European
Automobile
Manufacturers
Association

ACEA Position Paper on Methanol as a Gasoline Blending Component

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European Automobile Manufacturers Association

STATUS CONCERNING METHANOL

In many of today's discussions about alternative fuels, the role of methanol continues to be frequently discussed. One of the main reasons for this is that the production of methanol is relatively easy and cheap. Any kind of energy carrier (eg biomass, natural gas, coal) can be transferred via synthesis gas (H_2, CO) into methanol. Given that such feedstock are cheap, methanol might be even cheaper than gasoline on an energetic base [(1)]. In addition, for example in China, methanol is seen to have a potential role in domestic energy security and to support (Chinese) regional development.

Despite these apparent advantages, methanol as a fuel component remains of low interest worldwide. After its European introduction in the 1980s the use of methanol was not further developed. Only a few countries still use methanol (coal as feedstock) and certain regions in China are perhaps the most important and most challenging ones.

The methanol market in China is fragmented due to the fact that besides two national standards for M100 (pure methanol for blending) and M85 (85% methanol blending with 15% gasoline), several regional standards exist (eg M5, M10, M15, M50). In addition, fuel samples have been taken in China that were labelled as 'M15' but, on subsequent analysis, were found to contain up to 20% methanol. A China national M15 standard was being prepared but its status is now unclear.

In the latest version of the World-Wide Fuel Charter (WWFC5) [(2)] the worldwide automobile industry (represented by the European Automobile Manufacturers' Association, the Japan Automobile Manufacturers Association, the Truck and Engine Manufacturers Association and the Alliance of Automobile Manufacturers) strongly requests a ban on the use of methanol as a gasoline blending component. Other oxygenates like ethers (ETBE, MTBE) are preferred. Ethanol up to 10%v/v is allowed if permitted by existing regulation, provided that the blend-stock ethanol meets the requirements of the E100 Guidelines under the World-Wide Fuel Charter [(3)]. Methanol is not allowed due its nature of being an aggressive

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(1) See: Asia Methanol Market Outlook 2012, http://www.icis.com/Articles

(2) See: http://www.acea.be/publications/article/worldwide-fuel-charter

(3) See: Worldwide Fuel Charter, www.acea.be

material that can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers.

This paper justifies this position with various facts and figures.

VEHICLE IMPACTS USING METHANOL

The vehicle impact when exposed to methanol in gasoline is evaluated based on the status quo, ie methanol is present as a fuel component in gasoline that may be used in conventional gasoline engines that are not specifically designed for a certain methanol blend rate.

Methanol shows some beneficial fuel properties, for example a high octane number (RON > 104; MON > 90) which will result, in specifically designed engines, in a high efficiency of the combustion (4). In such particular engines, lower emissions of carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx) have been achieved (5).

On the other hand, methanol has several severe disadvantages, due to the chemical and physical properties (small polar molecule). Such disadvantages occur independently of the type of engine methanol may be used in, and become increasingly severe with the content of methanol in the blend.

1. **Calorific value (20 MJ/kg versus 44 MJ/kg):**

   Given that the fuel will be used in conventional gasoline engines, the lower calorific value will result in an accordingly lower mileage pre unit of fuel consumed. There is no efficiency gain if methanol is used. Since the engine management computer is not adjusted for a low calorific value fuel, the driver will also suffer, for example, from a loss in engine power resulting in poor acceleration, smoothness of driving etc.

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(4) See: SAE 2002-01-2743.

(5) See: Journal of Scientific & Industrial Research Vol. 62, January-February 1990,pp 97- 105; ISSN 1047-3289 *J. Air Waste Manage.* Assoc. 40:747-756 (1990).

2. **Theoretical air/fuel mixture (6.5 versus 14.6):**

   The high oxygen content of methanol leads to a much lower air-to-fuel ratio. This implies an inherent risk of lean mixture that would exceed the range of the engine calibration. In such a case combustion becomes rather less efficient, pollutant emissions might increase and customers might see the OBD light illuminated on the vehicle dashboard, informing them to seek repair. ***Figure 1*** shows that the impact on emissions of carbon monoxide (CO), hydrocarbons (HC) and oxides of nitrogen (NOx) is considerable if the injection pressure is not adjusted to the air-fuel mixture and calorific value of the fuel blend. This impact can occur from a baseline injection pressure of 0.33MPa due to the higher demand resulting from the lower calorific value of methanol gasoline blend.

3. **Latent heat of vaporization (1.2 MJ/kg versus 0.2 … 0.8 MJ/kg):**

   The high latent heat of vaporization has a cooling effect and this characteristic results in poor cold engine startability. The ambient temperature at which conventional port fuel injected engines will just start is around 10°C. Below this temperature a 100% methanol fuel will not run in conventional engines (6).

4. **Permeation:**

   High permeation involves material challenges like swelling stress of elastomers and gasket materials as well as higher evaporative emissions (see ***Figure 2***). Resulting higher evaporative emissions means a vehicle will not comply with the current evaporative emission regulation (which is likely to get tougher within the Euro 6 timeframe).

5. **Corrosion:**

   Methanol can cause corrosion of metallic components of fuel systems and the degradation of plastics and elastomers (see ***Figure 3*** and ***Figure 4***).

(6) See: V. Battista, et al., 'Review of the Cold Starting Performance of Methanol and High Methanol Blends in Spark Ignition Engines: Neat Methanol', SAE Paper 902154, 1990; L. G. Dodge, et al., 'Development of an Ethanol-Fuelled Ultra-Low Emissions Vehicle', SAE 981358, 1998.

The impact of degradation on elastomers' performance is severe. Besides resulting in higher evaporative emissions it will also result in fuel leakage in areas of the fuelling system where these materials are commonly used.

In particular the corrosion of aluminium will affect fuel pumps and valves. The related corrosion products will lead to injector coking if no suitable additive is added to the fuel. Methanol is also aggressive against some magnesium-based metallic alloys.

6. **Azeotropic increase of vapour pressure:**

   Due to the formation of azeotropic mixtures of methanol and other gasoline components, the addition of 2-3% methanol leads to a significant increase in the vapour pressure as well as a change in the fuel distillation behaviour.

7. **Polarity/strongly hygroscopic:**

   Due to its polar nature, phase separation/miscibility has to be considered in any case. With increasing content of methanol, the tendency to separate increases until a maximum is reached. Depending on the aromatic content of the base fuel the absolute miscibility will differ (see ***Figure 5***) and can reach ambient temperatures of the order of 0°C / -5°C. At this temperature two phases methanol and gasoline will be present with respective impact on materials and combustion, as described above.

   In case of water or moisture being present this becomes even worse; 0.3% of water is sufficient to decrease miscibility to 30°C (see ***Figure 6***). In order to overcome this challenge a suitable co-solvent needs to be applied in the right dosage (up to 20% of the actual methanol content). In addition to ensuring this in the entire tank infrastructure, it also might imply economic challenges. If the need for co-solvents is neglected this can result in a total de-mixing of the water-methanol phase and the hydrocarbon phase causing serious vehicle operation problems.

8. **Risk of incompatibilities versus engine oil, risk of emulsions formation, enrichment of additives, deposit forming:**

   Fleet tests in Europe have shown in the past necessity of special engine oils to be used for methanol fuels (M15 … M90). Otherwise severe coking in manifold, inlet valves, piston rings etc. as well as wear in the cylinder bore will occur. The latter might lead to a complete engine failure [DGMK-reports 260-03 and 260-13].

9. **Methanol and formaldehyde emissions:**

   Formaldehyde is the main combustion product of methanol if the combustion is insufficient. In addition unburned methanol reaches the exhaust. Therefore the amount of methanol and formaldehyde in the emissions for methanol is much higher than for conventional gasoline (7). In an older publication (SAE 881679), emissions of formaldehyde of a single cylinder SI engine showed an exponential increase when the methanol concentration in the fuel was varied from zero to 100% (see figure 23 on page 22 of the document). The effect is in principle the same for lean, stochiometric or rich equivalence ratios (8).

HEALTH IMPACTS

Methanol is highly toxic for humans via acute and chronic pathways.

- **Pharmacokinetics:**

Absorption: methanol is readily absorbed by all routes after ingestion, inhalation or dermal contact.

Distribution: methanol rapidly distributes in the body with the body fluid (blood, eye fluid, urine).

Metabolism: methanol is enzymatically oxidised in the human liver. Metabolic products include formaldehyde and formic acid. Formic acid is toxic because it inhibits essential enzymatic processes at the cellular level causing a lack in the oxygen supply and a disturbance of the acid-base balance, among a variety of other metabolic dysfunctions.

(7) Ronald L. Williams, Frank Lipari and Robert A. Potter, 'Formaldehyde, Methanol and Hydrocarbon Emissions from Methanol-fuelled Cars', J. Air Waste Manage. Assoc., 40, 1990, 747-756.

(8) A. Sapre, Properties, Performance and Emissions of Medium Concentration Methanol-Gasoline Blends in a Single-Cylinder Spark Ignition Engine, SAE 881679, 1988.

- **Acute toxicity:**

Acute methanol intoxication is manifested initially by signs of narcosis. This is followed by a latent period in which formic acid accumulates in the body causing metabolic acidosis. Severe abdominal, leg, and back pain occur and visual degeneration can lead to blindness. Poisoning by non-lethal doses can be described in three stages:

1) Narcotic stage similar to ethanol;
2) Latent period of 10-15 hours;
3) Visual disturbances and central nervous system lesions. Visual disturbances can lead to blindness due to edema of the retina and destruction of the optical nerve. Central nervous system lesions include headache, dizziness, abdominal, back, and leg pain, delirium that can lead to coma, and nausea. Formic acid production causes severe metabolic acidosis.

The ingestion of as little as 10-15 ml pure methanol can cause irreversible blindness and depression of the central nervous system as well as metabolic acidosis. 30ml are potentially fatal although the median lethal dosage is typically 100ml (1-2ml methanol / kg body weight).

Methanol exposure to eyes, skin and upper respiratory tract can result in irritating effects, eg redness of eyes, lacrimation, cough, skin degreasing and secondary inflammation.

- **Sub-chronic / chronic toxicity:**

Chronic exposure to methanol, either orally or by inhalation, causes headache, insomnia, gastrointestinal problems, and blindness.

The inhalation of methanol with an exposition of 1000ppm, as well as an extended contact with the skin may lead to a significant resorption of methanol resulting in systemic toxic effects.

CONCLUSIONS & RECOMMENDATIONS

In conclusion it has to be stated that the existing vehicle fleet is not capable of using high methanol blends. Due to the above mentioned drawbacks for direct blending of methanol in gasoline, the existing ban of methanol, respectively low usage (less than 3 vol %) in most of the existing fuel standards worldwide, is strongly confirmed and highly recommended.

In case methanol should be used widely in the transportation sector, its use as intermediate for etherification to MTBE/TAME or as feedstock for a MTG-process (methanol to gasoline) is strongly preferred. Both components, as well MTBE/TAME as MTG gasoline, are products that can be used in the entire fleet of gasoline vehicles.

FIGURES

Figure 1: Impact of injection pressure for MPI engines on exhaust pollutant emissions to adjust for different heating value and air to fuel ratio, baseline (0) is at 0.33MPa. Source: OEM in-house data.

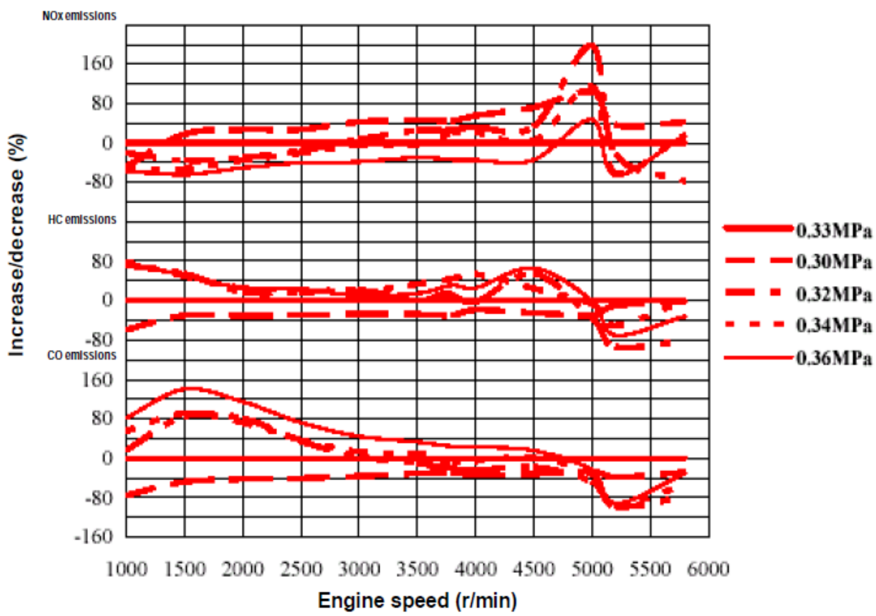
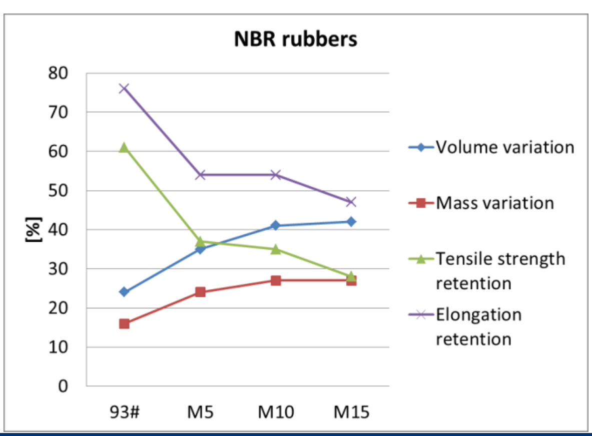


Figure 2: Impact of different methanol blends on different elastomers (rubber components). Source: OEM in-house data.



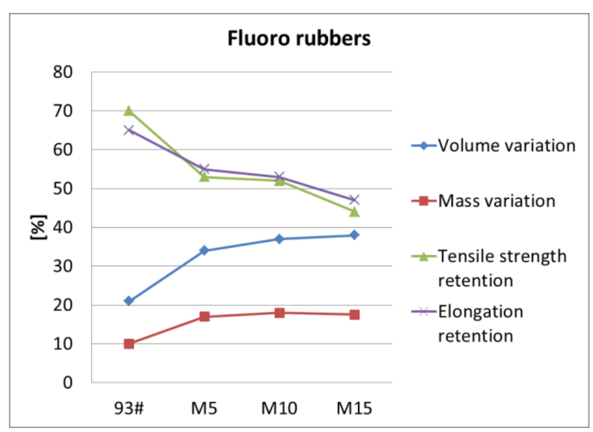


Figure 3: Impact of different methanol blend fuel on evaporative emissions. Source: OEM in-house data.

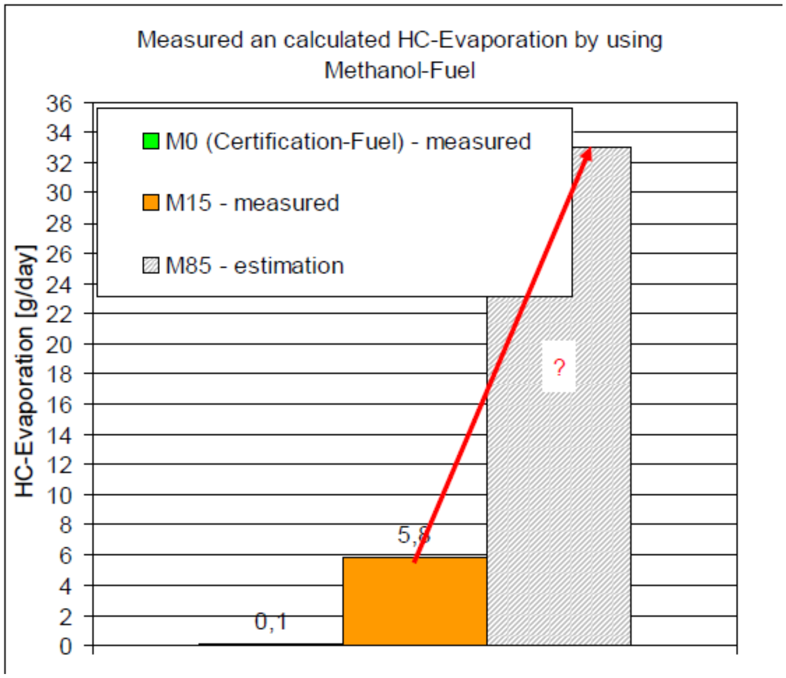


Figure 4: Corrosion impact of methanol blends with different inhibitors (1, 2, 3) on metals. Source: OEM in-house data.

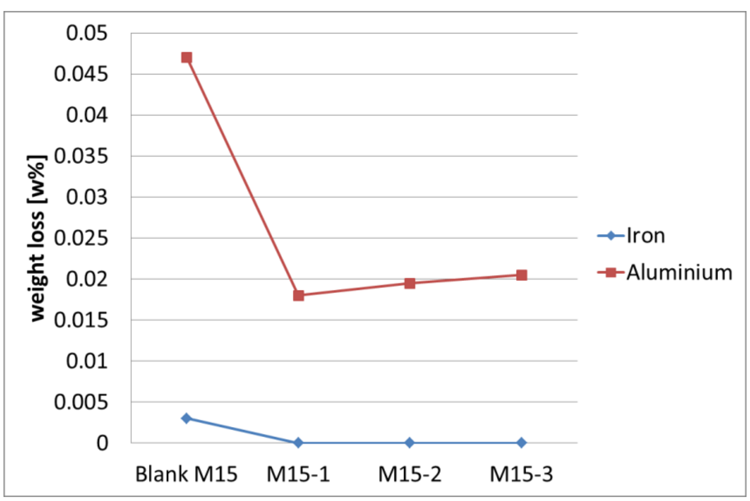


Figure 5: Miscibility methanol in different base fuels behaviour without water. Source: OEM in-house data.

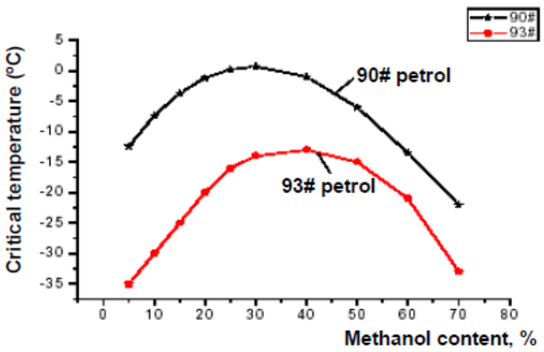


Figure 6: Impact of water on different methanol blends and phase separation behaviour. Source: OEM in-house data.

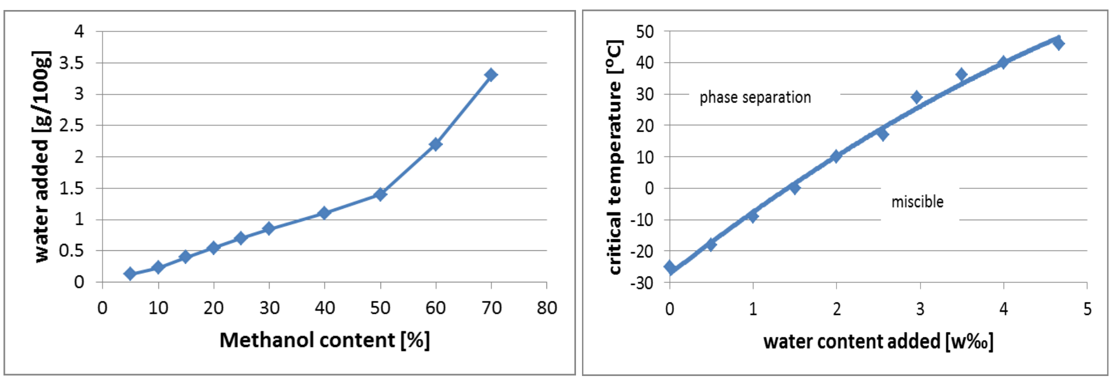


Figure 7: The effect of methanol blending on formaldehyde exhaust emissions.

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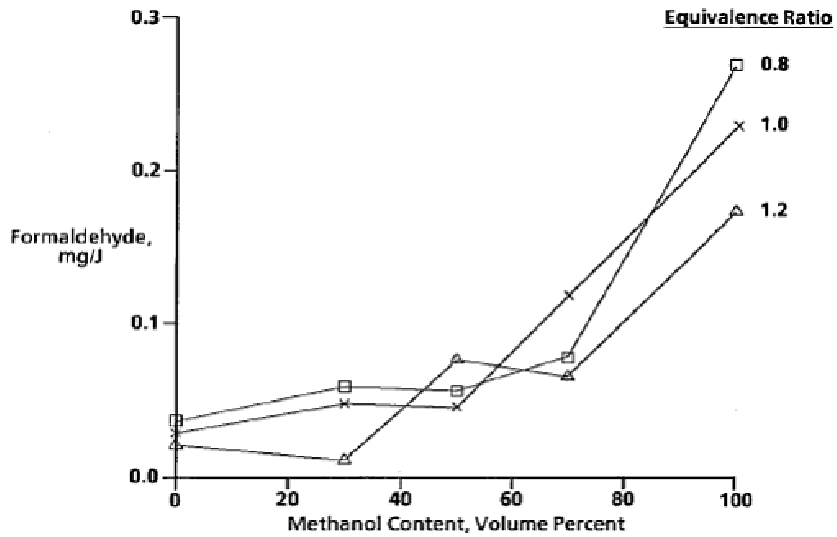

Figure 23. The Effect of Methanol Addition on Formaldehyde Emissions

European Automobile Manufacturers Association

ABOUT ACEA

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ABOUT THE EU AUTOMOBILE INDUSTRY

- Some 12.1 million people - or 5.6% of the EU employed population - work in the sector.
- The 3.1 million jobs in automotive manufacturing represent 10.4% of EU's manufacturing employment.
- Motor vehicles account for €396 billion in tax contribution in the EU15.
- The sector is also a key driver of knowledge and innovation, representing Europe's largest private contributor to R&D, with €41.5 billion invested annually.

European Automobile Manufacturers' Association – ACEA
Avenue des Nerviens 85 | B-1040 Brussels | www.acea.be
T +32 2 732 55 50 | M +32 485 886 647 | F +32 738 73 10 | info@acea.be | @ACEA_eu