# ALCOHOLS AND OTHER OXYGENATES AS MOTOR FUELS

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Alcohols and other low molecular weight oxygenates are known to be potentially valuable gasoline substitutes. While these are generally of interest in relation to the long-term need to secure future motor fuel supplies, there is a more urgent need for substitutes which will improve the octane rating of unleaded fuels. For environmental reasons, oxygenates including alcohols may be preferred to other fuel ingredients which are currently proposed or introduced to replace lead compounds. In addition to octane improvement qualities, oxygenates were assessed with regard to power output and exhaust emissions thus confirming that no great deficiencies in these parameters would be introduced.

## TEST PROCEDURES

Oxygenates were studied in a Fiat 127 903 cc engine connected to a Heenan Froude dynamometer to apply a steady variable load. A standard fuel-measuring device and Alcock viscous air flowmeter enabled fuel-air ratios to be closely monitored. Oil, cooling water, and air temperatures etc were continuously monitored to ensure that these remained within the normal range of operational variability. Compression ratios between the four cylinders ranged from 8.92 to 9.13 and this variation was deemed to be acceptable since our concern was to establish the comparative behaviour of these fuels in commercially available engines rather than in single-cylinder studies. The incidence of engine knock was readily detectable at low engine speeds. For routine detection at high engine speeds, a Bruel and Kjaer piezoelectric accelerometer and a CEL piezoelectric pressure washer were installed. The Bruel & Kjaer accelerometer required amplification through a Kistle charge amplifier to give a satisfactory oscilloscope signal, while the "knock" washer gave a satisfactory pressure trace without amplification.

A standard low-leaded base gasoline of the F-7 series was used for comparison and as a base for alcohol and oxygenate blends.

**Oxygenates used:**

The following alcohols, ethers, esters, and ketones were used in blends containing between 5 and 20% oxygenate in gasoline .

| | |
|---|---|
| **Alcohols** | Methanol |
| | Ethanol |
| | Tert Butanol |
| **Ethers** | Methyl tert butyl ether |
| | Diiso propyl ether |
| | Anisole |
| **Esters** | Dimethyl carbonate |
| | Methyl acetate |
| **Ketones** | 3 methyl butan-2-one |
| | 4 methyl pentan-2-one |
| | Acetone |
| | Methyl ethyl ketone |

The alcohols and MTBE are well known gasoline substitutes, some having been considered and used over the last sixty years. Other oxygenates in this list were chosen because of their branched structure, small molecular size and, in some cases, prior knowledge of their RON and MON. Current production cost was also important although bulk production and new methods of synthesis could make many other similar oxygenates viable.

The concentrations used in experiments were varied so as to limit total blend oxygen content to a maximum of around 4% by weight. This is within the limits of good drivability ie giving no observed problems caused by the leaning effect due to the extra oxygen in the combustion process.

The experiments aimed to test the various oxygenates with regard to improved octane rating and to test various mixtures of oxygenates combining two or more chemical types and changing individual components to assess whether a synergistic effect is exhibited.

The results obtained for single oxygenates showed several chemicals to have similar effects in similar concentrations provided that their oxygen content was comparable. Dual combinations of oxygenates were all tested as 10% vol/vol blends producing 2-4% wt/wt oxygen in the blends. Treble combinations were blended at 15% vol/vol.

Methanol/MTBE/3 methyl butan-2-one and methanol/MTBE/4 methyl pentan-2-one were seen to be superior while methanol/MTBE/TBA also exhibited good knock "protection". (Figs. 1 and 2)

Comparison of multicomponent blends with the effect of individual components is not always readily seen, since the individual effect of a smaller oxygenate percentage is not always very obvious. Comparing results on the basis of percentage weight of oxygen in the blend showed little significant correlation. Blending octane numbers cited in the literature vary dramatically with notable gaps for some of the ketones.

## EXPERIMENTAL RESULTS

**Octane Improvement** To determine apparent increase in quality due to oxygenate addition several engine runs were performed using the base fuel. Then oxygenate blends showed a clear comparison. Combinations of oxygenates were regarded as most important in order to study synergistic effects especially of mixtures of chemical type and components so as to establish where chemical type was of the greater importance.

The results initially suggested methanol plus MTBE with a ketone was better than average and methanol plus MTBE with TBA was promising. Later results showed dual blends may be equally valuable. For example MTBE and methanol was one of the best combinations while TBA and ketones in the triple blends were valuable in replacing the ether but did not improve the anti knock quality.

CFR tests were carried out and showed that the oxygenates led to a greater RON than MON increase. This is due to the higher sensitivity of the oxygenates compared with the base gasoline. However the replacement of MTBE by 4 methyl pentan-2-one reduced the sensitivity of the blend due to its own very low sensitivity. Small amounts of 4 MP2 imparted no change in RON but a decrease in MON.

**Power output** A number of blends showed increased power output when oxygenates were present with the greatest increase exhibited at low speeds. This may result in better acceleration performance with maximum power output largely unaffected. Increases of up to 5% were exhibited and in our work a 6:3:2 blend of methanol/MTBE/and 4 MP2 gave some of the best results.

## Viability of ketones as blending components

Acetone, MEK and 4 MP2 are among the hundred largest volume production organic chemicals, and some may be close in price to more usually accepted blending components. Their very high octane numbers make them worth further consideration. Tonnage production of such compounds may, however, be dependent on other industrial useage. For example, 4 MP2 is used widely as a solvent and degreasant. Tonnage used as an automobile paint solvent is being reduced in an attempt to reduce evaporative emissions to the atmosphere. Replacement by water-based solvents should release large tonnages of this ketone for fuel blends in the medium term as production plants are left with reduced total demand. Although this reduction may not augur well for future price stability, the medium term availability may provide a period in which the merits of 4 MP2 as an engine fuel ingredient could be well established.

## CONCLUSIONS

This work showed that combinations of oxygenates including alcohols, ethers and ketones can be highly advantageous in raising octane ratings by 3 or 4 without modification to engine and fuel system. Lower exhaust emissions are to be expected with more oxygen in the fuel and these and improved power output are additional benefits.

Alcohols and MTBE are used individually by many countries and some, notably Switzerland, include them together in some gasoline blends. Increasing interest is being shown in other ethers (such as dimethyl ether in the USA and elsewhere) and production plants for such fuel components are coming to be seen as potentially viable. The higher cost of ketones such as 4 MP2 has limited the interest in these as gasoline substitutes but current demand changes may release lower cost supplies and a world wide interest, increasing production for automobile fuel use, could well bring massive economies of scale.

The inexorable moves to unleaded fuels will bring these oxygenates a higher profile as potentially viable gasoline substitutes with major advantages in terms of octane requirement, power output and atmospheric quality.

Clean air legislation in the USA and elsewhere is giving a boost to several of the oxygenates which we have studied. For example, the 1990 US Clean Air Act placed tough restrictions on gasoline blending while tightening constraints on exhaust emissions. A 25% reduction in high octane aromatic compounds is called for by 1995. New blending ingredients are needed which meet the Act's requirements and replace the lost octane rating. MTBE has been widely recommended for this role[2] but Dimethyl ether (DME) may be equally promising.

A new one-step synthesis yields methanol **and** DME from CO-rich synthesis gas and is expected to show cost advantages over traditional catalytic dehydration of methanol. The DME/methanol product could be used as a transport fuel since the DME gives the methanol an improved cold-start facility. Thus, as a separate synthetic fuel or as an octane improver, DME could compete with MTBE without competing for a $C_4$ feedstock.

Another oxygenate which has attracted interest as an octane booster is di methyl carbonate (DMC). This compound was synthesised in the 1980's as a replacement for phosgene in carbonylation reactions[3]. Found to be "environmentally-friendly", DMC is finding other demands in pharmaceuticals and plastics but its greatest potential may be as an octane booster. Again it does not compete with MTBE being synthesised from methanol:

$$CO + 2CH_3OH + \tfrac{1}{2}O_2 \longrightarrow (CH_3O)_2CO + H_2O$$

A 12,000 t/y plant is operating in Italy and the feasibility of production in the USA is under consideration with methanol and methane more readily available. As a fuel blending component DMC reduces the amount of ozone emitted by the engines of older vehicles and shows the other cleaner exhaust properties typical of oxygenates.

As the world-wide trend towards unleaded fuels gathers pace, all the oxygenates will gain a higher profile as gasoline substitutes and octane boosters. Relying mainly on synthetic production routes the choice of "best oxygenate" will depend primarily on ease of synthesis to keep costs within reasonable limits.

Synthetic oxygenate mixtures such as the methanol/DME product referred to above could well prove the most viable. As with petroleum fractionation the usefulness of a mixture of compounds (c/f the "gasoline fraction") may well be decisive in settling which formulation will win the "best oxygenate" label.

Apart from compliance with the general constraints on emissions of CO, hydrocarbons, and NOX, there will be increasing concern to combat the "greenhouse effect". Apart from enhancing engine performance efficiency, alcohols, especially ethanol, may hold their place as the most "environmentally-advantageous" automobile fuels. This is especially true if the alcohol can be produced from a short-rotation biomass source such as cane-sugar. Agricultural production of the sugar cane absorbs $CO_2$. If one then produces ethanol by the well-known fermentation route, the subsequent combustion of the alcohol as motor fuel is merely **recycling** that $CO_2$ to the earth's atmosphere.

While the choice of feedstock for automobile fuel will remain largely dependent on price, such environmental issues will maintain the interest in the alcohols. In the next decade one may well see a range of fuels based on alcohols making further inroads into the world-wide gasoline demand.

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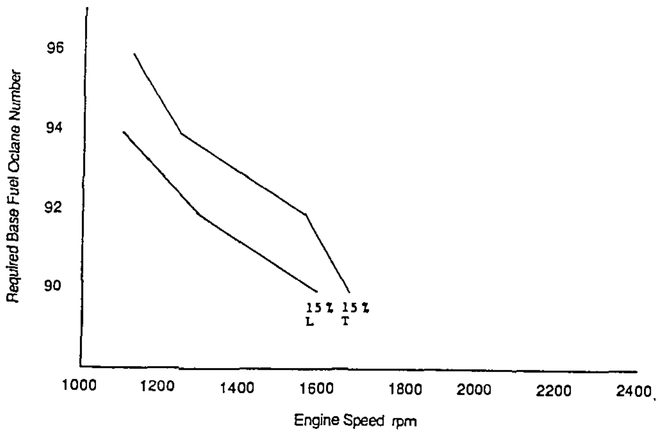


Figure 1 1 : 1 : 1 Methanol : MTBE : TBA

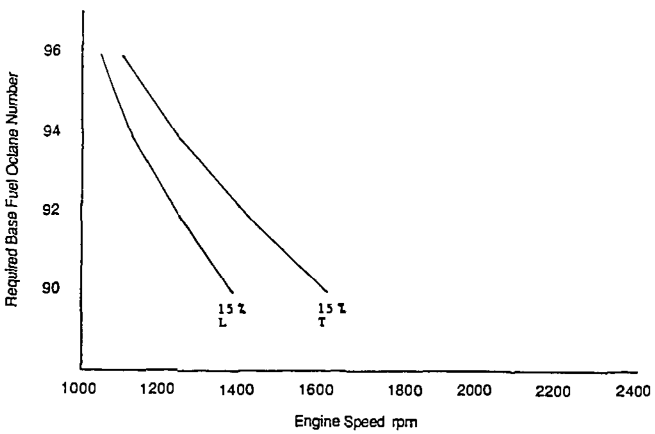


Figure 2 1 : 1 : 1 Methanol : MTBE : 3MB2