

CLEAN DIESEL FUEL: THE CASE FOR IGNITION-IMPROVED METHANOL

In the late 80's ICI Ltd, a UK chemical multinational, pioneered the use of methanol containing an ignition improver named Avocet™ as an alternative diesel fuel. Among many other demonstration projects around the world, a dozen SCRTD transit buses were converted to use the new fuel (the MASSCAR project). The demonstration was an outstanding success technically, proving the fuel to be not only clean burning, but also mechanically reliable. Unfortunately the new technology proved unable to compete on economic grounds since at that time methanol prices were rising due to high cost natural gas feedstock, and Avocet production cost was high because the advantages associated with high volume production could not be realized. Both these factors are now changed. Natural gas prices have fallen drastically, and new process technology will allow competitive pricing for Avocet™.

In view of the foregoing, since ICI Plc no longer exists, a new company has been formed to exploit the commercial opportunity offered by ignition improved methanol. Based on the original Avocet™ formulation and staffed by ex-ICI personnel, the new company is named Avocet Infinite Plc (UK) along with its wholly owned US subsidiary Avocet Solutions Inc.

1. AVOCET™ FUEL FORMULATION

Avocet as proposed to be distributed consists of the ignition improver admixed with small quantities of lubricity and anti-corrosion additives, optionally a dyestuff and bittering agent, and approximately 60% methanol co-solvent. The amount needed to be added to fuel methanol depends upon engine needs. Avocet Infinite believes that two fuel formulations may be required: 2% v/v addition of ignition improver for modern high compression diesels with electronic controls, and 5% v/v ignition improver addition for older retrofitted engines.

2.0 METHANOL AS A TRANSPORTATION FUEL

Any transportation fuel, to be acceptable, must satisfy multiple commercial criteria. (Note, M85 will not be considered here because it is adulterated with 15% gasoline. The addition of gasoline provides volatility for engine starting but does not enable the full benefits of methanol to be achieved).

The following identifies the major properties to be considered when assessing a potential new transportation fuel and an assessment of methanol with respect to these properties.

2.1 Production Cost. This factor is the most important because it ultimately determines the ability of a fuel to compete with gasoline or diesel in the marketplace. The key parameter is cost per unit of combustion energy, a definition which avoids problems associated with vehicular efficiency. To arrive at a true estimate of production cost inevitably involves assumptions. First however, must be the elimination of subsidies because these are temporary political constructions which distort long term realities. Methanol is a global commodity and its current US price of \$266 per tonne is determined by global trade. Its production cost is mainly determined by the cost of natural gas, the most cost effective

feedstock, and the capital costs associated with its synthesis. It is reasonable to infer that an average current global methanol production cost must therefore be in the region of \$150 to \$200 per tonne. However, recent trends in natural gas pricing indicate that much lower prices may be achievable. For example recent global spot prices for methanol have been reported at \$160 per tonne.

2.2 Octane Number and Compression Ratio. One of the main attractions of methanol is its high octane number (110) relative to regular gasoline. High octane fuel enables spark-ignition (SI) engines to be run at higher compression ratios so attaining greater engine efficiency.

2.3 Politics. A proposed novel fuel necessarily starts at a political disadvantage *vis a vis* gasoline or diesel. The crude oil industry is large, well-entrenched, and a major political force in nearly all countries. Any competition therefore faces considerable hurdles in terms of taxation, sympathetic regulation, infrastructure and available proven technology. These factors, while daunting, can be overcome, initially in niche markets, provided there are cogent reasons for adopting a new fuel.

2.4 Cold Start. A major drawback to the use of methanol in Spark-Ignited (SI) engines is its lack of sufficient volatility to facilitate cold starting. It is this drawback (among other factors) which caused the State of California to introduce 15% gasoline in its M85 program in the early 90's. (Gasoline, a mix of liquid hydrocarbons, contains a large enough fraction of highly volatile material to allow easy starting). The vapor pressure of a liquid is inversely proportional to its boiling point. The boiling point of methanol is 65° C. Avocet Fuel Solutions Inc. has patented technology, currently being validated, which can overcome the volatility deficiency.

2.5 NOx Emissions. NOx is without doubt the most dangerous pollutant found in the exhaust gases from internal combustion engines. In the form of NO₂ it is a respiratory irritant in its own right, but it is also the main actor in the formation of tropospheric ozone. The production of NOx occurs in the engine cylinder when air is heated to a high temperature, thus the rate of formation of NOx is exponentially proportional to the temperature reached by the cylinder gases. Methanol has an abnormally low theoretical flame temperature of 3550° F. It therefore burns with a relatively cool flame compared with any other fuel, and so produces less NOx on a comparable basis.

2.6 Particulate Emissions. The empirical methanol formula is CH₃OH. It is the simplest of the alcohol family and as a so-called C1 chemical, it possesses no carbon-carbon bonds. This means that it is almost impossible for methanol to give rise to smoke. Particulates, particularly those in the size range of 0.1 microns, are retained in the lungs. They have been shown to be a major hazard, associated with respiratory complaints as well as adverse effects on brain development. In addition, many of the polycyclic compounds which are found in the carbonaceous material of smoke are potent carcinogens. For these reasons and others, particulate emissions are considered to be the next most dangerous following NOx.

2.7 Ozone Reactivity. The mechanism for tropospheric ozone formation involves NO₂, sunlight and hydrocarbon vapors. The latter vary greatly in their ability to promote the ozone-forming reaction. Methanol has very low reactivity when compared with most other hydrocarbons found in the atmosphere.

2.8 Global Warming. Methanol has a lower output of CO₂ per unit of propulsive energy delivered than gasoline or diesel. As long as fossil fuels are used for energy production the global burden of CO₂ must increase. The rate of increase may be lowered by a judicious selection of fuel and its more efficient use. The introduction of methanol as a substitute offers the opportunity to reduce overall CO₂ emissions via engine efficiency increase as well as lower inherent CO₂ production.

2.9 Energy Security. Natural gas is much more widely distributed throughout the world than crude oil, so countries with access to gas can in principle become independent for transportation fuels. China represents an important and exceptional case because it has chosen to manufacture methanol using its extensive coal deposits as feedstock. It is now the foremost manufacturer of methanol in the world, and roughly one third of its output is dedicated to transportation in the form of an extender to gasoline. Any country with natural gas resources but no oil, has the option to synthesize methanol and use it to minimize crude oil imports. This strategy both increases energy security in the event of war, and conserves hard currency.

2.10 Sulfur. As part of the methanol production process, all sulfur compounds are removed from the natural gas feedstock prior to synthesis. Consequently methanol, unlike gasoline or diesel, is completely free of even trace amounts of sulfur. As sulfur is the main cause of reduced exhaust catalyst activity and longevity, the use of methanol offers not only lower costs associated with current vehicle catalyst systems, but also the potential consideration of novel and more cost effective catalysts which have hitherto been ruled out because of high sensitivity to sulfur.

2.11 Fire Properties. The low flame temperature and smoke-free combustion of methanol, coupled with its miscibility with water, mean that methanol fires are relatively benign. Methanol is difficult to ignite and fires are easy to extinguish. For these safety reasons it was the original fuel of choice for the Indianapolis 500 races in the USA. The US EPA has estimated that the adoption of methanol would lead to a 90% reduction in the overall costs of vehicular crashes. (See P. Machiele, "Summary of Fire Safety Impacts of Methanol as a Transportation Fuel" SAE Paper 901113, May 1990)

2.12 Fungibility and Transportation. Methanol can be conveniently shipped by pipeline, rail tankers, barges or bulk marine carriers. It has been produced and traded as a global commodity for more than fifty years, so its properties and associated shipping protocols are well understood.

2.13 Latent Heat of Evaporation. The latent heat of evaporation of methanol is 1100 kJ/kg., which is high compared with that of gasoline or diesel fuel. This property is of importance in determining the temperature within the cylinder, which in turn affects engine efficiency and NO_x production. The higher latent heat promotes lower temperature and therefore lower NO_x emissions.

2.14 Vapour Density. Defined as half the molecular weight, the vapour density of air is approximately 14.5, and methanol is almost identical at 16. This means that in the event of a spillage in a building or restricted area such as floors or basements, methanol vapour neither collects at floor level nor concentrates in a roof space, but will dissipate harmlessly via normal ventilation.

2.15 Energy Density. Fuels are not equivalent in terms of their energy content per unit volume. Energy density is important since it determines the cost of transport and storage, which is a function of volume. For any fuel used in transportation, the tank volume required per vehicular mile travelled is inversely proportional to its energy density. Methanol has a combustion energy of 19.9 MJ/kg which is just less than half the energy content of gasoline or diesel. Consequently a vehicle using methanol would require fuel tanks approximately double the capacity to achieve the same mileage range, or alternatively would require fueling twice as often.

2.16 Human Toxicity. Methanol is toxic upon ingestion. Fortunately there is no problem via skin absorption or inhalation since the body can metabolise methanol faster than it can be absorbed. However, wider availability of methanol gives rise to concerns regarding deliberate unauthorized consumption. This danger is real but can be ameliorated if necessary by the addition of non-potable additives to discourage consumption. It should also be noted that existing diesel and gasoline fuels contain proven carcinogens, to which the public would not be exposed if those fuels were supplanted by methanol. The literature on methanol toxicity is very extensive. References and data are available to interested parties on request.

2.17 Availability, Long Term and Current. As noted above, natural gas is the most cost effective feedstock for methanol and is over three times more plentiful than crude oil. In many parts of the world new gas reserves are not even being sought because there is insufficient demand. Therefore long term global energy supplies may be reasonably forecast to last for the next two centuries based on natural gas alone.

Currently, world production capacity for methanol is nearing 100 million tonnes per annum, and production capacity is expected to grow at approximately 8% per annum. In the near term any limitation, apart from market demand, on new capacity is not the availability of natural gas feedstock, but access to shipping, capital and plant construction. A transition to methanol as a transportation fuel would be slow given the size and scope of the concept, but will not present a long term logistical problem.

2.18 Energy Balance. This factor refers to the input of external energy required to manufacture the fuel in question. Methanol requires energy to produce and the overall process efficiency is around 75% -80% in modern large scale plants.

2.19 Spillages. The effect of methanol spillages on ecosystems in either aqueous or land-based environments has been shown to be negligible. As a metabolite methanol is quickly consumed by many different ambient organisms. Thus one of the major disadvantages of crude oil in terms of insurance costs and environmental damage can be completely avoided.

2.20 Atmosphere. Methanol occurs naturally in the environment and in consequence is a permanent constituent of the atmosphere. Wide scale adoption of methanol as a transportation fuel would inevitably lead to some evaporative losses. Adverse effects from such augmentation of the atmospheric global burden has been shown to be negligible under all foreseeable circumstances.

2.21 Extreme Climate Sensitivity. At extremely low temperatures such as those experienced in the Polar Regions during winter, diesel fuel will congeal, forming a slurry of waxy material and ultimately freezing solid. In order to overcome this problem, diesel-engined trucks, generators and similar heavy equipment which may be exposed to temperatures below 18° F (-8° C) need to be fueled with "winterized diesel" which contains anti-gel additives. The amount of additive required increases as the ambient temperature decreases and may be higher than 10%. In addition, trucks, storage tanks and engines are also preferentially kept warm by low grade heating throughout any period during which they are out of use. These precautions are both a source of risk and expense which can be completely avoided if ignition-improved methanol replaces diesel. The freezing point of methanol is -144° F (-98° C) which is far below any temperature reached on Earth, The advantages of avoiding the need to change fuel or having two supply systems is obvious, and, although largely irrelevant to the State of California, is of particular importance to the military.

2.22 Hydrophylicity. A subtle but important property of methanol lies in its hydrophylic nature. Fuels such as diesel or gasoline contain a mixture of non-polar hydrocarbons characterized by their immiscibility with water and their inability to dissolve polar molecules. This property precludes the use of a large number of additives which might otherwise confer beneficial properties to a hydrocarbon fuel. Methanol on the other hand is highly polar and fully miscible with water, salts and other polar molecules. It can therefore take advantage of many additive effects which are not available to gasoline or diesel fuels.

2.23 Interchangeability with Diesel Fuel. During the initial introduction of ignition-improved methanol a major barrier to acceptance will be its lack of widespread availability. It is therefore an important advantage that methanol fuel can be interchanged with diesel fuel in a vehicle tank without problem i.e., a truck driver can fill up with diesel fuel in the event that Avocet Fuel™ is unavailable and *vice versa*. This property also means that ignition-improved methanol can be stored and dispensed from an existing diesel facility.

3 EMISSIONS BENEFITS

In addition to the large amount of data generated by the various international projects referred to above, which encompassed a variety of engines operating in many climates, limited investigations of engine performance and emissions have been conducted over the past two years by Sonex Research based in Annapolis MD.. Their results were obtained using a single cylinder Honda GD-410 with and without EGR, and showed that acceptable engine performance can be achieved with 2% v/v addition of ignition improver and optimized EGR. Even under the most demanding conditions (low load, high revs) NOx emissions were reduced to 30% to 5% (depending on the precise running conditions) of the emissions measured using diesel fuel, while particulate emissions were uniformly zero. The actual results obtained by Sonex can be made available to CARB if required, noting that these results were obtained using small amounts of Avocet™ made on the laboratory scale. More sophisticated development work awaits production of larger quantities of Avocet™ and will involve investigation of such factors as compression ratio, electronic injection timing, turbocharging and optimal EGR on modern multi-cylinder diesel engines.

4 INTERCHANGEABILITY OF DIESEL AND AVOCET™ FUEL

During the transition between the two fuels, it would be highly desirable if a diesel truck fueled with Avocet™ Fuel could be filled up with diesel fuel on those occasions when the former was unavailable. This would be a convenience of considerable practical value to fleet operators whose vehicles may not always have access to Avocet™ Fuel. Avocet Infinite has made progress in determining the practicability of interchange. Methanol is slightly soluble in diesel fuel and is less dense. Therefore methanol will float on top when the two fuels are admixed in the fuel tank so the engine will encounter either 'pure' diesel or 'pure' methanol. Most modern engines have sufficient versatility built into their ignition control and injectors to cope with the transition. Older retrofitted engines present a more difficult problem and in the early stages of Avocet™ Fuel introduction it may be necessary for fleet owners to establish temporary fueling stations or provide itinerant trucks with supplementary fuel. An additional advantage is the possibility that existing diesel storage tanks may be easily converted to hold Avocet™ Fuel, thus circumventing one of the major problems encountered by the introduction of M85.

5 ECONOMICS

The cost of Avocet™ Fuel is determined by three variables:

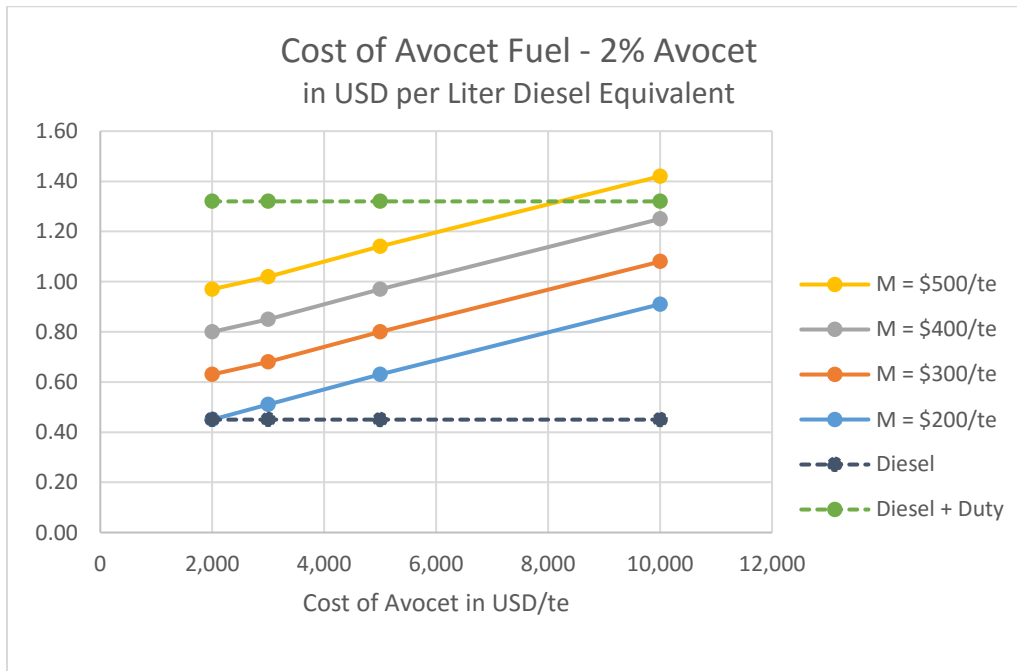
- The bulk price of Avocet™ in USD per tonne (a)
- The percentage v/v Avocet™ required (p)
- The bulk price of methanol in USD per tonne (m).

Given the density of Avocet™ (1.29 g/ml) and methanol (0.791 g/ml), the cost to a supplier/blender (C) per 1,000 liters of Avocet™ fuel in USD = $[(1,000 - 10p) \times (m/1264)] + (10ap/775)$. For diesel equivalence the result must be multiplied by 2.2.

To illustrate the sensitivity of Avocet™ Fuel costing with respect to the three major variables, the following ranges were chosen. The cost of Avocet™ is shown in cents per litre for ease of comparison with pump prices.

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|--|--------|--------|--------|----------|
| Bulk Price of Avocet per tonne (a): | \$2000 | \$3000 | \$5000 | \$10,000 |
| Percentage of Avocet Required (p): | 2% | 3% | 4% | 5% |
| Global Price Methanol FOB per tonne (m): | \$200 | \$300 | \$400 | \$500 |

The results are displayed in graphical form below only for the case where p = 2%. It is currently anticipated that the ignition improver will be available priced in the range \$5000 to \$6000 per tonne. Under these circumstances Avocet™ Fuel can be competitive with diesel fuel provided a favourable tax status can be achieved. Currently methanol is taxed on a volume basis rather than the more equitable energy based rate. Since methanol has slightly less than half the energy density of diesel it therefore suffers a severe disadvantage.



Avocet™ Fuel Cost versus Diesel

The above pricing data for bulk diesel fuel, methanol and Avocet™ result in the following comparison (cents per litre) based on November 2015 prices before tax:

| | |
|--|-----------|
| Current Diesel Fuel per litre (Dec. 2015) | 45 |
| Current Methanol High (diesel equivalent) | 62 (USA) |
| Current Methanol Low (diesel equivalent) | 54 (Asia) |
| Future Methanol Low (diesel equivalent) | 22-33 |
| Avocet Cost @ 2.5% v/v (diesel equivalent) | 14 |

Thus Avocet™ Fuel cost would range from a high 76 cents per litre to a possible low of 36 cents per litre for diesel equivalence. (It should be noted that methanol prices have fallen in parallel with diesel fuel prices over the past twelve months). The price of Avocet™ can therefore be anticipated to allow Avocet™ Fuel to be competitive with diesel in the near future even if diesel fuel prices continue to fall.

The above conclusions do not consider other important factors which will prove to be beneficial to the competitiveness of Avocet™ Fuel:

- Crude oil price increase
- Advantageous Tax rates
- Subsidies
- Technology advances enabling lower additive usage
- Premium value from low emissions

There are cogent reasons why each of the above factors should favor Avocet™ Fuel.

- Crude oil prices have probably bottomed out and will certainly climb again at some point.
- Advantageous tax rates may be applied to encourage alternative fuel use.
- Subsidies may become available for fuels which offer independence from oil.
- Avocet Infinite has patented technology currently being proven which will enable reductions in additive usage to be achieved.
- Regulations are being proposed which will ban diesel fueled vehicles from certain cities.

6 AVAILABILITY OF ENGINES

Existing diesel engines can be retrofitted, and new diesel engines can be designed, to run on Avocet™ Fuel. The need is to provide sufficient incentive to fleet users, stationary generator operators, and original equipment manufacturers (OEMs) to persuade them to do so.

A situation conducive to the acceptance of Avocet™ Fuel exists wherever certain factors are present. Diesel engine manufacturers are under considerable pressure to provide the public with low emission vehicles. Intrinsicly, diesel fuel will give rise to smoke and NO_x, and all diesel fuels contain sulfur compounds. The past thirty years have seen both engine manufacturers and oil companies make great efforts to decrease emissions on the one hand and reduce sulfur levels on the other. These efforts have been partially successful, but inevitably have added expense and compromised engine performance, both being costs which are ultimately suffered by the end user.

Avocet™ Fuel offers a way for the engine designer to minimize emissions of smoke and NO_x while improving engine performance and reducing costs. This is a potent combination of factors which can be enough to convince an OEM to invest the development resources needed. Avocet Infinite Plc. has begun the process of dialogue with OEMs, and will soon be in a position to provide Avocet™ Fuel for full scale testing purposes. The dialogue process will include conversion or design of engines powering construction equipment, farm vehicles, diesel powered generators, marine propulsion units and many other applications where diesel power is widely used.

Retrofitting fleets is a very direct and effective route to initial Avocet™ marketing, as mentioned above. The main issue of concern arises from the fact that methanol is chemically very dissimilar to diesel fuel. Methanol is a single pure polar liquid, while diesel fuel is a complex mixture of non-polar hydrocarbons. Since diesel engines and their fuel supply components have been designed and optimized for over a hundred years to operate with diesel fuel, it is not surprising that some of these components are incompatible with methanol. Provided such materials sensitivity is recognized, gaskets, pumps, tubing etc. which may be attacked by methanol can be replaced by suitably inert components. Such retrofitting has been successfully accomplished many times in the past, most notably by the MASSCAR fleet of buses operated by the Los Angeles Rapid Transit District in the late 80's and early 90's.

Another issue is the lower energy density of methanol which necessitates increasing fuel injection rates by a factor of 2.2 for equivalent performance. Although with older engines this may require replacement of injectors, most modern engines can cope with the requirement using existing software and electronic engine control. For equivalent mileage, tank volume will need to increase.

7 TECHNICAL ADVANCES

There are three technical considerations which offer opportunities to decrease the amount of Avocet™ required for Acceptable Engine Performance (AEP). Two of these have been patented by Avocet Infinite Plc and Avocet Solutions Inc. and are in the process of feasibility demonstration. For patent protection purposes no details can be exposed here, but both promise to lower the required percentage of Avocet to the region of 1% or less. The third relies on engine optimization, which includes turbocharging, exhaust gas recirculation, compression ratio, and injection timing. Most modern diesel engines benefit from electronically controlled injection and turbocharging. Both will enable the amount of ignition improver required for AEP to be minimized. A factor which should enable reduction of ignition improver

is Exhaust Gas Recirculation (EGR). Most modern engine incorporate this feature, which can add to the overall efficiency of engine operation.

The precise amount of Avocet™ needed for optimal running of specific engine configurations will perforce be the subject of development programs to be undertaken in conjunction with OEMs. At least some of the foregoing will be applicable to retrofitted older engines.

8 REGULATIONS AND POLITICS

Engines, fuels and the vehicles they power are heavily regulated by nearly all countries for safety, economic and political reasons. Although there is no reason to anticipate that Avocet™ Fuel will be unable to satisfy regulatory requirements, it is inevitable that obtaining necessary approvals will take considerable time and effort. This is particularly true for taxes. Some enlightened countries already tax methanol and other fuels on an energy density basis, which is rational, rather than on a volume basis, which greatly benefits gasoline and diesel. Ideally, as a nascent and environmentally benign fuel, methanol should be untaxed or even encouraged by subsidy as in the EU.

Bringing about a situation where methanol receives sympathetic treatment will need careful persuasion of the relevant Governmental agencies. This will not be a fast track process.

One potential snag involves the existence of a large global trade in chemical grade methanol. In the future, if fuel methanol is manufactured to be less pure, and therefore cheaper than chemical grade, and if it is either subsidized, untaxed, or taxed at a reduced rate (including possibly lower tariffs), then there will be a powerful inducement for unprincipled traders to convert fuel methanol to chemical methanol by distillation and so circumvent payment of taxes. This is analogous to the difference in tax status between home heating oil and agricultural diesel on the one hand versus on-road transportation diesel on the other. This difference is addressed by legislating red dye to denote heating oil and making it illegal to use home heating oil for transport use. Similarly we propose, where appropriate, to use a blue dye to denote fuel methanol.

CONCLUSION

There is no technical reason why ignition improved methanol should not be the winner in the competition to replace diesel fuel. Its merits have been well proven in a variety of engine tests in many parts of the world. Modern high volume production of ignition improver coupled with the availability of low priced fuel methanol based on widely available low cost supplies of natural gas will enable ignition improved methanol to compete cost effectively with diesel fuel. Modern diesel engines will be able to operate cleanly with high efficiency using the new fuel: the time is ripe for a switch to methanol.