoolefins have 4 isomers: 1-butene, cis-2-butene, trans-2-butene, and isobutene. Isomerization of one of the butene isomers to increase the supply of another has long been practiced commercially. For example, refineries maximize the octane number of hydrofluoric acid alkylate by installing a butene isomerization unit (e.g., the Hydrisom process) upstream of the alkylation unit. The isomerization process converts 1-butene to 2-butene, the preferred HF alkylation feedstock.

Normal butene isomerization has been extensively researched, with a variety of catalysts developed to overcome some technological difficulties— low conversion (equilibrium-limited reactions), rapid catalyst deactivation, and undesirable side reactions such as disproportionation and polymerization. The mandates for oxygenated fuels have renewed interest in this process. As MTBE production exhausts the available supplies of isobutene from traditional sources, additional isobutene is being produced on-purpose from field butanes through isomerization to isobutane and dehydrogenation to isobutene. Dehydrogenation is a very capital-intensive, and thus expensive route to MTBE. Consequently, much interest has been generated by the announcement of a new route to produce isobutene by butenes isomerization.

#### Normal Butene Isomerization Thermodynamics

Butenes isomerization is equilibrium limited. The equilibrium composition changes only slowly with temperature. For normal butene isomerization to isobutene, the yield in a single pass is limited to between 40 and 50 mol% in the normal reaction temperature range of 350-550°C (662-932°F). The branched isomer is favored by lower temperatures, but a faster reaction rate is favored at higher temperatures.

When the carbon skeleton is rearranged, mixtures of butenes result. Skeletal isomerization involves C-C bond rupture and reformation. Once a carbonium ion is formed in the presence of a strong acid, several side reactions also take place (e.g., polymerization, isomerization, hydrogen transfer). Therefore, it is unlikely to achieve a clean product slate. The typical isobutene selectivity ranges between 85 and 90%.

Table 1 lists processes offered for licensing, and Table 2 summarizes reported yields. These processes differ in conversion, selectivity, cycle length, and catalyst regeneration methods.

#### Diisopropyl Ether

In March 1992, Mobil Research & Development Corporation announced the development of a new process to produce DIPE by direct hydration of propylene to isopropyl alcohol (IPA), followed by etherification using shape-selective zeolite catalysts. DIPE's high octane and low vapor pressure gasoline blending qualities make it an attractive oxygenate blending candidate for reformulated gasoline mandated by the CAAA. Table 3 compares the blending properties of DIPE with MTBE, ETBE, and TAME. Another claimed advantage of DIPE is that, unlike MTBE, ETBE, and TAME, it is a completely refinery-based oxygenate, with no outside alcohol supply required.

UOP also unveiled a DIPE process in 1993. Its process is probably based on Union Carbide's IPA process.

Catalytic hydration of propylene to produce IPA is an established technology. The reaction steps are:



The direct propylene hydration to IPA and DIPE is thermodynamically limited with IPA as the main product and DIPE as a by-product. The use of a strong acidic catalyst can achieve direct propylene hydration under the moderate temperatures and pressures favorable to propylene conversion. Pressure is an important parameter determining propylene conversion—higher pressures increase the propylene conversion per pass. The water/propylene ratio is used to control IPA and DIPE production. A high water/propylene ratio favors IPA production, and a low ratio favors DIPE formation. The presence of excess water inhibits oligomer formation. The reaction temperature is normally kept as low as possible to minimize polymerization.

Although the hydration of propylene to IPA and DIPE is a known technology, the product recovery scheme is more complex than other etherification processes. The reactor effluent contains a mixture of unreacted feed (propylene and water), products (DIPE and IPA), and by-products (oligomers which are mainly C<sub>6</sub> olefins). Separating these components requires multiple distillation and extraction operations because binary azeotropes form between water/IPA, IPA/DIPE, and DIPE/water, and together they form a ternary azeotrope. Consequently, many separation schemes have been developed in order to reduce process complexity and operating cost.

#### OXYGENATE ECONOMICS

Figure 3 summarizes oxygenate product values for MTBE, ETBE, TAME and DIPE, including 10% depreciation and 25% pretax rate of return on investment. All economics are based on U.S. Gulf Coast overnight construction in 1993.

### MTBE Economics

The product values of MTBE, based on isobutene from refinery  $C_4$ s, steam cracker  $C_4$ s, TBA/PO, normal butene isomerization, and field butanes, are shown in Figure 3. The economics are developed for 2,400 b/d MTBE unit based on by-product isobutene, and 12,500 b/d MTBE plant from on-purpose isobutene—typical unit sizes for these applications. The value of isobutene is based on its value in alternative process uses. The major use for isobutene in refineries is alkylation feed. This comparison provides a picture of the current competitive situation.

From this comparison, we can conclude that MTBE production based on by-product isobutene sources is the least costly route. MTBE produced from isobutene derived from TBA/PO is the least expensive at an estimated product value of 70¢/gal. MTBE derived from steam cracking and FCC by-product isobutene has slightly higher product values of 74¢/gal and 78¢/gal, respectively. MTBE product values based on either an integrated normal butene isomerization unit or a dehydrogenation unit are of similar magnitude at \$1.10/gal and \$1.09/gal, respectively. These last two processes are considerably more costly than the traditional by-product isobutene sources. Integrating MTBE production with normal butene isomerization incurs higher raw material costs because normal butenes have a high alternative value as alkylation feedstock. Dehydrogenation technology uses less costly normal butanes as raw material, but is a highly capital-intensive process.

### TAME Economics

TAME, a high octane, low vapor pressure oxygenate, is becoming the second fastest growing oxygenate behind MTBE. Under the forthcoming complex model for RFG, amlenes will probably be restricted in the gasoline pool because of their high Reid vapor pressure (RVP) and high atmospheric reactivity. Factors for TAME's rapid growth are:

1. It removes light olefins in gasoline, which may be limited in RFG because of the high ozone formation tendency.
2. It provides an additional source of oxygenate without competing for isobutene.
3. The alternative for light olefins removed is  $C_3$  alkylation, which is less attractive [alkylation of  $C_3$ s increases acid consumption, and the slight octane improvement (90 versus 87  $(R+M)/2$ ), does not justify the additional processing cost].

Both as an oxygenate and as an octane enhancer, TAME's economics are attractive. TAME's product value is estimated to be 75¢/gal and 81¢/gal, based on isoamylene value use as an alkylation unit feed and a gasoline blending component, respectively. The product value of TAME is competitive with that for MTBE if isoamylene is valued as the alkylation feedstock—the more likely scenario for the future.

### ETBE Economics

Interest in ETBE has increased since the U.S. Treasury Department approved a 54¢/gal tax credit for ethanol used to produce ETBE. A similar tax credit is already allowed for ethanol used directly in gasoline blending. ETBE is preferred over ethanol as a blending component because it has a low vapor pressure (4 versus 19 psi). The tax credit extension makes production of ETBE more competitive with MTBE.

ETBE competitiveness hinges on the cost of ethanol. Currently, ETBE economics can be evaluated on the basis of three ethanol costs. Figure 3 illustrates that the product values of ETBE are estimated to be 83¢/gal for a 54¢/gal federal and state subsidy, \$1.03/gal for a 20¢/gal state subsidy only, and \$1.11/gal with no subsidy. ETBE is competitive with MTBE production from by-product derived isobutene only if ethanol continues to receive both federal and state subsidies. The subsidies make refinery operations dependent on government policy because the differential between methanol and grain-derived ethanol is unlikely to decrease substantially in the near future.

### DIPE Economics

One of DIPE's main attractions is that it is a totally refinery-based oxygenate process. Although inexpensive water provides the source of oxygen for DIPE, propylene is a relatively high valued raw material. In addition to its value as fuel products (e.g., LPG or feed to an alkylation unit), purified polymer grade propylene is an important commodity in the basic petrochemical industry. We estimate 308,000 b/d of

propylene is produced by FCC units in the U.S. refineries. Of this quantity, 48% is used in motor fuel either as alkylate or as polymer gasoline, 45% is used as chemical feedstock, and 8% is used in liquefied petroleum gas (LPG).

Figure 3 shows that DIPE economics are sensitive to propylene feedstock cost. DIPE product value varies from 74¢/gal, \$1.09/gal, and \$1.11/gal for propylene valued as fuel, alkylate feedstock, and polymer grade product, respectively. Our valuations indicate that DIPE is not competitive with MTBE in the United States where propylene is unlikely to be valued as fuel.

#### CONCLUSION

Before November 1, 1992, MTBE was used mainly as an octane enhancer for gasoline. Historical MTBE prices have been consistent with its octane blending value. This relationship existed because refiners could always choose between using MTBE or changing their operations to increase the octane of their gasoline pools. MTBE's oxygen value is unclear at this time, even though the United States has already gone through one winter with mandatory oxygenated fuel. Stockpiling before the 1992-1993 winter season and low gasoline prices combined to cause the MTBE price to collapse. The average 1993 MTBE price—between 70¢/gal and 75¢/gal—is below its octane value.

Figure 4 shows the values of various gasoline blending components as a function of their octane number. The economic risks of MTBE (by-product derived isobutene) and TAME are somewhat reduced because they can always be blended into the gasoline pool at their octane value. However, a price premium for oxygen content is required to justify the building of MTBE plants based on either normal butene isomerization or dehydrogenation technologies, and DIPE. ETBE economics are precarious because the federal subsidy for ethanol will expire in 2002. The continuation of subsidies depends strongly on corn state lobbying and the U.S. budget deficit.

#### LITERATURE CITED

- (1) *U.S. Petroleum Refining: Meeting Requirements For Cleaner Fuels And Refineries*, National Petroleum Council, August 1993.
- (2) P.R. Wilkes, "MTBE Plant financing Requires Effective Risk Management," *Fuel Reformulation*, July/August 1992, pp. 19-23.
- (3) "NPRAs Reports on MTBE Utilization and Capacity; 22 U.S. Plants Report," *Hydrocarbon Processing*, July 1991, p. 33.

Process Name	Developer	Licensor
Skeletal Isomerization	Lyondell	CDTech
SKIP	Phillips/Texas Olefins	Phillips
ISOFIN	BP and Mobil	Kellogg
Butesom	UOP	UOP
ISO-4	IFP	IFP
SISP-4	Snamprogetti	Snamprogetti

	SKIP	Skeletal Isomerization	ISOFIN	SISP-4	Equilibrium
Temperature, °C	480-550	370-440	350-430	450-490	350-520
Conversion, %	35	44	55-50	40-30	55-40
Selectivity, %	85-90	90	85-90	88-92	

Table 3 BLENDING PROPERTIES OF OXYGENATES						
	Ethers				Alcohols	
	MTBE	ETBE	TAME	DIPE	Methanol	Ethanol
Bolling point, °C	55.2	71.7	86.1	68	65	78
Density at 20° C, g/cm <sup>3</sup>	0.74	0.75	0.77	0.73	0.79	0.79
Molecular weight	88	102	102	102	32	46
Oxygen content, wt%	18.2	15.7	15.7	15.7	50	35
Heat of combustion, cal/g	8,940	9,440	8,408	8,100	5,423	7,094
Octanes						
Blending RON	118	119	112	110	126	129
Blending MON	102	103	99	97	101	101
Blending (R + M)/2	110	111	105.5	103	115	114
Blending RVP, psi	8	3.5	1	5.0	60	18
Maximum concentration, vol%	15	13	12	—	5	5

Figure 1  
IMPROVEMENT IN GASOLINE OCTANE, 1910-1990

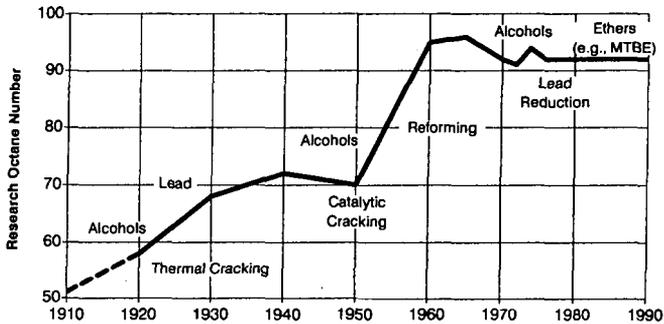


Figure 2  
WORLDWIDE MTBE PRODUCTION BY ISOBUTENE SOURCE

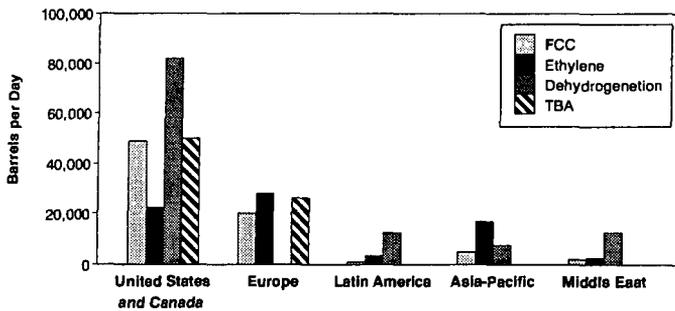


Figure 3  
OXYGENATE PRODUCT VALUES: U.S. GULF COAST, 1993

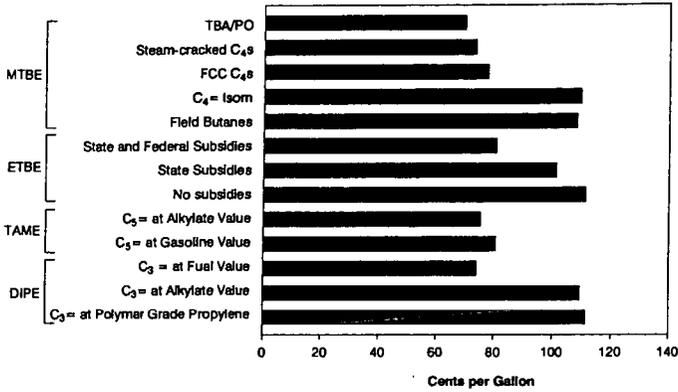
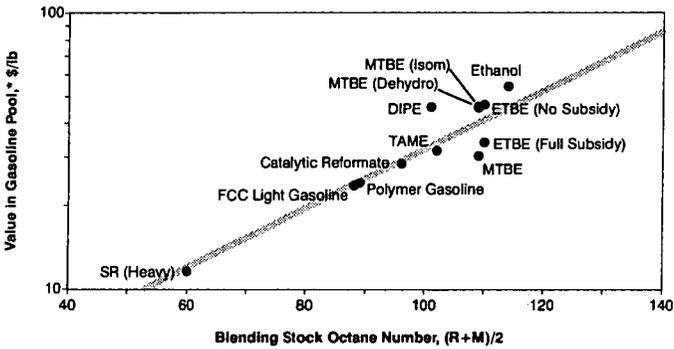


Figure 4  
VALUE OF GASOLINE POOL COMPONENTS AS A FUNCTION OF OCTANE NUMBER, 1993



\* Based on regular unleaded gasoline price of \$23.10/barrel.

GASOLINE RANGE ETHER SYNTHESIS FROM LIGHT NAPHTHA PRODUCTS OF  
FLUID CATALYTIC CRACKING OF FISCHER-TROPSCH WAX.

W. J. Reagan  
Amoco Oil Company  
Naperville, Illinois 60566

Keywords: Fischer-Tropsch wax, Fluid Catalytic Cracking, Ether Synthesis.

The Fluid Catalytic Cracking of Fischer-Tropsch wax ( $C_{20}^+$  paraffins) produces two to four times the concentration of reactive iso-olefins (isobutylene, isoamylenes, isohexenes) than observed from conventional gas oil feedstocks. Methanol reacts with these olefins to form the corresponding tertiary alkyl methyl ethers: MTBE, TAME and MTHE's. These etherification reactions are mildly exothermic and equilibrium limited. The reaction temperature and the olefin molecular structure are important variables for maximum ether yields. The base naphtha research octane number increases by 2-4 numbers after the etherification reaction. The presence of hydrogen has a detrimental effect on ether yields because of hydrogenation of reactive olefins to paraffins. The catalytic cracking of Fischer-Tropsch wax provides a non-conventional source of olefins for ether synthesis that can supplement existing and dwindling petroleum supplies.

#### INTRODUCTION

Fischer-Tropsch (F-T) synthesis technology (1) produces liquid hydrocarbons from synthesis gas (hydrogen and carbon monoxide) derived from the gasification of coal or reforming of natural gas. The F-T liquid product consists of a broad range of normal paraffins ( $C_3$ - $C_{30}^+$ ) and a small quantity of oxygenates and olefins. The distillate fraction,  $C_{12}$ - $C_{18}$ , is an excellent quality fuel. The largest product fraction,  $C_{18}^+$ , is primarily wax and is useless as a transportation fuel. These products are further treated by conventional petroleum processes, such as hydrotreating, reforming and catalytic cracking to produce conventional gasoline and distillate fuels. (2) Fluid catalytic cracking and hydrocracking studies have been reported by Mobil (3) and UOP. (4) Heavy wax ( $C_{20}^+$ ) fractions have also been treated with hydroisomerization and hydrocracking processes at Exxon. (5) Hydrodewaxing and catalytic cracking treatments of heavy wax from slurry F-T processing are also reported by Mobil. (6) In addition, pure component cracking studies (decanol, decanal) over the intermediate - pore zeolite HZSM-5 have been reported. (7) The catalytic cracking of F-T liquids was examined in some detail by Wojciechowski over large-pore Faujasite (zeolite Y) and over HZSM-5 zeolite catalysts. (8,9) Governmental regulations, most recently in the Clean Air Act Amendments of November, 1990, have resulted in the phase-out of lead additives, lowering of the Reid vapor pressure of gasoline and in some geographical areas, the mandated use of oxygenates. Several types of ethers are now commercially produced and used as gasoline blending components. (10) Recent studies of methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME) suggest that these compounds may reduce automotive carbon monoxide emissions, have high blending gasoline octane ratings, R+M/2, (MTBE=108, TAME=102) and have low Reid vapor pressure. These ethers are produced commercially by the etherification of the appropriate olefin by methanol (MTBE, isobutylene; TAME, isoamylenes). (11,12) There is less information in the open literature about the etherification reactions of  $C_6$  olefins that are also present in significant quantities in fluid catalytic cracking product naphthas. The Etherol process (13) produces a mixed ether product from  $C_6$ - $C_7$  reactive iso-olefins in naphthas. One report (14) provides some information about the reaction of  $C_6$  iso-olefins with methanol to produce the higher ethers, MTHE's, methyl tertiary hexyl ethers. MTBE has attracted the most attention in recent years. The growth rate for its production could reach 25% per year by 1995. (15,16) There is a growing need for alternative sources of olefins for ether syntheses as demand for these materials escalates beyond the capacity of conventional petroleum processes. There are no reported studies of the catalytic cracking processing of F-T liquids to produce  $C_3$ - $C_6$  olefins as feedstocks for the synthesis of gasoline range ethers.

#### EXPERIMENTAL.

The feedstock for this work is a sample of reactor wax from a commercial fixed bed F-T unit operated by Sasol, Limited. The analytical characterization of this feedstock is available in other studies. (4) The small scale (1 gram of feed, 3-5 grams of catalyst) catalytic cracking tests were performed on a Micro Activity Test unit (MAT) similar in design to the unit described in ASTM procedure, D3907-86. This test unit is equipped for detailed analyses of gas and liquid products and coke yields. The pilot plant tests were conducted in a circulating catalyst unit similar to a design described by ARCO. This unit operates with 2 to 3 kilograms of

catalyst and feed rates of 10-30 grams/minute. The ether synthesis experiments were carried out in a conventional high pressure micro-reactor. Three FCC catalysts, containing zeolite Y, zeolite Beta and zeolite HZSM-5 are the primary catalysts for the FCC studies. The Y zeolite catalyst is an Ultrastable Y faujasite (USY) zeolite catalyst taken from one of Amoco's commercial FCC units. The HZSM-5 catalyst is a commercial sample produced by Intercat Corp. The Beta sample was prepared in our laboratory by spray drying a commercially available Beta zeolite and a conventional silica-alumina matrix. Two commercial ion exchange resin catalysts, Rohm and Haas's Amberlyst 15 and Bayer's K 2634, were used in the ether synthesis runs.

## RESULTS AND DISCUSSION.

### A. Catalytic Cracking Tests.

Initial catalytic cracking runs with the small scale test system provide some insights into the catalytic cracking behavior of the wax feedstock. The initial choice of fluid catalytic cracking (FCC) catalyst and process conditions focuses on comparisons with conventional gas oil, the usual feedstock to commercial FCC units. At these conditions, (970°F reaction temperature, 3 catalyst to oil weight ratio), the wax feedstock readily converts (85%+ conversion) to high yields of C<sub>4</sub>- gas (high in propylene and C<sub>4</sub> olefins) and naphtha (C<sub>5</sub>-430°F). A summary of this comparison is presented in Table I. The conversion level is defined by convention as the sum of the products: naphtha, gas and coke. This high catalytic cracking conversion level for the wax feedstock agrees with the published Mobil data (3,6) on F-T wax cracking. In addition, historical pure component hydrocarbon cracking studies (17) suggest that long chain paraffins crack at much greater rates than the shorter chain paraffins. The low coke yield of the wax feedstock will be an important parameter when commercial heat balanced operations are evaluated. The relatively low octane number of the wax product naphtha results from the higher concentrations of low octane number paraffins compared to the gasoline from the more aromatic gas oil feedstocks. The octane numbers in the Table I are estimated results from detailed naphtha analyses by gas chromatography and correlations with octane engine tests. The target of these studies is to optimize the yields of branched olefin intermediates (isobutylene and isoamylenes) for ether synthesis. Three FCC catalysts, containing zeolite Y, zeolite Beta, and zeolite HZSM-5, were tested for wax conversion and product selectivity as a series of blends with an inert solid. Table II presents the detailed product distributions for the three catalysts at a similar conversion level of about 83%. Both the Beta and HZSM-5 catalysts produce much higher yields of the desirable olefins. However, this occurs at the expense of naphtha product. In addition, the HZSM-5 catalyst produces very high yields of propylene. These screening test results show that FCC catalyst variations can provide for widely different product distributions.

### B. Pilot Plant Catalytic Cracking Tests.

Some initial wax catalytic cracking screening tests on the pilot plant unit are presented in Table III. The high conversions of the wax feedstock in the pilot plant agree with the small scale test results. The Beta zeolite catalyst converts a greater fraction of the wax feedstock to light olefins, including propylene, isobutylene and isoamylenes, than the Y zeolite catalyst. The higher olefin yields are offset by a significantly lower naphtha yield for the Beta zeolite catalyst compared to the standard Y zeolite catalyst. The test results for the HZSM-5 catalyst mixture are similar to the Beta zeolite. High yields of the target light olefins are produced but the naphtha yield is much lower than the Y zeolite catalyst. This trade-off of light olefin and naphtha yields can be adjusted by the amount of the HZSM-5 additive. The total liquid products from several pilot plant catalytic cracking runs were combined and distilled (ASTM Method D-2892) to produce light naphtha (<200°F) fractions for the etherification studies.

### C. Ether Synthesis.

Since the reaction of isobutylene and methanol to form MTBE is well known, this study will focus on the production of TAME and MTHE ethers from the light naphtha products of the pilot plant wax cracking studies. A small, fixed bed unit was used for these etherification studies. The initial test runs involve the reaction of 2-Methyl-2-butene with methanol to produce TAME. Table IV shows the comparison of TAME yields (conversion of isoamylenes to TAME: moles TAME out/moles isoamylenes in\*100). The test conditions are: variable temperatures, 200 PSIG unit pressure, 0.66 WHSV (olefin) and 1.2 mole ratio of methanol/olefin. The catalyst for these runs is Amberlyst 15, a commercial etherification catalyst. The reaction temperature is a major factor in this etherification reaction. The sharp

rise in TAME yield at 150°F and the decline at 200°F suggests that equilibrium limitations exist at these temperatures and reaction conditions. The maximum yields of ethers will occur at these equilibrium conditions. Table V presents the detailed composition of the light naphtha samples from the pilot plant wax catalytic cracking runs. The iso-olefin contents of the samples, feeds "B" and "C", are higher from the pilot plant wax catalytic cracking runs than the light naphtha sample, feed "A". This is due to the use of high olefin selective FCC catalysts, Beta and HZSM-5, in the pilot plant runs, Nos. 940-01,02 and 941-01. The same Y zeolite catalyst was used in the runs for feed "A" and "C". The high iso-olefin content of feed "C" results from the lower conversion level. The reactive isoamylenes, 2-Methyl-2-butene and 2-Methyl-1-butene for TAME synthesis and the reactive C<sub>6</sub> iso-olefins, 2-Methyl-1-pentene, 2-Methyl-2-pentene, 2,3-Dimethyl-1-butene, and cis and trans 3-Methyl-2-pentene for MTHE synthesis are the important components. This light naphtha, feed "A" sample and methanol are the feedstock for a series of etherification runs at the same process conditions for the 2-Methyl-2-butene/methanol tests. Due to the limited availability of the naphtha, only two reaction temperatures are available. A summary of the conversion of the various C<sub>5</sub> and C<sub>6</sub> iso-olefins to their respective methyl ethers, Table VI, shows that reaction temperature is a major factor in the etherification reaction. The decrease in conversion with the increase in the carbon number of the iso-olefin agrees with other literature etherification studies. (18,20) The reaction products from these runs have a significant yellow color, especially at the higher reaction temperature of 150°F. This color is not present for the pure component 2-Methyl butene-2 tests. It is likely that polymerization of olefins to C<sub>10</sub>+ hydrocarbon "color bodies" is responsible for the colored product. The color of the ether product could be a significant product quality issue. Table VII presents the results of the etherification runs with the "B" and "C" light naphthas at 150°F. In these runs, both Amberlyst 15 and another commercial etherification catalyst, Bayer's K2634 are under study. The Bayer catalyst contains a noble metal in addition to the strong acid functionality. The noble metal is available for olefin isomerization and diolefin saturation, in the presence of hydrogen. The nominal reaction conditions from the previous set of runs, 200 PSIG, 2.9 grams of catalyst, methanol 1.37 g/hr, naphtha, 5.5 g/hr are the same except that only one reaction temperature, 150°F, is available. The iso-olefin conversion results are similar for both catalysts and the three feedstocks, in the absence of hydrogen gas in the reactor. The calculated research octane values for the products of these etherification runs are 2-4 numbers higher than the starting light naphtha feedstocks, Table VIII. As expected, this octane increase depends to some extent upon the concentrations of the ethers in the product. Blending octane numbers for the mixed ether light naphtha fractions are also shown in Table VIII. There is a fair agreement with the calculated (by GC) octane numbers. When hydrogen gas is present, Run No. 034-1, Table VIII, there is a major loss of iso-olefin conversion. These reaction conditions result in the hydrogenation of both reactive iso-olefins and linear olefins. This is an undesirable result since both the production of ethers and the octane number of the product decreases significantly. The run with added hydrogen gas, 034-1, has a lower research octane rating (79.5) than the feedstock (84.6) or the run with no added hydrogen, 034-3, (85.8). This octane loss is due to the conversion of high octane value olefins to low octane value paraffins. There is a significant improvement in the color of the etherification products in the presence of hydrogen gas.

These etherification runs clearly demonstrate that the light naphtha fractions from the catalytic cracking of Fischer-Tropsch wax are excellent ether synthesis feedstocks.

#### ACKNOWLEDGEMENT.

This work was supported by the U. S. Department of Energy, Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania under Contract No. DE-AC22-91PC90057. D. Kovach and R. Brown performed the experimental work. J. Newbury provided the GC naphtha analyses.

#### REFERENCES

1. Anderson, R. B. The Fischer-Tropsch Synthesis; Academic (New York), 1984.
2. Stuart, J. S., et al. Oil & Gas Journal, August 31, 1981, 62.
3. Kuo, J. C. W., et al. 1988 AIChE Annual Meeting (Washington, DC, 11/17/88, Preprint No. 61D); 1984 AIChE Annual Meeting (Anaheim, California, Preprint No. 11D); Department of Energy, Final Report, October, 1985, DOE/PC/60019-9A.
4. Shah, P. P., et al. "F-T Wax Characterization and Upgrading"; Final Report, Department of Energy, June 6, 1988, DOE/PC/80017-T1.
5. Exxon R&E Company, U.S. 4,832,819, May 23, 1989.

6. Mobil Oil Company, U.S. 4,684,756, August 4, 1987.
7. Riley, M.; Anthony, R. G. J. Catal., 103, 87-94, 1987.
8. Abbot, J.; Wojciechowski, B. W. Ind. Eng. Chem. Prod. Res. Dev. 1985, 24, 501-507.
9. Kobolakis, I.; Wojciechowski, B. W. Can. J. Chem. Eng., 63, April 1985, 269-277.
10. Piel, W. J. Energy Progress, 8, No. 4, 201, 1988; Oil & Gas J., December 4, 1989, 40.
11. Reychler, A. Bull. Soc. Chim. Belg.; 21, 71 (1907).
12. Ancillotti, F., et al., J. Catalysis; 46, 49-57 (1977).
13. Halsig, C. P., et al., NPRA, 1986 Annual Meeting, Paper AM-86-94.
14. Krause, A. O. I., et al., 8th Int. Cong. Catal., 5, 553, 1984.
15. Oil & Gas J., January 27, 1992, 21.
16. Oil & Gas J., November 30, 1992, 48.
17. Gorra, A.; Wojciechowski, B. W. Catal. Rev.-Sci. Eng., 27(1), 29-150, 1985

TABLE I

**INITIAL COMPARISONS OF FISCHER-TROPSCH MAX CRACKING AND CONVENTIONAL GAS OIL FEEDSTOCKS**

MAT Test Results: 970°F, 3 C/O, Equilibrium Catalyst  
Product Distribution and Product Properties

	Gas Oil	Max
Conversion, wt%	61.6	88.1
<b>Products, wt%:</b>		
C <sub>1</sub>	2.6	1.8
C <sub>2</sub> + C <sub>3</sub>	11.6	31.4
C <sub>4</sub>	6.9	15.9
C <sub>5</sub> - 430°F	36.2	36.8
430°F+	38.4	11.9
Coke	4.3	2.2
Isobutylene	1.3	4.5
Isoamylenes	2.3	5.8
Naphtha, RON	90.4	85.8
MON	79.8	77.6

TABLE II

**MAT TEST RESULTS--CATALYST COMPARISONS AT 880°F**

Catalyst Type	Zeolite T	Zeolite Beta	Zeolite HZSM-5
Run No.	031	042	055
Conversion, wt%	83.0	83.3	83.8
<b>Product Yields, wt%:</b>			
C <sub>1</sub>	0.6	0.6	1.5
C <sub>2</sub>	7.4	8.9	17.5
C <sub>3</sub>	0.8	0.9	2.7
C <sub>4</sub>	13.2	17.7	27.4
C <sub>5</sub>	3.7	3.6	3.6
C <sub>6</sub>	11.7	13.5	13.9
C <sub>7</sub>	3.6	2.2	2.0
C <sub>8</sub> - 430°F	41.7	35.8	15.3
430°F+	17.0	16.8	16.2
Coke	0.3	0.2	0.1
Isobutylene	5.8	9.4	12.3
Isoamylenes	7.7	9.2	9.8
C <sub>5</sub> - 430°F	57.0	51.4	31.1
RON	85.2	84.4	84.4
MON	76.2	74.6	76.0

TABLE III  
PILOT PLANT RUNS

RUN NO.	939-05	940-2	941-1
Reaction Temp., °F	879	910	965
C/O Ratio	2.25	3.35	2.84
WHSV (hr <sup>-1</sup> )	42.2	61.5	54.61
Catalyst	Steamed eq. USY	Steamed Beta	Steamed eq. USY (75%)/HZSM-5 (25%)
Conversion, wt%	85.0	96.5	89.0
Product Yields, wt%:			
C <sub>2</sub>	0.51	0.66	1.22
C <sub>2</sub> <sup>n</sup>	6.28	13.68	16.03
C <sub>3</sub>	0.90	1.81	2.47
iC <sub>3</sub>	3.40	7.66	3.40
nC <sub>3</sub>	0.99	2.09	1.92
iC <sub>3</sub> <sup>n</sup>	6.75	12.99	12.95
tC <sub>3</sub> <sup>n</sup>	3.19	5.44	5.33
cC <sub>3</sub> <sup>n</sup>	2.31	3.98	3.76
iC <sub>4</sub>	3.35	3.73	2.16
nC <sub>4</sub>	0.96	1.51	1.40
Total C <sub>3</sub> <sup>n</sup>	10.54	10.24	12.47
C <sub>7</sub> -430°F	46.08	31.53	24.81
430°F+	14.06	3.67	11.60
Coke	0.68	1.00	0.47

TABLE IV  
TAME PRODUCTION  
Methanol/2-Methyl-2-butene feedstock

Reaction Temperature, °F	TAME YIELD <sup>a</sup>
125	50
150	80
200	59

<sup>a</sup>TAME YIELD = moles TAME out/moles isoamylenes in \* 100.

TABLE V  
HYDROCARBON COMPOSITION OF 200°F NAPHTHAS

Feed ID:	92-0490-01A Feed A <sup>a</sup>	93-0024-01A Feed B	93-0024-01C Feed C
Pilot Plant Run Nos.	939-01, + 02 eq. USY catalyst conversion = 93.6%	940-01, 02 941-01 Beta/HZSM-5 catalyst Conversions = 90, 96%	939-04 eq. USY catalyst conversion = 83%
Total Paraffins wt%	6.69	8.44	4.32
Total Iso-paraffins wt%	42.71	17.64	22.88
Total Aromatics wt%	1.74	2.62	0.35
Total Naphthenes wt%	3.96	5.55	3.16
Total Olefins wt%	44.51	64.47	68.6
Reactive iso-olefins wt%			
C5's			
2-methyl-1-butene	1.25	2.15	1.76
2-methyl-2-butene	4.26	5.67	5.64
C6's			
2,3-dimethylbutene	0.8	0.73	0.97
2-methyl-1-pentene	2.35	2.49	3.02
2-methyl-2-pentene	4.01	5.27	5.46
3-methyl-trans-2-pentene	2.49	3.13	3.29
3-methyl-vis-2-pentene	3.98	5.48	5.35

TABLE VI  
**REACTIVE ISO-OLEFINS CONVERSION TO ETHERS**  
 Reaction Temperature (Averages of Three Weight Balance Tests)

Feed A		
Iso-olefin Component	125°F	150°F
	wt%	wt%
C5		
2-Methyl-1-butene	85.4	89.9
2-Methyl-2-butene	29.9	65.5
C6		
2,3-Dimethyl-1-butene	56.5	83.4
2-Methyl-1-pentene	65.9	87.5
2-Methyl-2-pentene	20.7	48.6
3-Methyl-cis-2-pentene	21.7	38.6
3-Methyl-trans-2-pentene	20.8	29.8

TABLE VII  
**REACTIVE ISO-OLEFINS CONVERSION TO ETHERS**

	Feed A	Feed B				Feed C	
200°F- Naphtha	92-049-01A	92-0024-01A				93-0024-01C	
Reaction Temp, °F	150	150	150	150	150	150	
Catalyst	Amberlyst 15	Amberlyst 15	K2634	K2634	K2634	K2634	
			No H2	H2	H2	No H2	
<i>iso-olefin component</i>							
C5's							
2-Methyl-1-butene	89.9	90.2	87.1	77.2	78.1	87.7	
2-Methyl-2-butene	65.5	62.2	66.2	42.9	38.2	61.2	
C6's							
2,3,0imethyl-1-butene	83.4	---	---	---	---	---	
2-Methyl-1-pentene	87.5	85.5	84.1	72.2	78.6	86.9	
2-Methyl-2-pentene	48.6	56.1	62.7	44.2	31.5	51.5	
3-Methyl-cis-2-pentene	38.6	31.0	43.4	23.8	7.3	25.8	
3-Methyl-trans-2-pentene	29.8	32.2	43.7	25.9	20.7	33.3	

TABLE VIII  
**LIGHT NAPHTHA ETHERIFICATION RUNS HYDROCARBON COMPOSITION OF FEED AND PRODUCTS**

Run No.	Reaction Temp	Catalyst	Research Octane Number*	Blending Research Octane Number
<b>Feed A</b>				
92-0490-01A	---	---	80.92	66.9
15586-024-2	125°F	Amberlyst 15	80.09	77.9
15586-024-6	150°F	Amberlyst 15	83.76	79.9
15586-024-8	150°F	Amberlyst 15	83.88	---
<b>Feed B</b>				
93-0024-01A	---	---	83.12	83.9
15586-031-2	150°F	Amberlyst 15	87.43	87.9
05586-033-1	150°F	Bayer K2634	87.48	85.9
15586-033-3	150°F	Bayer K2634	85.78	84.9
<b>Feed C</b>				
93-0024-01C	---	---	84.56	95.9
15586-034-1	150°F	Bayer H2 K2634	79.47	88.9
15586-034-3	150°F	Kayer no H2 K2634	85.78	95.9

\*Calculated

TABLE VIII  
**LIGHT NAPHTHA ETHERIFICATION RUNS HYDROCARBON COMPOSITION OF FEED AND PRODUCTS**  
 (Continued)

Run No.	Paraffins	Iso-paraffins	Aromatics	Naphthenes	Olefins	Oxygenates	Unknowns
<b>Feed A</b>							
92-0490-01A	6.689	42.712	1.736	3.956	44.507	0.071	0.33
15586-024-2	7.804	40.230	1.995	4.474	33.762	11.406	0.34
15586-024-6	6.463	40.429	2.247	4.574	29.671	16.296	0.32
15586-024-8	6.337	40.466	2.263	4.586	29.58	16.436	0.33
<b>Feed B</b>							
93-0024-01A	8.437	17.637	2.623	5.349	64.472	0.17	1.11
15586-031-2	7.417	17.989	3.687	6.424	41.847	21.815	0.821
05586-033-1	7.381	17.340	3.691	6.583	41.716	22.445	0.844
15586-033-3	8.205	17.668	3.62	6.512	45.889	17.277	0.83
<b>Feed C</b>							
93-0024-01C	4.315	22.881	0.353	3.161	68.651	0.15	0.49
15586-034-1	14.535	24.733	2.405	5.436	35.369	17.382	0.19
15586-034-3	5.921	22.489	1.977	4.497	43.51	21.192	0.415

\*Calculated

## SYNTHESIS OF OXYGENATES FROM H<sub>2</sub>/CO SYNTHESIS GAS AND USE AS FUEL ADDITIVES

Richard G. Herman, Kamil Klier, Owen C. Feeley, and Marie A. Johansson  
Zettlemoyer Center for Surface Studies and Department of Chemistry,  
7 Asa Drive, Lehigh University, Bethlehem, PA 18015.

Keywords: Oxygenates, Synthesis Gas, Ethers, MTBE, Alcohols

### ABSTRACT

Alternative processes for synthesizing fuel-grade oxygenates are centered on conversion of synthesis gas into C<sub>1</sub>-C<sub>3</sub> alcohols and ethers. Over Cs/Cu/ZnO-based catalysts, mixtures of methanol/ isobutanol are predominantly formed. It has been found that these alcohols can be directly coupled over certain strong acid organic-based catalysts to form unsymmetric C<sub>4</sub> ethers, mainly the kinetically favored methyl isobutyl ether (MIBE) with some of the thermodynamically favored methyl tertiarybutyl ether (MTBE), the symmetric ethers of dimethylether (DME) and diisobutylether (DIBE), or selectively dehydrated to form isobutene over sulfated zirconia. Based on these reactions, a 2-stage, dual catalyst configuration can be utilized to give MTBE as the dominant ether product. The octane numbers and cetane ratings of the oxygenates have been determined and are compared, e.g. adding 10 vol% MIBE and MTBE to 82.3 MON gasoline altered the MON of the gasoline by -1.5 and +1.4 units, respectively, and MIBE has a high cetane number of 53, compared to 42 for typical U.S. diesel fuel.

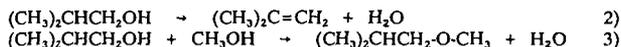
### INTRODUCTION

Beginning in the 1970s, environmental concerns led to a phasing out of lead in gasoline, and recent legislative requirements are inducing the lowering of aromatics and light (high vapor pressure) hydrocarbons in reformulated gasoline. To maintain the required octane level of gasoline and to provide environmental benefits, oxygenate additions, either as alcohols or ethers, to gasoline have been steadily increasing. At the present time, the preferred oxygenate is methyl tertiarybutyl ether (MTBE) because it compensates for the loss in octane number caused by a reduction in aromatics, reduces the vapor pressure of the gasoline fuel, and provides some reduction in vehicle tailpipe hydrocarbon and carbon monoxide emissions [1]. Currently, MTBE is manufactured from methanol and isobutene *via* a liquid phase synthesis over acid resin catalysts, as represented by Equation 1, where isobutene is usually obtained as a side product from petroleum refinery FCC units [2-4]. Although older FCC units can produce 8 wt% C<sub>4</sub> products in their output [5], the typical FCC refinery product slate now contains 1.4 wt% C<sub>4</sub> compounds [6], and improved processes utilizing catalytic additives such as improved ZSM-5 tend to decrease the yield of C<sub>3</sub> and C<sub>4</sub> olefins in the light ends further still [7]. Thermal cracking of the isobutane in the light ends can also be carried out to obtain isobutene [6]. Although cracking processes are being modified to yield more C<sub>4</sub> as a by-product, the availability of refinery supplied isobutene is limited.



Alternative feedstocks and processes not directly dependent on isobutene for the synthesis of oxygenates are highly desirable, and new catalysts and catalytic processes are being investigated and developed. One of the alternative processes that have been developed for the synthesis of pure isobutene is the endothermic dehydration of tertiary butanol [8]. Another possible source of isobutene for ether synthesis is dehydration of isobutanol, represented by Equation 2, that is produced from synthesis gas. An overall scheme of using coal as the initial resource involves gasification of the coal to synthesis gas, purification (and water gas shifting if necessary) of the synthesis gas, higher alcohol synthesis, and direct synthesis of ethers from the alcohols. Both the

alcohols and ethers can be used as fuels and fuel additives as desired. Methanol and isobutanol are the predominant products formed from  $H_2/CO$  synthesis gas over alkali-promoted  $Cu/ZnO$ -based catalysts [9-14], as well as over non-copper-containing high temperature alkali-promoted alcohol synthesis catalysts [15,16]. Since the two alcohols are produced together, direct coupling of these two alcohols to produce fuel-grade ethers is also of interest. It has been shown [17,18] that over acid resin catalysts, the dominant reaction is direct coupling that results in the formation of methyl isobutyl ether (MIBE), Equation 3. However, if a selective catalyst were found for converting isobutanol to isobutene (even as a transient intermediate) with subsequent reaction with methanol (Reaction 2 followed by Reaction 1), a desirable route to high octane MTBE from natural gas or coal-derived synthesis gas would be provided [19]. Such a process would alleviate isobutene dependence on petroleum feedstocks.



## EXPERIMENTAL

A variety of organic resin catalysts and inorganic oxide and zeolite catalysts have been probed for alcohol conversion reactions [20,21], and the catalysts investigated in the current study consisted of Amberlyst-15 (used as received) and sulfated zirconia. The sulfate-modified zirconia ( $SO_4^{2-}/ZrO_2$ ) was prepared as described by Hino and Arata [22]. Zirconium chloride octahydrate ( $ZrOCl_2 \cdot 8H_2O$ ) was added to aqueous ammonia to precipitate high surface area  $Zr(OH)_4$ , that was washed and then dried at  $100^\circ C$  overnight. The dried  $Zr(OH)_4$ , e.g. weighing  $\approx 10$  g, was placed on a folded filter paper, and 150 ml of 1 N  $H_2SO_4$  was poured through it. The wet powder was dried at  $110^\circ C$  overnight and then calcined in air at  $620^\circ C$  for 3 hr. The BET surface area of this catalyst was found to be  $60$   $m^2/g$  and the sulfur content was 0.84% by weight.

The catalysts were tested for ether synthesis from binary methanol/isobutanol (2-methyl-1-propanol) reactant mixtures in the vapor phase in a downflow stainless steel bench-scale reactor system that is automated so that testing can be carried out under continuous operation at designed experimental conditions. A schematic of the reaction system was shown previously [19]. Typically,  $N_2/He$  gas was utilized as the carrier/inlet gas, and the alcohol mixture was added at the top of the reactor via a high pressure Gilson pump or an ISCO piston pump provided by Air Products and Chemicals, Inc. The conversion and product composition was monitored by *continual sampling*, e.g. 0.5 hr, of the exit stream by GC analysis using in-line, heated, automated Valco sampling valves and by collection of the liquid product for analyses by GC, NMR, and GC/MS.

The dedicated Hewlett-Packard Model 5890 Series II gas chromatograph (GC) with a capillary column (25 m x 0.32 mm ID wall coated open tube (WCOT) with a chemically bound 5.0  $\mu m$  thick methyl silicon coating) is interfaced and controlled by a PC data station using chromatographic software (Chrom Perfect) from Justice Innovations, Inc. At the same time, the GC is interfaced with a Hewlett-Packard Model 3396 Series II recorder/integrator, which can also produce a hardcopy of each chromatogram and listing of the associated integrated peak areas.

All of the catalytic tests reported here were carried out at 1 atm. According to our standard procedure, the catalysts were diluted with 0.5 or 3 mm Pyrex beads to a total volume of 20 ml. The catalyst bed was centered in the stainless steel reactor between two glasswool plugs. The remainder of the reactor volume was filled with 3 mm Pyrex beads that served to preheat and mix the entering gas, as well as minimizing dead volume in the reactor. The charged reactor was brought to the reaction temperature in a flow of approximately 80% He and 20%  $N_2$ . When the temperature was stabilized, the equimolar alcohol mixture was pumped into the reactor at the preset flow. The reaction was carried out at each temperature for at least 3-6 hr. Steady state conversions of methanol and isobutanol were usually obtained within the first 1-2 hr time-on-stream.

## RESULTS AND DISCUSSION

Direct Coupling or Dehydration of Alcohols Over Amberlyst-15 and  $\text{SO}_4^{2-}/\text{ZrO}_2$ . Thermodynamic calculations of the direct coupling of methanol and isobutanol indicate that low temperatures, i.e. 50-90°C, are necessary to achieve favorable selectivity to desired products, especially MTBE and MIBE [18,19]. The upper temperature of 90°C was chosen for this study in order to maximize conversion. Low pressure, i.e. 1 atm, is utilized in these reactions in light of the findings of Nunan et al. [17,18] that indicated lower pressures favored greater isobutene formation, the precursor of MTBE. The alcohol partial pressure was chosen such that no condensation would occur within the reaction system, and this was determined empirically under reaction conditions. A summary of the experimental conditions used with the Amberlyst-15 catalyst is given below:

Catalyst weight	5.00 g (dry)	MeOH flow rate	1.72 mol/kg cat/hr
Reaction temperature	90°C	i-BuOH flow rate	1.72 mol/kg cat/hr
Total Pressure	1 atm	He + N <sub>2</sub> flow rate	16 mol/kg cat/hr.

The space time yields (STY) of the products are given in Table 1. It is seen that the molar yields of DME, butenes, and MIBE were comparable, while only 0.5% of each reactant was converted to MTBE. The entry "Butenes" includes iso-, *trans*-2-, and *cis*-2-butene with isobutene predominating (greater than 85% of the butene content).

The *sulfate-modified zirconia* catalyst (5 g) was tested under the same conditions employed with Amberlyst-15, but higher temperatures were also utilized. At 90°C, only MIBE was detected, but the yield was very low. However, at higher temperature isobutanol was selectively dehydrated to butenes in the presence of methanol. Indeed, at 175°C, the  $\text{SO}_4^{2-}/\text{ZrO}_2$  showed 95% conversion with over 80% selectivity to butenes, principally *isobutene* (Table 1). At the latter temperature, small amounts of C-8 and C-12 products (0.5 mol%) were observed. Non-sulfated zirconia was found to be totally inactive for the dehydration of either methanol or isobutanol over the temperature interval tested (90-175°C).

Dehydration of Isobutanol Only Over the  $\text{SO}_4^{2-}/\text{ZrO}_2$  Catalyst. The activity and selectivity of dehydrating isobutanol over  $\text{SO}_4^{2-}/\text{ZrO}_2$  in the absence of methanol was investigated. The  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalyst (5 g) calcined to 620°C was centered in the reactor as described previously. The reaction conditions utilized included the temperatures of 125, 135, 150, 175, 200, and 225°C and isobutanol feed rates of 1.69-20.28 mol/kg catalyst/hr while maintaining the He + N<sub>2</sub> flow = 18.78 mol/kg catalyst/hr. The isobutanol space velocity of 1.69 mol/kg cat/hr was used in an initial temperature dependence study from 125 to 175°C. At 175°C, 85% of the isobutanol was converted to butenes. Comparison to the first entry row in Table 1 indicates that absence of the methanol reactant produced only a small increase in isobutanol conversion.

At the temperature of 200°C, the isobutanol flow rate was raised sequentially to 6.76, 13.52, and 20.28 mol/kg cat/hr. A final test was performed at 225°C using 20.28 mol isobutanol/kg cat/hr. Testing was carried out for several hours at each point of temperature and space velocity. The only major products observed with the on-line GC analysis were isobutene, *trans*-2-butene, and *cis*-2-butene. Trace amounts of octenes and C<sub>8</sub> ethers were seen. At higher reaction temperatures, small amounts of methanol and other products believed to be cracking products of isobutanol were seen as was seen for isobutanol only dehydration over H-mordenite. The yields of the major products under these conditions are presented in Table 1. It can be seen that the predominant product was isobutene in each case. The highest productivity of isobutene of 11.35 mol/(kg cat. × hr) was obtained at 225°C and a flow rate of 20.28 mol isobutanol/kg cat/hr. The selectivity of isobutene among the butenes at this high productivity was 79% (12.2 mol% *trans*-2-butane and 8.7 mol% *cis*-2-butene). This production of isobutene corresponds to 1.1 kg isobutene/kg cat/hr, and therefore the dehydration of isobutanol over  $\text{SO}_4^{2-}/\text{ZrO}_2$  is a fast reaction at this temperature.

Dual Reactor Synthesis of MTBE. The concept of this experiment was to selectively dehydrate isobutanol in the reactant alcohol mixture to isobutene over one catalyst and then to couple the isobutene with methanol to form MTBE over a second catalyst. In this dual bed experiment at ambient pressure, the first catalyst bed contained 5 g of  $\text{SO}_4^{2-}/\text{ZrO}_2$ , calcined to 620°C, while the second bed contained 0.5 g of Amberlyst-15. The reactant gas flow of the methanol/isobutanol = 1/1 mixture was 1.72 mol/kg cat/hr of each alcohol with a carrier gas flow of 17.2 mol/kg cat/hr of  $\text{N}_2$  and He. The first bed was maintained at 175°C to effect the selective dehydration of isobutanol to isobutene, while the second bed consisting of the resin catalyst was kept at 90°C for the MTBE synthesis reaction. A short line of copper tubing connected the two beds and served as a heat exchanger. The space time yields of the products are given in Table 1.

In this experiment, the conversions of isobutanol and methanol corresponded to  $\approx 77$  mol% and  $\approx 20$  mol%, respectively. This productivity of MTBE is more than an order of magnitude higher than that obtained by the direct coupling of methanol and isobutanol over the Amberlyst-15 resin at 90°C. The butenes consisted of 0.90, 0.09, and 0.08 mol/kg cat/hr of isobutene, *trans*- and *cis*-2-butene, respectively. In addition, 0.03 mol *tert*-butanol/kg cat/hr was also observed. It was observed that lowering the second bed temperature to ca. 40°C (non-steady state conditions) increased the yield of MTBE to  $\approx 0.35$  mol/kg cat/hr, which principally reflected the enhanced reaction of methanol with the isobutene that is favored by lower reaction temperatures. Indeed, the decrease in the yields of "butenes" was due solely to a lower amount of isobutene ( $\approx 0.70$  mol/kg cat/hr) in the product mixture, while the *trans*- and *cis*-2-butene yields remained constant.

This experiment under unoptimized conditions shows that it is feasible to considerably increase the yield of MTBE formed from alcohols via a 2-step process, although the yield obtained under these conditions was limited by the low pressure and high temperature employed, as well as the small amount of Amberlyst-15 used as the second catalyst bed. In these experiments, water was not separated from the product stream between the beds.

Fuel Characteristics of Oxygenates. Determination of the octane numbers of MIBE and MTBE was performed by AMOCO Oil Company. The standard ASTM methods D-2699 and D-2700 were used for Research Octane Number and Motor Octane Number, respectively. Cetane determinations were carried out at the Southwest Research Institute. Octane number were determined for MIBE, MTBE, and a 50/50 by volume mixture of MIBE and MTBE. MTBE was obtained from Aldrich, while the MIBE was synthesized in-house by the Williamson ether synthesis as described previously [19]. For the purpose of octane number determination, this product was distilled under nitrogen to yield a >96% purity of MIBE, as determined by gas chromatography. The major impurity was isobutanol. The peroxide level of the ether samples was <20 ppm and was considered to be acceptable for all three samples.

The results obtained by AMOCO Oil Co. are summarized in Table 2. It can be seen that MTBE increased the research octane number by 2.8 units and the motor octane number by 1.4 units, which is in good agreement with values obtained by Spindelbaker and Schmidt [23]. MIBE, on the other hand, decreased both the research octane number and motor octane number by 3.2 and 1.5 units. The gasoline/ether mixture containing both MIBE and MTBE (5 vol% of each) had the same values as the base unleaded regular gasoline. In this case, an appreciable amount of oxygen was added to the ULR gasoline without altering its octane rating.

The blending octane numbers were calculated according to the following equation: Blending Research Number = RON (component A)  $\times$  (percent component A) + RON (component B)  $\times$  (percent component B). Table 3 lists the blending numbers for MIBE and MTBE. MTBE and MIBE are structurally not very different, but it is clear from the results presented above that MTBE is superior to MIBE for octane enhancing purposes. Comparisons of the blending octane and cetane numbers of oxygenates are given in Table 4. In this table, ETBE = ethyltertiary-

butylether, IPTBE = isopropyltertiarybutylether, DIPE = diisopropylether, and TAME = tertiary-amylnmethyl ether. Changes ( $\Delta$ ) in RON and MON were determined at 10 vol% levels of the oxygenates in gasoline. It is clear that MIBE has a poor octane number but a high cetane number.

#### ACKNOWLEDGEMENT

This research was supported in part by the U.S. Department of Energy (Pittsburgh Energy Technology Center), principally under Contract No. DE-AC22-90PC90044.

#### REFERENCES

1. "Critical Technologies: The Role of Chemistry and Chemical Engineering," National Research Council, National Academy Press, Washington, D.C., pp 22-23 (1992).
2. Chase, J. D. and Galvez, B. B., *Hydrocarbon Process.*, **60**(3), 89 (1981).
3. Chase, J. D., in "Catalytic Conversions of Synthesis Gas and Alcohols to Chemicals," ed. by R. G. Herman, Plenum Press, New York, 307 (1984).
4. *Hydrocarbon Process.*, **68**(11), 96 (1989); and Satterfield, C. N., "Heterogeneous Catalysis in Industrial Practice," 2nd Ed., McGraw-Hill, Inc., New York, 260 (1991).
5. Haggin, J., *Chem. Eng. News*, **67**(23), 31 (1989).
6. Monfils, J. L., Barendregt, S., Kapur, S. K., and Woerde, H. M., *Hydrocarbon Process.*, **71**(2), 47 (1992).
7. Krishna, A. S., Hsieh, C. R., English, A. R., Pecoraro, T. A., and Kuehler, C. W., *Hydrocarbon Process.*, **70**(11), 59 (1991).
8. Abraham, O. C. and Prescott, G. F., *Hydrocarbon Process.*, **71**(2), 51 (1992).
9. Klier, K., Herman, R. G., and Young, C.-W., *Preprints, Div. Fuel Chem., ACS*, **29**(5), 273 (1984).
10. Klier, K., Herman, R. G., Nunan, J. G., Smith, K. J., Bogdan, C. E., Young, C.-W., and Santiesteban, J. G., in "Methane Conversion," ed. by D. M. Bibby, C. D. Chang, R. F. Howe, and S. Yurchak, Elsevier, Amsterdam, 109 (1988).
11. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C.-W., and Herman, R. G., *J. Catal.*, **116**, 195 (1989).
12. Nunan, J. G., Herman, R. G., and Klier, K., *J. Catal.*, **116**, 222 (1989).
13. Herman, R. G., in "New Trends in CO Activation," ed. by L. Guzzi, Elsevier, Amsterdam, 265 (1991).
14. Herman, R. G., Klier, K., Young, C.-W., Nunan, J. G., Feeley, O. C., and Johansson, M. A., *Proc. 9th Intern. Pittsburgh Coal Conference*, 409 (1992).
15. Tronconi, E., Ferlazzo, N., Forzatti, P., and Pasquon, I., *Ind. Eng. Chem. Res.*, **26**, 2122 (1987).
16. Tronconi, E., Lietti, L., Forzatti, P., and Pasquon, I., *Appl. Catal.*, **47**, 317 (1989).
17. Nunan, J. G., Klier, K., and Herman, R. G., *J. Chem. Soc., Chem. Commun.*, 676 (1985).
18. Nunan, J. G., Klier, K., and Herman, R. G., *J. Catal.*, **139**, 406 (1993).
19. Klier, K., Herman, R. G., Bastian, R. D., DeTavernier, S., Johansson, M., Kieke, M., and Feeley, O. C., in "Proc. Liquefaction Contractors' Review Meeting"-September 1991, U.S. DOE-PETC, Pittsburgh, PA, ed. by G. J. Stiegel and R. D. Srivastava, 20-49 (1991).
20. Klier, K., Herman, R. G., Johansson, M. A., and Feeley, O. C., *Preprints, Div. Fuel Chem., ACS*, **37**(1), 236 (1992).
21. Feeley, O. C., Johansson, M. A., Herman, R. G., and Klier, K., *Preprints, Div. Fuel Chem., ACS*, **37**(4), 1817 (1992).
22. Hino, M. and Atara, K., *J. Chem. Soc., Chem. Commun.*, 851 (1980).
23. Spindelbaker, C. and Schmidt, A., *Erdoel, Erdgas, Kohle*, **102**, 469 (1986).

**TABLE 1.** Product yields (mol/kg cat/hr) over the single bed and dual bed catalysts from methanol = isobutanol = 1.72 mol/kg cat/hr reactants and from isobutanol only at different flow rates at 1 atm at the temperatures utilized in this study.

	T <sub>Reaction</sub>	DME	Butenes	MIBE	MTBE	C8 Ether
SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub>	175°C	0.10	1.29	0.05	0.01	trace
Amberlyst-15	90°C	0.04	0.04	0.05	0.01	0.01
Dual Reactor <sup>a</sup>	1. 175°C	0.06	1.07	0.06	0.16	trace <sup>b</sup>
	2. 90°C					
	2. 40°C	0.06	0.87	0.06	0.35	trace <sup>b</sup>
(SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> ) <sup>c</sup>	175°C	-----	1.44	-----	-----	trace <sup>b</sup>
(SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> ) <sup>d</sup>	200°C	-----	4.45	-----	-----	trace <sup>b</sup>
(SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> ) <sup>e</sup>	200°C	-----	6.80	-----	-----	trace <sup>b</sup>
(SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> ) <sup>f</sup>	200°C	-----	7.75	-----	-----	trace <sup>b</sup>
(SO <sub>4</sub> <sup>2-</sup> /ZrO <sub>2</sub> ) <sup>f</sup>	225°C	-----	14.37	-----	-----	trace <sup>b</sup>

<sup>a</sup>The catalyst in Reactor 1 was ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup> and in Reactor 2 was Amberlyst-15.

<sup>b</sup>Plus trace of octenes.

<sup>c</sup>The reactant consisted of isobutanol only with a flow rate of 1.69 mol/kg cat/hr.

<sup>d</sup>The reactant consisted of isobutanol only with a flow rate of 6.86 mol/kg cat/hr.

<sup>e</sup>The reactant consisted of isobutanol only with a flow rate of 13.5 mol/kg cat/hr.

<sup>f</sup>The reactant consisted of isobutanol only with a flow rate of 20.3 mol/kg cat/hr.

**TABLE 2.** Octane numbers of the ether/gasoline fuel mixtures.

Sample	Research Octane Number	Motor Octane Number	Peroxide (ppm)
Unleaded Regular Gasoline (ULR)	92.1	82.3	-
10% MTBE in ULR	94.9	83.7	14
10% (MTBE/MIBE) in ULR	92.0	82.4	6
10% MIBE in ULR	88.8	80.8	17

TABLE 3. Blending research octane number (BRON) and blending motor octane number (BMON) of MTBE and MIBE in unleaded regular gasoline.

Sample	BRON	BMON
MTBE in ULR	120.1	96.3
MIBE in ULR	60.8	67.0

TABLE 4. Selected properties of hydrocarbon fuels and oxygenated additives.

Oxygenate (or Fuel)	Blending Octane Number (R+M)/2	Cetane No.	$\Delta$ RON <sup>a</sup>	$\Delta$ MON <sup>a</sup>
MIBE	64	53 <sup>b</sup>	-3.3 <sup>c</sup> -1.9 <sup>d</sup>	-1.5 <sup>c</sup> -3.0 <sup>d</sup>
MTBE	108 109 <sup>e</sup> , 110 <sup>e</sup> , 108 <sup>e</sup>	<10	+2.8 <sup>c</sup> +3.4 <sup>d</sup>	+1.4 <sup>c</sup> +2.8 <sup>d</sup>
ETBE	110 <sup>e</sup> , 112 <sup>f</sup>		+2.1 <sup>d</sup>	+2.2 <sup>d</sup>
IPTBE	100.5 <sup>e</sup> , 113 <sup>f</sup>			
DIPE	104.5 <sup>e</sup> , 105 <sup>f</sup>			
TAME	104.5 <sup>e</sup> , 105 <sup>f</sup>			
Methanol	116 <sup>e</sup> , 108 <sup>f</sup>	3		
Ethanol	113 <sup>e</sup> , 115 <sup>f</sup>	8		
i-Propanol	108.5 <sup>e</sup> , 106 <sup>f</sup>			
1-Butanol	87 <sup>e</sup>	25	+1.0 <sup>d</sup>	+0.6 <sup>d</sup>
i-Butanol	102 <sup>f</sup>	13	+3.1 <sup>d</sup>	+2.1 <sup>d</sup>
t-Butanol	101 <sup>e</sup> , 100 <sup>f</sup>		+1.9 <sup>d</sup>	+2.0 <sup>d</sup>
Butane	94 <sup>e</sup>			
Gasoline	-----		-----	-----
Diesel Fuel	-----	> 42	-----	-----

<sup>a</sup>Determined at the level of 10 vol% of additive in gasoline.

<sup>b</sup>Determined by the Southwest Research Institute with a sample submitted by us; J. Erwin, private communication.

<sup>c</sup>Determined by AMOCO Oil Co. with samples submitted by us using an unleaded gasoline having RON = 92.1 and MON = 82.3; W. J. Reagan, private communication.

<sup>d</sup>From Reference 23 using an unleaded gasoline having RON = 82.4 and MON = 76.6.

<sup>e</sup>From G. H. Unzelman, *Oil & Gas J.*, 33 (April 10, 1989).

<sup>f</sup>From W. J. Piel, "Proc. First Biomass Conf. of the Americas," Burlington, VT (1993).

<sup>g</sup>From W. J. Piel, *Energy Prog.*, 8(4), 201 (1988).

## The Mechanism of Higher Oxygenate Synthesis over Supported Rh Catalysts

Steven S. C. Chuang, Raja Krishnamurthy, Mark A. Brundage, Michael W. Balakos  
Department of Chemical Engineering,  
The University of Akron,  
Akron, Ohio 44325-3906

Keywords: Rhodium, Higher oxygenates, Infrared spectroscopy

Extensive mechanistic studies have shown that higher oxygenates are formed from the insertion of CO into adsorbed alkyl species that is generated from CO dissociation and partial hydrogenation. The reduced Rh surface is known to be responsible for the formation of alkyl species. However, little is known about the nature of the active sites for CO insertion on various promoted Rh catalysts that are active for higher oxygenate synthesis. *In situ* infrared spectroscopy reveals linear CO on the single reduced Rh site as the most active adsorbed CO species for CO insertion on Rh/SiO<sub>2</sub> and Cu-, Ag-, Ce-, and Mn-promoted Rh/SiO<sub>2</sub> catalysts. Tilted CO exhibiting a band below 1700 cm<sup>-1</sup> is identified as a spectator that does not participate in CO insertion. Increasing reaction pressure causes an increase in the residence time of alkyl intermediate allowing CO insertion to occur. The selectivity toward higher oxygenates can be improved by increasing the relative concentration of linear CO sites and by increasing reaction pressure.

### INTRODUCTION

The catalytic synthesis of oxygenates from synthesis gas, i.e., CO/H<sub>2</sub>, is an important route to the production of clean fuels and chemical feedstocks from indirect coal liquefaction (1-12). There are a considerable number of experimental studies on the mechanism of higher oxygenate synthesis on Rh/SiO<sub>2</sub> and Cs-Cu-ZnO catalysts. Mechanistic study on Cs-Cu-ZnO reveals that Cs promotes  $\beta$  addition between surface species resulting in an increase in selectivity toward 1-propanol and 2-methyl-1-propanol, the principal higher alcohol products (6,7). The Cs-Cu-ZnO catalyst is more active and selective toward methanol than higher alcohols (7). Promoted Rh catalysts have been found to exhibit selectivity up to 75% for the formation of C<sub>2+</sub> oxygenates in the conditions ranging from 0.07 MPa to 10 MPa and 473-573 K (13). Although the reaction pathway and the nature of active sites for higher oxygenate formation on Rh/SiO<sub>2</sub> catalysts have been identified (13-16), the effect of promoter and support on the nature of active sites remains unclear.

At present, there is no satisfactory single step synthesis that permits economic production of higher oxygenates (17). An in-depth understanding of the mechanism is a key step toward rational design of selective catalysts for higher oxygenate synthesis and the development of a more selective route to higher oxygenates.

This paper reports the use of *in situ* infrared (IR) spectroscopy to investigate the nature of CO insertion sites and the residence time of intermediates involved for CO insertion on Cu-, Ag-, Ce-, and Mn-promoted Rh/SiO<sub>2</sub> catalysts. *In situ* characterization of reaction intermediates is essential for the development of a fundamental understanding of catalytic processes (18-20). *In situ* infrared spectroscopy has been one of the most important tools for studying the nature and structure of adsorbed species and its coverage on supported catalysts under reaction conditions (16,21-26). The structure of adsorbed species is closely related to the nature of the sites.

Investigation of the nature and reactivity of adsorbed species will provide information on the activity of sites to which the adsorbed species bonds.

## EXPERIMENTAL

A 0.5 wt% Rh/SiO<sub>2</sub> was prepared by impregnation of SiO<sub>2</sub> (Strem, 350 m<sup>2</sup>/gm) with an aqueous solution of rhodium chloride. Cu-Rh/SiO<sub>2</sub> catalyst with 3 wt% Rh loading was prepared by coimpregnation of aqueous solutions of copper and rhodium nitrates with Cu to Rh molar ratio of 1.0. Ag-Rh/SiO<sub>2</sub> with Rh loading of 3 wt% was prepared by the coimpregnation of aqueous solutions of silver and rhodium nitrates with Ag to Rh molar ratio of 1.0. A Ce-Rh/SiO<sub>2</sub> catalyst with 5 wt% Rh loading and Ce to Rh molar ratio of 0.74 was prepared by coimpregnating the silica support with a mixture of rhodium chloride and cerium nitrate solutions. Mn-Rh/SiO<sub>2</sub> catalyst with 4 wt% Rh loading and Mn to Rh molar ratio of 0.1 was prepared by sequential impregnation of manganese nitrate and rhodium chloride solutions. The ratio of solution to the support material used was 1 ml to 1 gm. After impregnation the catalyst samples were dried in air at 303 K and then reduced in flowing hydrogen at 673 K for 16 hr. The reduced catalysts were pressed into a self-supporting disk and then placed in the IR cell for *in situ* studies.

CO adsorption and the reaction of preadsorbed CO with C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> were carried out in an infrared (IR) reactor cell. The IR cell can be operated at temperatures up to 723 K and at a pressure of 6.0 MPa (16). Infrared spectra were measured by a FTIR spectrometer with a DTGS detector at a resolution of 4 cm<sup>-1</sup>. CO adsorption was conducted by exposing the catalyst to 0.1 MPa of CO at 303 K. Gaseous CO was removed by flowing helium. The infrared spectra of adsorbed CO were recorded at 0.1 MPa of CO or He. The reactivity of the adsorbed CO for CO insertion was investigated by introducing C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> (molar ratio of C<sub>2</sub>H<sub>4</sub>:H<sub>2</sub> = 1:1) to the adsorbed CO in the IR cell that served as a batch reactor. The infrared spectra of adsorbed CO and intermediates during the reaction were measured as a function of reaction time.

## RESULTS AND DISCUSSION

It has been proposed that the formation of C<sub>2+</sub> oxygenates over Rh-based and IFP catalysts involves the insertion of CO into adsorbed C<sub>n</sub>H<sub>x</sub> that is produced from CO dissociation and hydrogenation as shown in Fig. 1 (12-16,27-29). Higher alcohols such as ethanol can be produced from either the hydrogenation of acetaldehyde or direct hydrogenation of acyl species. A high selectivity (up to 75% carbon efficiency) has been achieved on promoted Rh catalysts at 573 K and 10 MPa (3,29). The selectivity can be compared to the maximum selectivity of 25% for C<sub>2</sub> products predicted by Anderson-Schulz-Flory distribution (29). The reaction pathway in Fig. 1 also suggests that CH<sub>4</sub> and C<sub>2+</sub> oxygenates are produced from the same C<sub>1</sub> precursor, i.e., CH<sub>x</sub>. Thus, it has been suggested that C<sub>2+</sub> oxygenates should be viewed as C<sub>1</sub> compounds in Anderson-Schulz-Flory distribution that could, in principle, be produced with 100% selectivity (29). However, high hydrogenation activity of Rh catalyst and thermodynamically favorable formation of CH<sub>4</sub> usually lead to a substantial yield of CH<sub>4</sub>. The challenge is how to suppress hydrogenation and enhance CO insertion in higher oxygenate synthesis.

The nature of active sites for CO hydrogenation has been a subject of extensive studies (13-16,27-29). It is generally agreed that CH<sub>x</sub> is formed from CO dissociation followed by hydrogenation on the reduced Rh sites. However, the number of surface atoms (i.e., the size of ensemble) required for CO dissociation remains unclear.

Much controversy has existed on the nature of the active site for CO insertion on Rh catalysts for more than a decade (16). Since CO insertion is a key step toward the formation of

higher oxygenates, clarification of CO insertion sites is essential for the development of a comprehensive mechanism for  $C_2$  oxygenates synthesis. Recently, we have employed ethylene hydroformylation as a probe reaction to determine the nature of active sites for CO insertion on the Rh catalysts. In ethylene hydroformylation, ethylene is hydrogenated to adsorbed ethyl species that may undergo CO insertion leading to the formation of propionaldehyde; adsorbed ethyl species can also be hydrogenated to ethane as shown in Fig. 2 (16,27). CO insertion into adsorbed ethyl species is analogous to CO insertion into  $CH_x$  species. Investigation of CO insertion into adsorbed ethyl species produced from  $C_2H_4$  and  $H_2$  provides direct information for elucidation of CO insertion sites without the complication resulting from CO dissociation and hydrogenation.

Our previous study on the reactivity of adsorbed CO on a reduced 3 wt% Rh/SiO<sub>2</sub> reveals that the linear CO adsorbed on a single Rh site is involved in CO insertion leading to the formation of propionaldehyde (16). Bridged CO and gem-dicarbonyl CO exhibit little reactivity towards CO insertion. Similar studies were conducted on the oxidized Rh/SiO<sub>2</sub> catalysts and showed that single Rh<sup>+</sup> sites are more active for CO insertion than the single Rh<sup>0</sup> sites (16). However, Rh<sup>+</sup> sites are not able to withstand the reducing atmosphere of CO/H<sub>2</sub> above 393 K.

The high activity of linear CO sites and the lack of activity of bridged CO sites has led to preparation of supported Rh catalysts containing primarily linear CO sites. Adsorbed sulfur blocked the bridged CO sites, increasing the concentration of linear CO sites resulting in an increase in CO insertion selectivity and activity. Low-loading supported Rh catalyst contains highly dispersed Rh crystallite. Highly dispersed Rh which contains primarily single Rh sites may chemisorb linear CO. In contrast, CO adsorption on the 0.5 wt% Rh/SiO<sub>2</sub> produced bands at 2027 and 2004 cm<sup>-1</sup> that can be assigned to weakly adsorbed Rh(CO)<sub>4</sub> as shown in Fig. 3 (30). The intensity of the bands decreased in flowing helium suggesting that the species was weakly adsorbed. The exposure of this adsorbed CO to ethylene and hydrogen did not result in any reaction at 303 K. CO adsorption at 323 K also produced weakly adsorbed Rh(CO)<sub>4</sub> bands at 2027 and 2004 cm<sup>-1</sup> similar to those observed at 303 K. Exposure of adsorbed CO to ethylene and hydrogen at 323 K produced a propionaldehyde band at 1708 cm<sup>-1</sup> after approximately 20 min of reaction. An increase in the amount of propionaldehyde formed is shown by the increase in the intensity of the adsorbed band with time as observed in Fig. 3. An increase in the hydrocarbon band near 2983 cm<sup>-1</sup> is also observed with reaction time. The simultaneous formation of propionaldehyde and ethane indicates that CO insertion into adsorbed ethyl species competes with ethylene hydrogenation.

CO adsorption on a Cu-Rh/SiO<sub>2</sub> catalyst produced a linear CO band at 2058 cm<sup>-1</sup>, a bridged CO band at 1875 cm<sup>-1</sup>, and gem-dicarbonyl bands at 2091 and 2027 cm<sup>-1</sup> as shown in Fig. 4. A band at 2127 cm<sup>-1</sup> assigned to CO adsorbed on Cu is also observed. Reaction of  $C_2H_4$  and  $H_2$  with adsorbed CO on Cu-Rh/SiO<sub>2</sub> catalyst shows the formation of propionaldehyde 1 min after addition of the reactants. A decrease in the bands at 2127 cm<sup>-1</sup> and 2058 cm<sup>-1</sup> and the formation of propionaldehyde indicates that the linear CO on Rh and CO adsorbed on Cu participate in CO insertion into the adsorbed ethylene. The rate of propionaldehyde formation is much faster on the Cu-Rh/SiO<sub>2</sub> catalyst in comparison to the highly dispersed Rh/SiO<sub>2</sub> catalyst. A decrease in intensity was observed in the gem-dicarbonyl bands after approximately 10 min of reaction with the simultaneous formation of ethane at 2983 cm<sup>-1</sup> and a small amount of CO<sub>2</sub> at 2341 cm<sup>-1</sup>. Thus, the addition of Cu appears to increase the rate of CO insertion as indicated by the higher rate of formation of propionaldehyde on the Cu-Rh/SiO<sub>2</sub> catalyst as compared to the dispersed Rh/SiO<sub>2</sub> catalyst.

CO adsorption on Ce-Rh/SiO<sub>2</sub> produced linear CO band at 2048 cm<sup>-1</sup>, bridged CO band at 1857 cm<sup>-1</sup>, gem-dicarbonyl bands at 2090 and 2027 cm<sup>-1</sup>, and a tilted CO at 1766 cm<sup>-1</sup>. CO

adsorption on Mn-Rh/SiO<sub>2</sub> produced linear CO band at 2040 cm<sup>-1</sup>, bridged CO at 1835 cm<sup>-1</sup>, weakly adsorbed gem-dicarbonyl band at 2090 cm<sup>-1</sup>, and a tilted CO band at 1670 cm<sup>-1</sup>. CO adsorption on Ag-Rh/SiO<sub>2</sub> produced linear CO band at 2072 cm<sup>-1</sup>, a weak bridged CO band at 1879 cm<sup>-1</sup>, and gem-dicarbonyl bands at 2095 and 2030 cm<sup>-1</sup>.

The linear CO was found to be active for CO insertion. There is no obvious correlation between the wavenumber of linear CO and its CO insertion reactivity. The tilted CO that has been suggested to be highly active for CO insertion is in fact a spectator that does not participate in the reaction.

In conclusion, linear CO site is active for CO insertion. The selectivity toward higher oxygenates can be improved by increasing the relative concentration of linear CO sites and increasing reaction pressure.

## REFERENCES

1. Ellgen, P. C., Bartley, W. J., Bhasin, M. M., and Wilson, T. P., *Adv. Chem. Ser.*, 178, 147 (1979).
2. Yoneda, Y., *Progress in C<sub>1</sub> Chemistry in Japan*, (Research Association for C<sub>1</sub> Chemistry, Eds.) Elsevier, New York-Tokyo, 1989.
3. Anderson, R. B., *Fischer Tropsch and Related Synthesis*. Academic Press, New York, 1983.
4. Klier, K., *Adv. Catal.*, 31, 243 (1982).
5. Sachtler, W. M. H., *Proceedings of 8th International Congress on Catalysis*, Vol. 1, p. 151 (1984).
6. Nunan, J. G., Bogdan, C. E., Klier, K., Smith, K. J., Young, C. Y., and Herman, R. G., *J. Catal.*, 116, 195 (1989).
7. Nunan, J. G., Herman, R. G., and Klier, K., *J. Catal.*, 116, 222 (1989).
8. Murchison, C. B., Conway, M. M., Stevens, R. R., Quarderer, G. J., *Proceedings of 9th International Congress on Catalysis*, Vol. 2, p. 626 (1988).
9. Cochran, G. A., *Eur. Patent Appl.* 841029325, 1984.
10. Courty, P., Forestiere, A., Kawata, N., Ohno, T., Raimbault, C., and Yoshimoto, M., in "Industrial Chemicals via C<sub>1</sub> Processes." ACS Symposium Series No. 328, p. 42, Washington, D. C., 1985.
11. Courty, P., Durand, D., Freund, E., and Sugier, A., *J. Mol. Catal.*, 17, 241 (1982).
12. Pan, W. X., Cao, R., and Griffin, G. L., *J. Catal.*, 114, 447 (1988).
13. Ichikawa, M., *Chemtech.*, 674 (1982).
14. Chuang, S. C., Tian, Y. H., and Goodwin, J. G., Jr., *J. Catal.*, 96, 449 (1985).
15. Bell, A. T., *Catal. Rev. Sci. Eng.*, 23, 203 (1981).
16. Chuang, S. S. C., and Pien, S. L., *J. Catal.*, 135, 618 (1992).
17. "Coal Liquefaction: A Research Needs Assessment Executive Summary," DE-AC01-87ER30110, A report prepared for the U. S. Department of Energy, 1989.
18. Delgass, W. N., Haller, G. L., Kellerman, R., and Lunsford, J. H., "Spectroscopy in Heterogeneous Catalysis," Academic Press, New York, 1979.
19. Rabo, J. A., in "Proceedings of the 10th International Congress on Catalysis," Part A, p. 1, Akademiai Kiado, Budapest, 1993.
20. Tamaru, K., "Dynamic Relaxation Methods in Heterogeneous Catalysis", in *Catalysis: Science and Technology*, vol. 9, J. R. Anderson and M. Boudart (eds.), p. 87, Springer-Verlag, Berlin-Heidelberg-New York, 1991.
21. Yates, J. T. Jr., and Madey, T. E., Eds. "Vibrational Spectroscopy of Molecules on Surfaces," Plenum Press, New York, 1987.

22. Hicks, R. F., Kellner, C. S., Savotsky, B. J., Hecker, W. C., and Bell, A. T., *J. Catal.*, 71, 216 (1981).
23. Li, Y. E., and Gonzalez, R. D., *Catal. Lett.*, 1, 229 (1988).
24. Moser, W. R., Cnossen, J. E., Wang, A. W., and Krouse, S. A., *J. Catal.*, 95, 21 (1985).
25. Chuang, S. S. C., and Pien, S. I., *J. Mol. Catal.*, 55, 12 (1989).
26. King, D. L., *J. Catal.*, 61, 77 (1980).
27. Sachtler, W. M. H., and Ichikawa, M., *J. Phys. Chem.* 90, 4752 (1986).
28. Biloen, P., and Sachtler, W. M. H., *Adv. Catal.* 30, 165 (1981).
29. van den Berg, F. G. A., Ph. D. Thesis. University of Leiden. The Netherlands, 1984.
30. Hanlan, L. A., and Ozin, G. A., *J. Amer. Chem. Soc.*, 96, 6324 (1974).

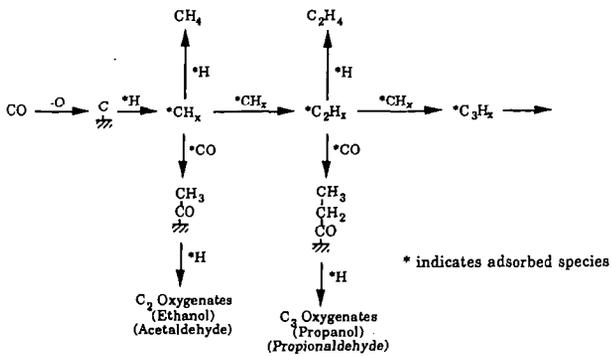


Figure 1. Reaction pathway for higher oxygenates synthesis on Rh- and IFP-based catalysts.

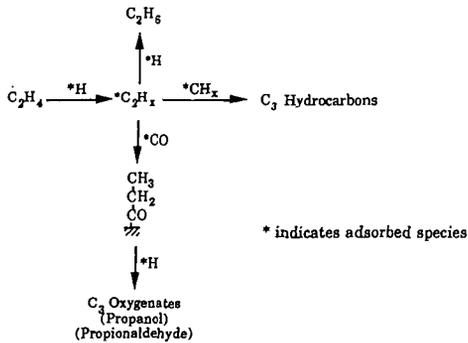


Figure 2. Reaction pathway for ethylene hydroformylation.

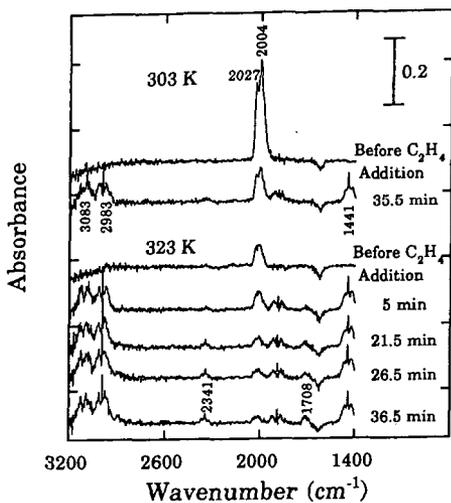


Figure 3. C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> addition to CO (ads.) on 0.5% Rh/SiO<sub>2</sub>

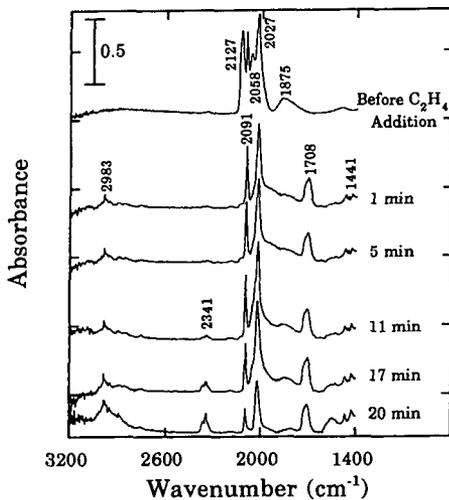


Figure 4. C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub> addition to CO (ads.) on Cu-Rh(1:1)/SiO<sub>2</sub>

## OXYGENATES FROM SYNTHESIS GAS

Wolfgang Falter and Willi Keim  
Institut für Technische Chemie  
RWTH Aachen  
Worringerweg 1  
52074 Aachen, Germany

Keywords: Oxygenates, Synthesis Gas, Isobutanol

The direct synthesis of oxygenates starting from synthesis gas is feasible by homogeneous and heterogeneous catalysis. Homogeneous Rh and Ru based catalysts yielding methyl formate and alcohols will be presented.

Interestingly, modified heterogeneous catalysts based on "Isobutyl Oel" catalysis, practiced in Germany (BRD) up to 1952 and in the former DDR until recently, yield isobutanol in addition to methanol. These "Isobutyl Oel" catalysts are obtained by adding a base such as Li < Na < K < Cs to a Zn-Cr<sub>2</sub>O<sub>3</sub> methanol catalyst. Isobutanol is obtained in up to 15% yield.

J. Seibring [1] synthesized, with a ZrO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub>-CuO-ZnO-K<sub>2</sub>O catalyst, isobutanol in yields up to 22%. G. Kollé-Gorgen [2] produced with a ZrO<sub>2</sub>-MnO<sub>2</sub>-Pd-K<sub>2</sub>O catalyst isobutanol in yields up to 30%.

Our best catalyst a Zr-Zn-Mn-Li-Pd catalyst produced isobutanol up to 60% at a rate of 740g isobutanol per liter catalyst and hour. The reaction conditions with T = 715K, p = 25 MPA, GHSV = 20,000 h<sup>-1</sup> are rather severe. With changing pressure the selectivity to isobutanol changes. There is a significant temperature impact, which is evident from Fig. 1

Whereas at 625K about 72% methanol is formed, this portion decreases to 6% at 725K. In parallel, the isobutanol portion in the liquid product increases from 4% to 625K to 45% at 715K. The catalyst is quite stable over a run of about 720 hours. In catalyst preparation, the pH of the precipitation is critical. Fig. 2 outlines best values for isobutanol rest and around pH-values. Finally Fig. 3 exhibits a typical selectivity pattern obtained in various runs.

1. J. Seibring. *Thesis RWTH Aachen* 1985.
2. G. Kollé-Gorgen, *Thesis RWTH Aachen* 1985.

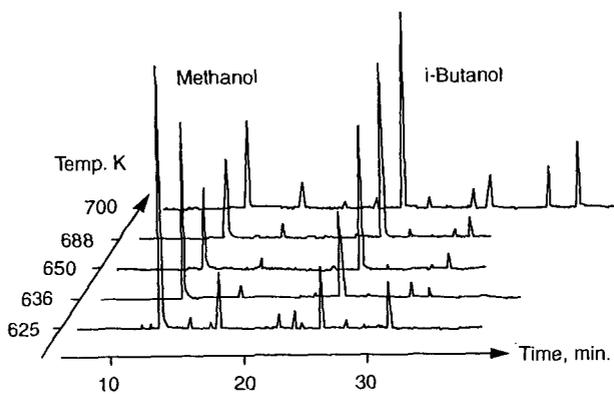


Figure 1. Temperature dependence i-BuOH selectivity (Zr-Zn-Mn-Li-Pd catalyst, 10 MPa, GHSV 10,000 h<sup>-1</sup>)

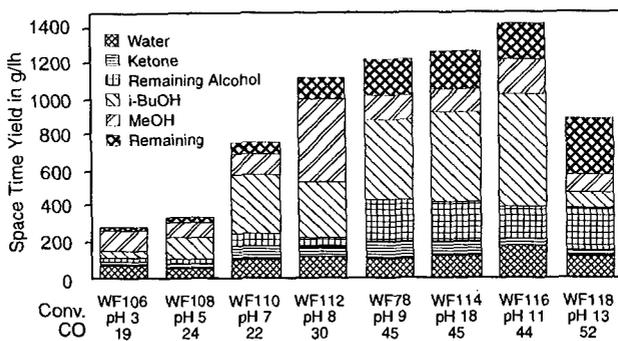


Figure 2. Impact of pH-value on catalyst preparation Zr-Zn-Mn-K-Pd, T = 700 K, p = 25 MPa, GHSV = 20,000 h<sup>-1</sup>

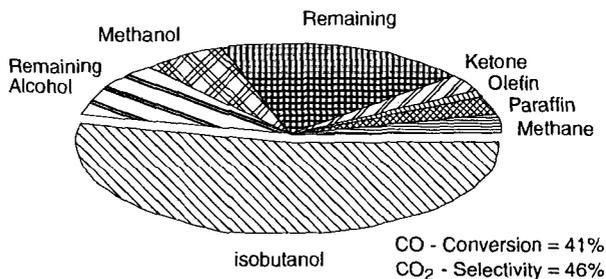


Figure 3. Product selectivity Zr-Zn-Mn-Li-Pd catalyst T = 715 K, p = 25 MPa, GHSV = 20,000 h<sup>-1</sup>

## DIMETHYL CARBONATE PRODUCTION FOR FUEL ADDITIVES

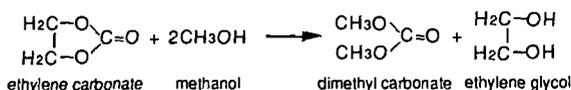
Y.Okada, T.Kondo, S.Asaoka  
R&D Center, Chiyoda Corporation  
3 - 13 Moriya-cho Kanagawa-ku Yokohama 221, Japan

Key words : Dimethyl carbonate, Octane enhancing oxygenates, Zeolite catalysts

### INTRODUCTION

Dimethyl carbonate is very attractive as for use as an oxygenate for fuel additives. A feasible method of mass production at a low cost is needed for producing dimethyl carbonate for fuel additives.

The transesterification process is one of the dimethyl carbonate production processes<sup>(1)</sup>. In this process, ethylene carbonate with methanol is transesterificated to dimethyl carbonate.



In the transesterification process, ethylene glycol is co-generated with dimethyl carbonate. The ethylene glycol is considered to correspond economically with the conventional product from hydration of ethylene oxide, because the quality of the ethylene glycol produced by transesterification is equal to the quality of the conventional product and the demand for ethylene glycol is growing year by year. Therefore, development of the dimethyl carbonate process through the transesterification is indicated.

Oxidative carbonylation processes in both the liquid-phase and vapor-phase are known as the other dimethyl carbonate processes. Liquid-phase oxidative carbonylation is the oxidation of carbon monoxide with oxygen in methanol in the presence of copper chloride<sup>(2)</sup>. A catalyst is used in a slurry mixture. In the vapor-phase oxidative carbonylation, the reaction of carbon monoxide and methyl nitrite by the oxidation of methanol and nitric oxide in the presence of both palladium chloride and copper chloride is used<sup>(3)</sup>. These processes are based on oxidation due to the presence of both oxygen and chloride.

Transesterification is a mild reaction with small exotherm, and is carried out in the liquid phase without toxic chemicals and corrosiveness. These features will be the merit of scale up with a low fixed capital.

We started transesterification process development for dimethyl carbonate production from the above considerations. Zeolites were studied as catalysts for this transesterification, due to their properties of resistance to heat and organic solvents. Zeolite catalysts can be used in fixed bed reactors without a catalyst separation unit. Chiyoda has developed processes using zeolites, for example, the Z-forming process to produce BTX from light hydrocarbons, the 2,6-DIPN production process using zeolite adsorbent, etc.

## **EXPERIMENTAL**

### **Catalysts**

Almost all of the popular industrial zeolites, for example the A, X, Y, L, Mordenite, ZSM-5 type, etc., were used in the catalysts screening. Several types of zeolites with adjusted cation species were screened next. Those catalysts were provided to reaction tests after calcination.

### **Test units**

Reaction tests were performed in batch reactors and fixed bed reactors. Stainless steel was used for the reactors. Fixed-bed flow reactors were operated automatically under good material balance and well controlled of catalysts bed temperature.

## **RESULTS**

The catalysts screening were performed from the points of activity, selectivity and sustainability. The reaction condition, the regenerating method, etc., were studied in order to develop the process for dimethyl carbonate production through transesterification. We will discuss some results of the catalysts screening and catalytic performance tests. The details of catalysts design will be discussed in the future.

### **Catalysts screening**

Various structure types of zeolites were examined during the first step of the catalysts screening based on activity, selectivity and sustainability. The influence of the cation species of zeolite on catalytic ability was studied next in several types of zeolites. A part of the results for the catalysts screening of commercially available zeolites is as follows.

#### **Zeolite types**

Na form zeolites with Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> molar ratios varying from 0.04 to 0.5 were used.

The activity is varied according to the types of zeolites as shown in Fig.1. It is considered that the order of activity depends on  $Al_2O_3/SiO_2$  which represents the quantity of active site of the zeolites. Zeolite A with the largest  $Al_2O_3/SiO_2$  ratio of 0.5 shows the highest activity, and ZSM-5 with the small  $Al_2O_3/SiO_2$  of 0.04 has a very low activity. It seems that the activity depends on the quantity of active sites of the zeolites. Zeolite A has the most active sites, because the maximum value of  $Al_2O_3/SiO_2$  in the zeolites is at 0.5. After that, the catalysts with the same  $Al_2O_3/SiO_2$  of different structures were examined.

#### Cation species

The influence of the cation species including proton on catalytic ability was studied for several types of zeolites. We will discuss a part of the results for commercially available zeolites having different cation species.

The H form zeolites shows no activity. Fig.2 shows a comparison of the activity with 3 A(KA), 4 A(NaA) and 5 A(CaA) zeolites which have same  $Al_2O_3/SiO_2$ . The 3 A (KA) zeolite shows the highest activity. The order of the activity in zeolites A is as follows; 3 A > 4 A > 5 A. As for A type of zeolites which have the same crystalline structure, the activity depends on the cation species.

Several types of K form zeolites were studied. Fig.3 gives a comparison of the activity of the industrially popular 3 A and L types of the zeolites, and the activity of the K form X type which is in adjusted cation species. The order of the activity for these zeolite types is A > X > L. The activity depends on the  $Al_2O_3/SiO_2$  and here zeolite A also shows the highest activity of the K form zeolites.

From the results of catalysts screening, the activity of the zeolite catalysts depends on the  $Al_2O_3/SiO_2$  which represents the quantity of active sites, and the activity level of the site depends on the cation species.

#### Catalytic performance tests

Catalytic performance tests were achieved in order to study the zeolite catalysts for use in fixed bed reactors. The content of the cation species, the temperature for calcination, the material for binder, etc., were studied in addition to the catalysts screening.

Table 1 shows an example of catalytic performance tests. A 46% of one pass dimethyl carbonate yield was obtained at 120 ( $^{\circ}C$ ) and 10 ( $kg/cm^2$ ).

## **CONCLUSION**

The catalytic activity of zeolites for the production of dimethyl carbonate for use an oxygenate for fuel additives was studied.

We studied the activity of some of the industrially popular zeolites by the catalysts screening based on activity, selectivity and sustainability. We found that the order of zeolite catalyst activity depends on the  $Al_2O_3/SiO_2$  which represents the quantity of active sites. Zeolite A with a maximum value of  $Al_2O_3/SiO_2$  at 0.5 in the various zeolite types shows the highest activity.

The influence of the cation species of the zeolites was studied using several types of zeolites. The order of the activity for industrially popular zeolites A is; 3A (KA) > 4A (NaA) > 5A (CaA). It is believed that the activity level of the site depends on the cation species. In the case of zeolite A, the order of activity for cation species is as follows;  $K^+ > Na^+ > Ca^{2+}$ .

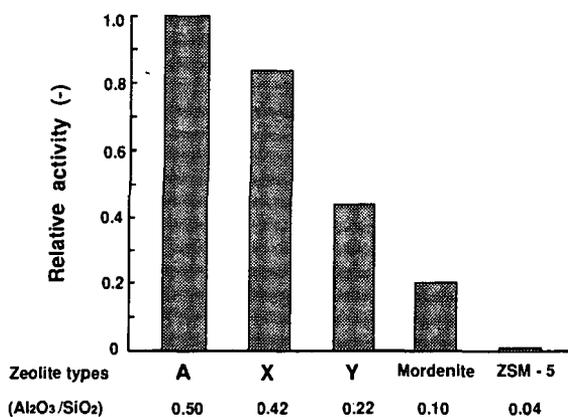
Catalytic performance tests were achieved to study zeolite catalysts for use in fixed bed reactors. A 46% of one pass dimethyl carbonate yield was obtained at 120 (°C) and 10 (kg/cm<sup>2</sup>). Zeolite catalysts can be used in fixed bed reactors with significant properties of resistance to heat and organic solvents in comparison with ion exchange resin. The zeolite catalysts for dimethyl carbonate production by transesterification were prepared using commercially available zeolites by a simple ion exchange treatment.

## **REFERENCES**

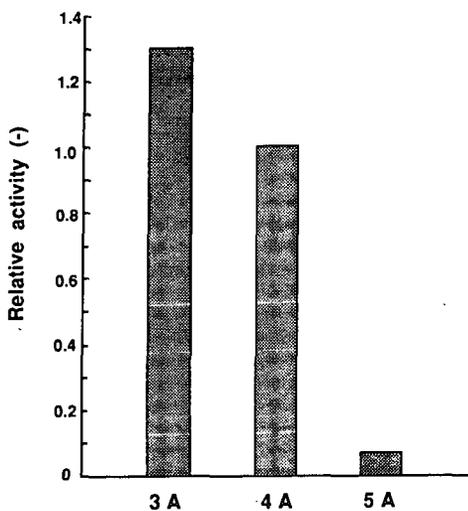
- 1) John F. Knifton et al, J.of Molecular Catalysis, vol.67, 389-399 (1991)
- 2) Ugo Romano et al., Ind. Eng. Chem. Prod. Dev., vol.19, 396-403 (1980)
- 3) EP 425197 (1990)

**Table 1 Fixed- bed flow reaction test**

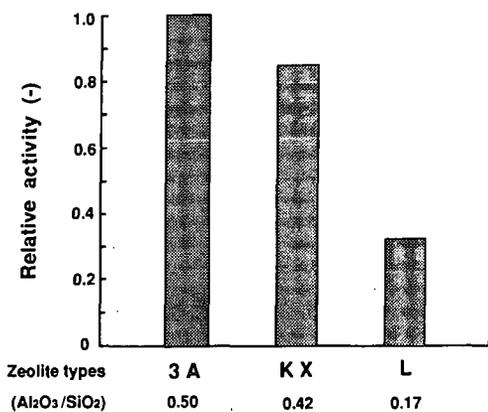
Temp. ( °C )	Press. ( kg/cm <sup>2</sup> )	DMC Yield ( % )
<b>120</b>	<b>10</b>	<b>46</b>



**Fig.1 Activity of various types of zeolites**



**Fig.2 Activity of A type zeolites**



**Fig.3 Activity of K form zeolites**