report no. 3/08

Guidelines for blending and handling motor gasoline containing up to 10% v/v ethanol

Guidelines for blending and handling motor gasoline containing up to 10% v/v ethanol

Prepared for the CONCAWE Fuels Quality and Emissions Management Group by its Special Task Force, FE/STF-24:

B. Engelen (Chair) L. Baldini J. Baro J. Delgado Diestre N.G. Elliott E.B.M. Jansen

- P-M. Martinez Sánchez
- S. Mikkonen
- M. Mortier
- P. Scorletti
- R. Terschek
- J. Woldendorp

K.D. Rose (Technical Coordinator) N.D. Thompson (Technical Coordinator)

Reproduction permitted with due acknowledgement

© CONCAWE Brussels April 2008

ABSTRACT

This report provides guidance on handling and blending ethanol at up to 10% v/v concentrations in motor gasoline. The major challenges associated with ethanol-containing gasolines are discussed as they relate to the conformity of the finished fuel to typical specifications, especially those in the European unleaded motor gasoline specification (EN228). This report focuses on the production, distribution, and supply of motor gasoline containing up to 10% v/v ethanol and does not address issues related to higher ethanol blends, specifically E85 fuels (up to 85% v/v ethanol in gasoline).

For the purposes of this report, the terms motor gasoline and unleaded petrol (as defined in European Standard EN228) are considered to be synonymous.

KEYWORDS

Ethanol, motor gasoline, unleaded petrol.

INTERNET

This report is available as an Adobe pdf file on the CONCAWE website (www.concawe.org).

NOTE

Considerable efforts have been made to assure the accuracy and reliability of the information contained in this publication. However, neither CONCAWE nor any company participating in CONCAWE can accept liability for any loss, damage or injury whatsoever resulting from the use of this information.

This report does not necessarily represent the views of any company participating in CONCAWE.

CONTENTS			Page	
SUMMARY				
1.	INTRODU 1.1. 1.2.	JCTION MAJOR CHALLENGES OTHER CHALLENGES	1 1 1	
2.	CHALLEI 2.1. 2.2. 2.3. 2.4. 2.5. 2.6. 2.7. 2.8. 2.9. 2.10. 2.10.1. 2.10.1. 2.10.2. 2.10.3. 2.11. 2.11.2. 2.11.2. 2.11.3. 2.11.4. 2.11.5. 2.11.6. 2.12.	NGES AND GUIDELINES VAPOUR PRESSURE DISTILLATION OCTANE HYDROCARBON BLENDSTOCK QUALITY HYDROPHILIC NATURE REMOVAL OF DIRT MATERIAL COMPATIBILITY, CORROSION AND PERMEABILITY SULPHATE ISSUES DENATURANTS ISSUES TRANSPORT OF ETHANOL BLENDS Transport via Multi-Product Pipelines Transport by Road and Rail Transport by Barge SAFETY & FIRE FIGHTING MEASURES Safe Handling Surface Spills and Leaks Fire Protection and Fire-Fighting Agents for Fires Involving Ethanol/Gasoline Blends Storage Sources of Ignition Drain or Waste Water Handling ADDITIVE EFFECTS	2 2 3 4 5 5 7 8 11 11 11 11 12 12 12 12 12 12 12 12 12	
3.	BLENDIN 3.1. 3.2.	IG GUIDELINES REFINERY BLENDING TERMINAL BLENDING	15 15 15	
4.	GLOSSA	RY	16	
5.	ACKNOWLEDGMENTS		17	
6.	REFERENCES		18	

SUMMARY

The production of motor gasolines containing ethanol will increase in Europe as a consequence of the EU Biofuels Directive 2003/30/EC and the subsequent EU Fuel Quality and Renewable Energy Directives that are expected to be adopted in 2008. The increased use of ethanol introduces new challenges to refinery and vehicle fuel systems and to an increased need for good housekeeping practices throughout the gasoline supply and distribution system. This report provides guidelines for the production, blending, distribution, and supply of motor gasolines containing up to 10% v/v ethanol.

1. INTRODUCTION

There is relatively little experience with biofuels in Europe although the production of motor gasoline¹ containing biomass-derived products, especially ethanol, is increasing as a result of the EU Bio Fuels Directive 2003/30/EC and the subsequent EU Fuel Quality and Renewable Energy Directives that are expected to be adopted in 2008. The increased use of ethanol introduces new challenges to refinery and vehicle fuel systems and an increased need for good housekeeping practices throughout the motor gasoline supply and distribution system.

Although new vehicle technologies (Flexible Fuel Vehicles) have been developed that can use fuel blends containing up to 85% v/v ethanol (also known as Ethanol (E85)), this document only addresses the challenges of motor gasoline blends containing up to 10% v/v ethanol.

Several general references on ethanol and ethanol/gasoline blends are also included in the bibliography section. [1,2,3,4,5,6]

1.1. MAJOR CHALLENGES

The chemistry of ethanol is very different from that of hydrocarbon fuels. As a result, blending ethanol into hydrocarbon fuels introduces some specific challenges that must be carefully addressed in the production, blending, distribution, and supply of motor gasolines, including:

- Effect of ethanol on vapour pressure, octane rating, distillation, and related properties,
- Quality of the hydrocarbon blendstock for ethanol blending to ensure fit-forpurpose motor gasoline performance, and
- Tendency of ethanol to increase the dissolved water content of motor gasoline.

1.2. OTHER CHALLENGES

Other challenges can also be expected as the use of ethanol increases. In general, these challenges are managed through proper specifications, procedures, and good housekeeping practices, and include:

- Removal of dirt, rust, and other solid contaminants,
- Compatibility of motor gasoline containing ethanol with materials commonly used in refinery, distribution, and fuel supply systems, especially the permeability and corrosion of these materials,
- Sulphate issues product handling and injector plugging in vehicle fuel systems,
- Denaturants issues,
- Transport of gasolines via multi-product pipelines,
- Safety and fire-fighting measures,
- Effects of corrosion inhibitor additives,
- Guidance on ethanol blending at refineries and terminals.

¹ For the purposes of this report, the terms motor gasoline and unleaded petrol (as defined by European Standard EN228) are considered to be synonymous.

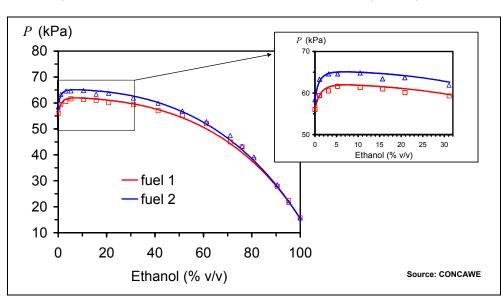
2. CHALLENGES AND GUIDELINES

2.1. VAPOUR PRESSURE

Although ethanol has a lower molecular mass than most of the hydrocarbons used in motor gasoline, ethanol is a liquid rather than a gas at ambient temperatures and pressures due to strong intermolecular hydrogen bonding interactions between ethanol molecules. These interactions are either very weak or absent in hydrocarbon mixtures. As a consequence, pure ethanol has a much lower vapour pressure (15-20kPa) than motor gasoline.

However, when ethanol is dissolved into a predominantly hydrocarbon mixture such as motor gasoline, these same intermolecular interactions increase the volatility of the hydrocarbon-ethanol blend, most significantly at low concentrations of ethanol. For example, the maximum increase in vapour pressure occurs at an ethanol concentration of only about 1-5% v/v ethanol in a hydrocarbon blend. This positive deviation from ideal mixture behaviour (Raoult's Law) occurs because the intermolecular interactions between ethanol and hydrocarbon molecules are less than they are in the two pure liquids making it easier for molecules to volatilize from the ethanol-hydrocarbon mixture.

As shown in **Figure 1**, addition of only about 2% v/v of ethanol into unleaded gasoline can increase the vapour pressure of the mixture by 6-8 kPa potentially leading to non-compliance with the requirements of European Standard EN228, EU's quality standard for motor gasoline. The vapour pressure increase with low concentrations of ethanol is also observed to be larger when the vapour pressure of the base gasoline is reduced.



Vapour Pressure of Mixtures of Unleaded Gasoline 95 (ULG95) and Ethanol

Because of this effect, mixing hydrocarbon-only and ethanol-containing gasolines in the fuel distribution and supply system, for example, can also result in a vapour pressure increase that can cause the mixture to exceed vapour pressure specification limits. For this reason, it is recommended that hydrocarbon-only motor

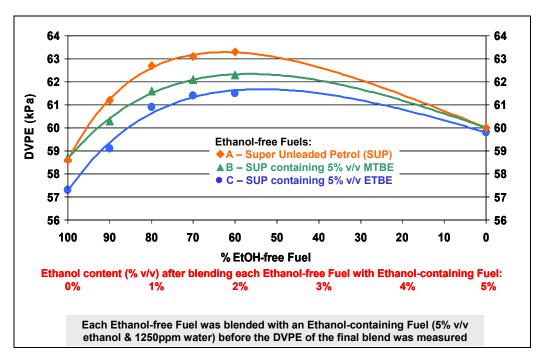
Figure 1

gasoline is not re-introduced into a section of the fuel distribution system once ethanol-containing gasoline has been introduced. Mixing of hydrocarbon-only and ethanol-containing gasoline cannot be avoided in the vehicle's tank, however, and cannot be controlled by fuel suppliers' procedures.

Figure 2 shows the change in Dry Vapour Pressure Equivalent (DVPE) of three different ethanol-free gasolines when blended with a 5% v/v ethanol-containing gasoline (also containing 1250 ppm of water). The final ethanol content of these blends ranged from 0% to 5% v/v ethanol.



Dry Vapour Pressure Equivalent (DVPE) of Blends of Ethanol-free and Ethanol-containing Motor Gasolines



Source: DGMK [7]

At the first introduction of ethanol-containing gasolines into the fuel distribution system, the vapour pressure for delivered fuel should be targeted with an extra margin in vapour pressure in order to ensure that marketed fuels do not exceed vapour pressure specifications at the service station. From experience, this is more easily managed in the winter time. Following first introduction, seasonal transitions during the spring and autumn periods must also be carefully managed.

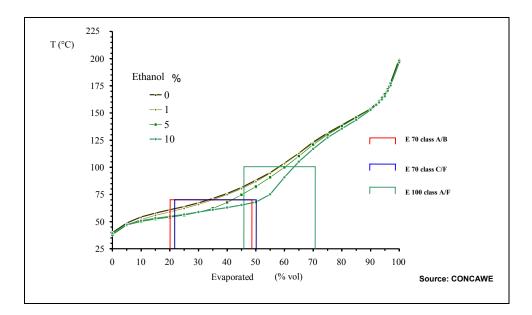
2.2. DISTILLATION

In addition to its impact on vapour pressure, ethanol also changes the distillation characteristics of the gasoline/ethanol mixture and the evaporated fraction at 70°C (E70) is changed most significantly.

As shown in Figure 3, E70 increases by about 8% v/v when 5% v/v ethanol is blended into base gasoline. An 18% v/v increase in E70 is observed when 10% v/v

ethanol is blended into base gasoline. These changes are significant and can be compared to the 28% v/v overall range of E70 that is defined in the EN228 specification for all volatility grades (for example, for Class A motor gasolines, the allowed E70 range is 20 to 48% v/v, or 28% v/v, in the EN228 specification).





2.3. OCTANE

Equation 1 can be used to estimate the RON and MON of gasoline blended with ethanol based on the ethanol content and properties of the base and blended fuels.

Equation 1: ON_{g+a}

$$ON_{g+a} = \frac{C_a}{100} \cdot I_a + (1 - \frac{C_a}{100}) \cdot ON_g$$

where:

ON_{g+a} is the octane number (RON or MON) of the gasoline-ethanol mixture,

 ON_{g} is the octane number (RON or MON) of the base gasoline,

 $C_{\rm a}$ is the ethanol content (% v/v), and $I_{\rm a}$ is the octane blending index of ethanol.

(C_a and I_a are dependent variables).

The octane blending index of ethanol, I_a , depends on the properties of the base motor gasoline, and can only be determined by preparing and measuring the properties of trial blends.

Since the octane of ethanol is higher than that of gasoline, there will normally be a boost in motor gasoline octane after blending with ethanol and typical values are shown in the table:

Typical Boost in Octane Number After Ethan		mber After Ethanol Addition
	RON	MON
2% v/v ethanol	0.5	0.3
5% v/v ethanol	1.3	0.8

Notes:

- (1) The octane number boost depends upon the composition of the base gasoline, particularly its aromatics content.
- (2) The octane blending index for ethanol increases as the octane number of the base gasoline decreases.

2.4. HYDROCARBON BLENDSTOCK QUALITY

For refiners producing motor gasolines containing ethanol, an important consideration is the production and properties of the hydrocarbon blendstock for ethanol blending, often called a Blendstock for Oxygenate Blending (BOB). This hydrocarbon blendstock must be produced with properties that are appropriately adjusted in order to take into account any changes that will occur after the ethanol has been added, either at the refinery or terminal (see Section 3).

The current EN228 petrol specification permits the addition of up to 5% v/v ethanol and this specification and its corresponding national annexes apply to motor gasoline sampled at the service station nozzle. For this reason, the following parameters should be considered when manufacturing the hydrocarbon blendstock intended for blending with ethanol:

- Percentage volume of ethanol to be blended into the hydrocarbon blendstock
- The properties of the final motor gasoline that will be impacted by adding ethanol to the hydrocarbon blendstock, such as:
 - Vapour pressure (see Section 2.1)
 - Distillation characteristics (see Section 2.2)
 - Octane number (see Section 2.3)
 - Oxygen content
- Seasonal adjustments and other local volatility requirements.

2.5. HYDROPHILIC NATURE

Due to the presence of the hydroxyl (-OH) group, ethanol exhibits strong hydrogen bonding interactions, very similar to those found in liquid water. This effect means that ethanol is hydrophilic in nature and has a strong affinity for water.

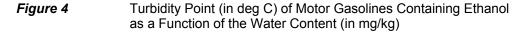
As a consequence, ethanol has a tendency to absorb water that may be present in distribution, storage, and vehicle fuel systems even when the ethanol is only present at low concentrations in gasoline. This tendency means that extra precautions are required especially when ethanol is first introduced into the supply and distribution

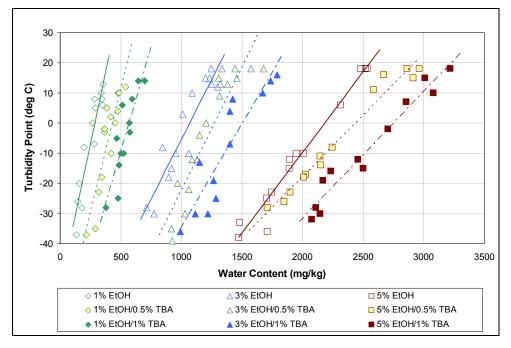
system and good housekeeping practices are needed thereafter following its first introduction.

The turbidity point, or haziness, is a good measure of the onset of phase separation as a function of the water content of the fuel blend. If excess water is present, ethanol can increase the concentration of dissolved water in gasoline before phase separation (turbidity) is observed.

As shown in **Figure 4**, at the same turbidity point, the dissolved water content of gasoline increases as the ethanol concentration in the blend increases. At the same ethanol content, the addition of a co-solvent, tertiary-(n-butyl) alcohol (TBA) in this example, increases the dissolved water content of the gasoline even further before the onset of haziness or turbidity.

For example, at 1% v/v ethanol and at -10°C, gasoline becomes hazy at a water concentration of 200 mg/kg. At an ethanol content of 5% v/v and at the same temperature, haziness occurs at a much higher dissolved water concentration of about 2000 mg/kg. In other words, ethanol is an effective co-solvent for dissolving water in hydrocarbon fuels.





Fuels tested in this study included:

- Regular unleaded motor gasoline with vapour pressure ~90 kPa and 25% aromatics
- Regular unleaded motor gasoline with vapour pressure ~90 kPa and 35% aromatics
- Super unleaded motor gasoline with vapour pressure ~60kPa and 25% aromatics
- Super unleaded motor gasoline with vapour pressure ~60 kPa and 35% aromatics

All fuels contained no ETBE or MTBE and the turbidity points were tested twice at each condition. (Source: DGMK [7])

If phase separation does occur, the gasoline in the upper phase will usually contain less ethanol than does the lower phase and may be out of specification for other key properties, such as octane, vapour pressure, and distillation properties.

The lower phase will usually contain ethanol (\sim 70%), water (\sim 20%), and hydrocarbons (\sim 10%). Any water soluble denaturants, such as methanol, may also be more soluble in the water phase than in the gasoline phase. Obviously, vehicles will have difficulty running on a phase-separated mixture of this kind.

If it is found that phase separation has occurred, all dispensers should be immediately deactivated and it is imperative that water bottoms are removed from the storage tank. The remaining hydrocarbon mixture should be tested to ensure that it is still in specification and, if not, appropriate action should be taken to remedy the situation. Since the water bottoms will contain some level of ethanol and hydrocarbons, this mixture may be flammable and appropriate precautions should be taken during handling and disposal, consistent with local safety and environmental regulations.

Extra precautions are also needed to avoid water entering tanks. Tank cleaning, regular water checks and, if necessary, tank draining are advisable. It is also recommended that tanks are adequately dried before their first use. Terminal storage tanks should have fixed roofs with a floating internal cover. In-tank blending is not recommended unless water entry is properly controlled. When checking gasoline storage tanks for water, ethanol-compatible water paste should be used in order to guarantee proper indication.

Because existing automatic water detection systems are disabled in the presence of ethanol-containing gasoline, the use of ethanol in pipeline systems is not recommended without taking special precautions (see 2.10.1). Ethanol-containing gasoline can also interfere with the protection offered by commonly used corrosion inhibitors in pipeline systems.

2.6. REMOVAL OF DIRT

Ethanol-gasoline blends may loosen sediment and sludge from storage tanks and filling lines due to the solvency of the blend. For this reason, tanks should be clean and free of water and sediment before they are used for ethanol-containing gasolines.

The first load of ethanol-containing gasoline should fill the tank to at least 80% capacity. If this is not accomplished with the initial load, a second load should be brought in as soon as possible after the first load. This allows the solvency of the ethanol-gasoline blend to loosen any sediment and varnish type deposits from the sides and upper portions of the tank.

It is also recommended that storage tanks are kept as full as possible during the first seven to ten days to accelerate this process and to run a few litres of fuel product through each dispenser to flush the system. As soon as the dispensed fuel product is clear and bright, the tank can be placed back in service. Dispenser filters should also be changed if needed and $10\mu m$ (nominal) ethanol-compatible dispenser filters are recommended for this purpose.

2.7. MATERIAL COMPATIBILITY, CORROSION AND PERMEABILITY

Only the fuel distribution system is considered in this section, and not the fuel system components commonly used on vehicles.

With respect to the compatibility with materials typically used in fuel supply and distribution systems, ethanol is different from fuel hydrocarbons in three important ways:

- The presence of the polar hydroxyl (-OH) group,
- The relative size of the ethanol molecule, and
- The higher conductivity of ethanol (and of ethanol/gasoline blends).

Because of these differences, various components in the fuel distribution system may be less compatible with ethanol/gasoline blends than they are with hydrocarbon-only fuels.

- 1. Many fuel system elastomers that have excellent compatibility with hydrocarbon-only fuels are themselves characterized by polar constituents. These constituents contribute to the stability of the elastomer through hydrogen-bonding and other interactions. These interactions may be vulnerable to substitution by the hydroxyl group of the ethanol. For this reason, some elastomers can lose their structural integrity over time due to the loss of stabilizing hydrogen bonding interactions when the elastomer is exposed to ethanol/gasoline blends. Ethanol can also extract plasticizers in the elastomers, reducing the flexibility and toughness of the elastomer products. Fuel system components such as seals, gaskets and piping that are made from polymers and elastomers must be designed to retain their structural integrity, strength and flexibility after extended exposure to ethanol/gasoline blends.
- 2. Because ethanol is a smaller and more polar molecule than MTBE, ETBE, and other oxygenates, there is a lower energetic barrier for ethanol diffusing into and through elastomeric materials. Over time, ethanol can accumulate in these materials, causing them to swell and soften, leading to an overall weakening of the elastomeric structure.
- 3. In comparison to hydrocarbons, ethanol has a high conductivity and contains an active oxygen functionality. This can contribute to corrosion and wear problems of some metal components. Furthermore, the suspension of water within the ethanol/gasoline blend may enhance rusting and/or galvanic corrosion. The tendency of ethanol to loosen varnish and gum deposits can also have a significant impact. By loosening these deposits, ethanol may accelerate wear of metallic components that are in regular contact with fuel by scouring internal surfaces with suspended particles. The use of corrosion inhibitors can help mitigate this problem although the compatibility of these additives with ethanol/gasoline blends must be thoroughly evaluated.

Tables 1 and **2** provide an overview of materials that are either recommended for use or should be avoided when handling ethanol or ethanol/gasoline blends.

Table 1Recommendations for Materials Considered for Use in Ethanol and
Ethanol/Gasoline Blend Applications [3]

Material	Recommended	Not Recommended	
Metals	Carbon steel with post-weld heat	Zinc and galvanized materials	
	treatment of carbon steel piping and internal lining of carbon steel tanks ² Stainless steel Bronze	Brass	
		Copper	
		Lead/tin coated steel	
		Aluminium (may be an issue for	
	Aluminium	E100)	
Elastomers	Buna-N (hoses & gaskets)	Buna-N (seals only)	
	Fluorel	Neoprene (seals only)	
	Fluorosilicone	Urethane rubber	
	Neoprene (hoses & gaskets)	Acrylonitrile-butadiene hoses	
	Polysulfide rubber	Polybutene terephthalate	
	Viton		
Polymers	Acetal	Polyurethane	
	Polypropylene Polyethylene Teflon Fibreglass-reinforced plastic	Polymers containing alcohol groups (such as alcohol based pipe dope)	
		Nylon 66	
		Fibreglass-reinforced polyester and epoxy resins	
		Shellac	
Others	Paper	Cork	
	Leather		

This list is not comprehensive and the quality of the material must be appropriate for the intended application. It is strongly advised that the manufacturers of these products are consulted before ethanol or ethanol/gasoline blends are introduced.

² During the past decade, there have been some reports of stress corrosion cracking of unlined carbon steel storage tanks and non-heat-treated piping in contact with fuel ethanol. [8,9] At the time of this writing, the American Petroleum Institute (API) is preparing a recommended practice related to ethanol storage.

Table 2	Compatibility of Ethanol with Materials Commonly Used in Fuel
	Distribution Systems [3]

Item	Recommended	Not Recommended
Containment system (around tank and loading racks)		Clay liners. Ethanol may dry out the liner and allow cracks to develop
Tanks used for E5	Mild steel Fibreglass-reinforced plastic (newer types)	Some lining materials commonly used to prevent small leaks such as older types of epoxy or polyester resin-based materials. If a tank is relined, the manufacturer should be contacted for advice.
Tanks used for E100	May require a tank constructed of a special chemical resin	
Pumps used for	Carbon & ceramic seals	
E100	Teflon-impregnated packing materials	
Pipe sealants used for E5 and E100	Teflon tape	Alcohol based pipe sealants
Meters used for E5	When first converting to ethanol/gasoline blends, it is advisable to recalibrate meters after 10-14 days to ensure that the fuel change has not caused any meters to over-dispense	
Meters used for E100	Internal O-rings & seals should be selected that are specifically designed for use with ethanol	
Fuel Filters for E5	It may be necessary to change the fuel filter shortly after converting to ethanol/gasoline blends. Once the dispensed fuel is clear and bright, the filter life should be similar to those in regular gasoline applications.	Ethanol can dissolve the glue in filter elements that are not specifically designed for this service Filters containing shellac
Hoses used for E5	No problems reported	
Hoses used for E100	Contact the manufacturer	
Nozzles used for E5	No problems reported	

In this table:

- The term 'E100' refers to pure or denatured ethanol.
- The term 'E5' refers to blends of motor gasoline containing up to 5% v/v ethanol (EN228).

2.8. SULPHATE ISSUES

Flow meter and pump deposits as well as filter plugging and injector sticking incidents have been reported in the USA after they were exposed to some ethanol/gasoline blends. According to work reported by ASTM, insoluble sulphates have been implicated in these deposits and are believed to originate from sulphates carried over from the ethanol manufacturing process. Specifications for fuel grade ethanol should ensure against manufacturing impurities, including insoluble sulphates.

2.9. DENATURANTS ISSUES

Customs and Excise agencies use denaturants to prevent the ingestion of ethanol that is not intended for human consumption. Because there is evidence that some denaturants can impact engine operation and performance, only denaturants that have been demonstrated to have no detrimental effect on engine performance should be used where they are allowed. Motor gasoline conforming to EN228 specifications that contains MTBE, ETBE, TBA, isobutanol, or isopropanol denaturants is expected to show satisfactory performance.

2.10. TRANSPORT OF ETHANOL BLENDS

2.10.1. Transport via Multi-Product Pipelines

A review of current pipeline practices in other parts of the world indicates that the pipeline shipment of ethanol/gasoline blends is not common practice. Pipeline operating companies in the USA, for example, prohibit the shipment of ethanol/gasoline blends.

If pipelines are to be used for this purpose, they must be completely dehydrated prior to the shipment of ethanol/gasoline blends because of the affinity of ethanol for residual water. Dehydrating a pipeline system is a major and potentially costly endeavour and will require additional filtration and/or coalescer equipment to be successfully completed.

If ethanol is transported via a pipeline system, more frequent cleaning and inspection should occur due to the capacity of ethanol to pick-up dirt (rust, sediments, etc.) throughout the system. Corrosion inhibitors that are compatible with ethanol should be selected.

In multi-product pipelines, the potential contamination of jet fuel by ethanol is a very serious concern. Because of the affinity of ethanol for water, higher concentrations of dissolved water can be carried through the pipeline system and jet fuel filter/coalescer performance may be impaired. On the other hand, in South Africa, two trial shipments of ethanol/gasoline blends were carried out in multi-product pipelines, without reported deterioration of the jet fuel quality.

Although the use of pipelines to transport ethanol/gasoline blends may not be excluded, significant capital investments will be required to guarantee a completely dry system, including additional filtration equipments and quality monitoring systems.

Prior to granting approval for such pipeline shipments, large scale trials should be carried out with the active participation of all stakeholders, including the pipeline operators, oil companies, aviation companies, and OEMs.

2.10.2. Transport by Road and Rail

In principle, the distribution of ethanol/gasoline blends by road truck and rail is done in the same way as conventional motor gasoline. However, special precautions should be taken to avoid contamination of the ethanol/gasoline blend with water, dirt, rust, and gum. In particular, the ethanol/gasoline blend should not be mixed with hydrocarbon-only fuel in order to avoid increases in vapour pressure.

2.10.3. Transport by Barge

Due to the affinity of ethanol for water, the transport of ethanol/gasoline blends by barge should be avoided. If this is not possible, then extra precautions and procedures should be put in place to ensure safety, cleanliness, and product integrity following transport.

In particular, vessels that occasionally use product tanks as ballast water tanks should not be used for transporting ethanol/gasoline blends. Any commingling of ethanol/gasoline blends and water should be strictly avoided.

2.11. SAFETY & FIRE FIGHTING MEASURES

2.11.1. Safe Handling

Safety precautions and equipment for storing and handling ethanol/gasoline blends are similar to those used for conventional gasoline. Protective equipment including gloves should always be worn. Skin exposed to fuel should be washed with soapy water. The relevant Safety Data Sheet (SDS) should also be reviewed for recommendations on safe handling, type of gloves, and related procedures before beginning work with ethanol and with ethanol/gasoline blends.

2.11.2. Surface Spills and Leaks

Spills and underground leaks of ethanol/gasoline blends should be treated in the same manner as motor gasoline spills and leaks, including notification of the proper authorities. The supplier's SDS should also be reviewed for recommendations on spill clean-up procedures.

2.11.3. Fire Protection and Fire-Fighting Agents for Fires Involving Ethanol/Gasoline Blends

Personnel should approach an ethanol/gasoline blend fire with the same caution as they would use in approaching a conventional gasoline fire, and similar fire-fighting techniques should be used.

The use of alcohol resistant foams is required when fighting fires involving fuels containing high levels of ethanol. For fighting fires involving gasolines containing up to 10% v/v ethanol, such foams may not be required but it is strongly advised that

responsible personnel review their specific operations and use appropriate equipment based on local safety recommendations and requirements.

Fires involving pure ethanol do not produce smoke and the flames are difficult to see in daylight.

2.11.4. Storage

Pure ethanol can be stored in fixed roof tanks with or without an internal floating cover (IFC)³. Tanks with external floating covers can allow some rain water to enter the tank and are not recommended for storing ethanol.

The vapour concentration above 100% liquid ethanol will be in the flammable range when the liquid temperature is between about 12 and 43°C. Because impurities in the ethanol can alter this range, however, it is good engineering practice to assume that the vapour phase above fuel-grade ethanol is always in the flammable range and procedures and equipment should be used that ensure safe storage conditions. The type of vent on a fixed roof tank will not greatly affect the average flammability condition whether the vents are open or Pressure/Vacuum (P/V) vents. (A P/V vent is a venting device that reduces the free flow of air and vapours in and out of the tank).

When used for storing pure ethanol, an internal floating roof tank with a P/V vent on the fixed roof is likely to be in the flammable range. An IFC with air scoops (that is, with slits in the tank walls to allow free venting, conforming to API 650H guidelines where permitted) will probably be outside of the flammable range as long as the floating roof seals are in good condition and the number and size of the vents are appropriate.

For this reason, procedures, similar to those used for gasoline storage, should be used to ensure against ignition, especially when fixed roof tanks are used to store liquid ethanol. These procedures can include the use of inerting gas systems to avoid a flammable mixture in the vapour space although this approach may not be practical in all situations. Ethanol and blended fuel storage must comply with prevailing legislation.

2.11.5. Sources of Ignition

The presence of ethanol does not substantially increase the risk of static electricity since ethanol has a high electrical conductivity. Lightning could be a problem but a well-grounded metal tank with a well maintained P/V vent or flame arrestor on the vent is considered safe. Excessive friction could cause ignition inside an internal floating roof tank if, for example, the floating roof were to develop a mechanical problem.

Obviously, hot repair work or other human activities near the open vent of an inservice tank must be avoided because these practices could cause ignition to occur. Procedures, similar to those used for conventional gasoline tanks, should be in place to avoid these problems.

³ An internal floating cover (IFC) is one in which the cover deck is located inside the fixed roof storage tank in order to reduce tank vapour emissions.

2.11.6. Drain or Waste Water Handling

Ethanol can be difficult to remove from drains and waste water because it is very soluble in water. For this reason, the only way to efficiently remove ethanol is through biological treatment.

If the bacteria in treatment facilities have not been acclimatised to ethanol, much of the ethanol will pass through the treatment plant before it is degraded. Several weeks to a month may be required before a treatment plant can efficiently process ethanol-containing waste streams. Facilities can gradually increase the ethanol content in their waste water system as the bacteria become more efficient at degrading ethanol. It is important to test degradation performance in the laboratory and analyse the plant effluent for ethanol content over time in order to determine the degradation rate.

Because terminals do not usually have biological treatment facilities, ethanol will most likely pass through the mechanical treatments that are commonly used. If the terminal sends its waste water to a municipal treatment plant, it is important to check with the treatment plant operators whether their facility can handle ethanol-containing waste.

In any case, the disposal of drain or waste water must be done in accordance with all local regulations and permits.

2.12. ADDITIVE EFFECTS

In order to ensure fit-for-purpose motor gasolines, corrosion inhibitors should be added to fuel grade ethanol by ethanol producers, distributors, and gasoline blenders. Only corrosion inhibitors that are effective in such applications and compatible with hydrocarbon-only gasolines should be used for this purpose.

3. BLENDING GUIDELINES

3.1. REFINERY BLENDING

Blending ethanol at the refinery is not preferred because of problems that can occur with the subsequent transport and storage of the ethanol/gasoline blend. Refinery blending may be appropriate, however, when ethanol/gasoline blends are directly supplied to the loading rack from the refinery.

3.2. TERMINAL BLENDING

Direct blending at the loading rack is the best approach to overcome the transport and handling issues associated with ethanol-containing fuels. To do this, the refinery must produce a special BOB (see Section 2.4) and supply it to the terminal. This typically results in additional costs for injection equipment and ethanol storage, as well as an increase in truck movements.

For product quality reasons, terminals should be designated either as ethanolblending or ethanol-free locations (unless they have segregated systems for storage and handling) and their service should not routinely change.

Blending ethanol at low ambient temperatures is not believed to cause any additional problems that are not also encountered at higher ambient temperatures.

The commingling of ethanol and motor gasoline can result in a small volumetric increase of the blend. This increase should be taken into account when considering product volumetric measurement and accounting.

4. GLOSSARY

API	American Petroleum Institute
BOB	Blendstock for Oxygenate Blending
DVPE	Dry Vapour Pressure Equivalent
E70	% evaporated at 70C
E100	% evaporated at 100C
EN228	European Standard for motor gasoline containing up to 5% v/v ethanol
ETBE	Ethyl Tertiary Butyl Ether
EtOH	Ethanol
EU	European Union
IFC	Internal Floating Cover
MON	Motor Octane Number
MTBE	Methyl Tertiary Butyl Ether
OEM	Original Equipment Manufacturer
P/V	Pressure/Vacuum
RON	Research Octane Number
RUP	Regular Unleaded Petrol
SDS	Safety Data Sheet
SUP	Super Unleaded Petrol
TBA	Tertiary Butyl Alcohol
ULG	Unleaded Gasoline

5. ACKNOWLEDGMENTS

FE/STF-24 wishes to acknowledge the contributions to this report from Dr. Neville D. Thompson, who was the CONCAWE Technical Coordinator for Fuels and Emissions from 2000-2006. Before his untimely death in August, 2006, Neville was instrumental in guiding STF-24 activities and ensuring a smooth start to this project. We will always remember him as a good friend, an esteemed colleague, and a true professional in his field.

6. **REFERENCES**

- 1. RFA (2005) Fuel ethanol industry guidelines, specifications and procedures. RFA Publ. No. 960501. Washington DC: Renewable Fuels Association
- API (2001) Alcohols and ethers a technical assessment of their application as fuels and fuel components. API Publ. 4261, 3rd edition. Washington DC: American Petroleum Institute
- 3. ADM (2001) Fuel ethanol technical information. Decatur IL: Archer Daniels Midland Company
- 4. Owen, K. and Coley, T. (1995) Automotive fuels reference book (2nd edition). Warrendale PA: Society of Automotive Engineers
- 5. NESCAUM (2001) Health, environmental, and economic impacts of adding ethanol to gasoline in the Northeast States. Vol. 2: Air quality, health, and economic impacts. Boston MA: Northeast States for Coordinated Air Use Management
- 6. Guibet, J.-C. (1999) Fuels and engines. Vol.1, p. 193-200, p. 220-224, p. 234-243. Paris: Éditions Technip
- 7. Terschek, R. and Ludzay, J. (2005) Laboratory test programme on the addition of ethanol to automotive fuels. Research Report No. 645. Hamburg: DGMK
- 8. Kane, R.D. et al (2004) Stress corrosion cracking in fuel ethanol: a newly recognized phenomenon. Paper No. 04543. Houston TX: NACE International
- 9. API (2007) Stress corrosion cracking of carbon steel in fuel grade ethanol: review, experience survey, field monitoring, and laboratory testing. API TR 939-D, 2nd edition. Washington DC: American Petroleum Institute

CONCAWE Boulevard du Souverain 165 B-1160 Brussels Belgium

Tel: +32-2-566 91 60 Fax: +32-2-566 91 81 e-mail: info@concawe.org website: http://www.concawe.org