Setting a Quality Standard for Fuel Ethanol

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1. EXECUTIVE SUMMARY

The purpose of this technical paper is to provide information on the quality and characteristics of fuel ethanol around the world, to be used as the basis of a discussion paper for public comment on a proposed Australian fuel ethanol quality standard. Fuel ethanol is that used in blends with petrol, in blends with diesel, and in dedicated 100% ethanol fuelled vehicles.

In light of Australia's commitment to harmonization with international standards, the process of developing fuel standards has initially turned to Europe. With regard to fuel ethanol, however, the European Union (EU) is in the process of developing a standard, and hence this paper draws mainly on the experience of those countries such as Brazil and the United States of America (U.S.) where ethanol has been used in automobiles for decades, since the 1930s and 1970s respectively. Within the EU, Sweden and Poland have promoted fuel ethanol use since 1985 and 1992, respectively, and the standards and practices in these countries are analyzed in more detail. Sweden does not have an official national standard, but Svensk Etanolkemi AB (Sekab) standards have become de facto in the industry. In the Asian region, India adopted a fuel ethanol standard in 2004, which has been included in the analysis.

A short history of fuel ethanol in each country has been captured. This encompasses the time frame during which ethanol has been in use, the approximate qualities of fuel ethanol consumed and it's penetration into the fuels market, as well as wherever possible, each country's rationale for the development of the standards and specifications for fuel ethanol. This background enables the specifications and practices adopted in each country to be compared with Australian conditions, leading to an assessment of each of the key parameters of fuel ethanol that impact vehicle emissions (including greenhouse gases), fuel consumption, and engine/fuel system durability and operability. The terminology "petrol" and "gasoline" are used interchangeably in this report.

With the exception of Brazil, anhydrous ethanol is more widely in petrol. Thus most countries use high purity anhydrous ethanol as a frame of reference when setting a fuel ethanol standard. For low percentage ethanol-petrol blends, the petrol standard is typically modified to include the allowed percentage of anhydrous ethanol meeting the specifications contained in the anhydrous ethanol standard, as well as any additives deemed necessary. Further standards derived from the anhydrous ethanol standard are typically adopted for other finished fuels such as 75% and 85% ethanol petrol (and up to 100% ethanol test fuels) used in automotive spark-ignition engines.

The U.S. has followed the above philosophy, and it appears to be the route the EU is taking in developing their fuel ethanol standard. Brazil has taken a slightly different approach than the other countries surveyed with regard to the components specified in the anhydrous ethanol standard. They claim that since the ethanol purity is high in the anhydrous standard, (99.3 ^{0} INPM minimum), most of the other components will have been removed during the purification process, and there is no need to specify additional parameters such as water, chloride or methanol content. Hence, of the parameters usually considered, Brazil's anhydrous ethanol standard limits only acetic acid and copper content. The Brazilian hydrous ethanol standard, however, includes several limits on components that are typically included by other countries in their anhydrous ethanol standards (see Chapter 5).

At this time, ethanol-diesel blends are regarded as test fuels in the U.S., and based on the anhydrous ethanol standard ASTM D 4806, with added water and specialty additive packages. Sweden has commercialized ethanol-diesel blends in Stockholm's bus fleet and uses Sekab's 95% hydrous ethanol standard in these blends, which differs from their anhydrous ethanol specification with respect to ethanol and water content. The same components deemed to be potentially detrimental to engine performance are limited in both the anhydrous and hydrous ethanol specifications. Brazil's hydrous ethanol standard can be compared with Sekab's hydrous ethanol standard and could be used for ethanol-diesel blends.

This paper focuses on a high purity anhydrous ethanol standard from which further finished fuel standards could be derived. The approach followed by the U.S. ASTM, Brazil, India and the EU, is to form a committee of stakeholders who debate the parameters that could be included in an ethanol standard. Australian stakeholders would include the ethanol producers (Manildra and CSR Distilleries), National Refiner's Association, Automobile Association, and the Australian Standards Bureau.

2. ETHANOL AS AN AUTOMOTIVE FUEL

Ethanol (or ethyl alcohol) is an organic chemical compound (i.e. a compound comprised of hydrogen, carbon and oxygen). The chemical structure of ethanol is shown in Figure 1.

Figure 1: Ethanol

```
     H   H
     I   I
H – C – C – OH
     I   I
     H   H
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Ethanol can be produced in two forms – hydrous (or hydrated) and anhydrous. Industrial ethanol production typically yields an azeotroph (i.e it boils without change) by distillation that is about 93% to 96% ethanol and 4% to 7% water by volume. Hydrous ethanol, therefore, typically has a purity of about 95% and has been used in Brazil since the late 1970's directly as a motor fuel in adapted alcohol vehicles with modified engines that are able to use fuel with 95% plus ethanol content. Hydrous ethanol has also been tested as a 15% emulsion in diesel and is used as a dedicated fuel in diesel engines in Sweden.

Since an azeotroph boils without change, further distillation will not remove the water from the ethanol. A second stage process is required to produce high purity anhydrous ethanol for use in petrol blends. Most countries require industrial ethanol, whether hydrous or anhydrous, to be denatured (to prevent oral consumption thereby differentiating it from potable beverage alcohol for taxation purposes) by the addition of small amounts (1% to 5 %) of unpleasant or poisonous substances.

An oxygenate (as defined by ASTM) is an oxygen-containing, ashless organic compound, such as an alcohol or ether, which may be used as a fuel or fuel supplement – hence, ethanol is an oxygenate and it has unique properties that cause petrol to burn more thoroughly, thereby improving combustion and reducing tailpipe carbon monoxide (CO) emissions. The importance of oxygenates has increased because they provide a means of extending the petrol pool (thereby reducing dependency on imported crude oil), help alleviate the octane shortage that resulted from the phasing out of lead anti-knock compounds and reduce vehicular emissions.

In general, the type of emissions from vehicles using ethanol will be similar to those from petrol-powered vehicles, but the amount of emissions will be less. The greater the percentage of ethanol, the lower the resulting emissions. The quantity of pollutants released also depends upon how well the vehicle's emission control system captures and burns emissions, and how well the engine is designed and "tuned" for using fuel ethanol.

2.1 ANHYDROUS ETHANOL IN LOW PERCENTAGE PETROL BLENDS

Because ethanol is hygroscopic and easily picks up water from ambient air and the distribution system, the water content of the denatured fuel ethanol must be limited when blended with gasoline to reduce the risk of phase separation (see Chapter 5, section 5.1 point 5).

Anhydrous ethanol is typically blended up to 10 volume % (vol%) in petrol for use in unmodified engines. Certain materials commonly used with petrol are totally incompatible with alcohols. This will be discussed further in the next section. In fuel blends up to 5% (EU) and 10% (U.S.), no problems are expected and conventional petrol vehicles can be operated under full manufacturer warranty. Low percentage ethanol blends are dispensed in many service stations worldwide with almost no reported incompatibility with materials and equipment.

When ethanol is blended into fuel at levels above 10 vol%, some engine modifications may be necessary, although the exact ethanol percentage at which modifications are needed varies with local conditions such as climate and altitude. Anhydrous ethanol has been used up to 25 vol% in petrol blends in Brazil (and in some cases even higher) with adjustments to improve drivability and material compatibility. Since ethanol has a higher octane than petrol, most Brazilian vehicles are tuned to operate with a fuel rich mixture (fuel/air ratio above stoichiometric), which helps explain why the drivability and fuel economy have not been greatly affected. Cars with electronic fuel injection built for the Brazilian market have ethanol-resistant elastomers, and there have been few reported complaints about drivability or corrosion. The latest model vehicles with onboard sensors are able to detect the higher octane of ethanol blends and automatically adjust the timing, resulting in greater fuel efficiency.

Two types of emissions are released from vehicles – exhaust and evaporative. The use of a 10% ethanol blend in gasoline is widely documented to achieve a 25% or greater reduction in exhaust CO emissions. Exhaust emissions of most toxic hydrocarbons (HCs) such as benzene, also reduce when ethanol is added to gasoline, primarily because of the dilution of the petrol that emits them. Emissions of acetaldehyde, formaldehyde and peroxyacetyl nitrate (PAN) will likely increase when ethanol is added. Studies conducted throughout the world on nitrogen oxide (NOx) exhaust emissions from ethanol-blended fuels are often contradictory, and it appears the emissions are about the same for ethanol and petrol vehicles.

In terms of evaporative emissions, ethanol has fewer highly volatile components than petrol, and so in its pure form, it has fewer emissions resulting from evaporation. However, when added to petrol, the vapor pressure of the blend is increased, increasing evaporative emissions. This is because in its pure form, ethanol molecules are polar and bond to each other via the hydroxyl (OH) groups. These forces of attraction prevent the molecules from leaving the liquid. However, in the presence of hydrocarbons, this bonding does not take place for the first 2 vol% to 3 vol% of ethanol added to petrol. Thereafter, increased addition of ethanol will not further boost the vapor pressure. Using a petrol base-stock for ethanol blending that initially has a lower vapor pressure negates this effect.

2.2 ANHYDROUS ETHANOL IN DEDICATED & FLEXIBLE FUELLED VEHICLES

Ethanol vehicles are conventional vehicles that have metallic and rubber based materials replaced with ethanol compatible substitutes. In addition, the timing is adjusted to ensure complete combustion of the ethanol. These vehicles require a set fuel mixture that typically contains up to 85% anhydrous ethanol, in order to operate efficiently.

During the past few years, several major automobile manufacturers have developed flexible fuel vehicles (FFVs) that can run on petrol or E85 fuel (85% ethanol by volume) or any blend of ethanol and petrol from 0% to 85% ethanol. The main differences between ethanol FFVs and petrol vehicles are the materials used in the fuel management system and modifications to the engine calibration system.

The corrosive effect of a fuel rises with increasing ethanol content. Materials that normally would not be affected by low percentage ethanol blends have been found to dissolve in the presence of higher ethanol concentrations, including aluminium, brass, zinc and lead. Even if the parts made from these materials do not fail, insoluble compounds will be introduced into the fuel, causing plugged vehicle fuel filters. Terne (lead-tin-alloy) plated steel, commonly used for petrol fuel tanks, and lead-based solder are also incompatible with high concentrations of fuel ethanol. Non-metallic materials that degrade when in contact with high concentrations of fuel ethanol include natural rubber, polyurethane, cork gasket material, leather, polyvinyl chloride (PVC), polyamides, methyl-methacrylate plastics, and certain thermo and thermoset plastics. The swelling and embrittlement of rubber fuel lines and o-rings can, in time, lead to component failure.

These problems are eliminated in dedicated ethanol vehicles and FFVs by using unplated steel, stainless steel, black iron and bronze, which have all shown acceptable resistance to ethanol corrosion. Non-metallic materials successfully used with E75 and E85 include thermoset reinforced fiberglass, thermo plastic piping, neoprene rubber, polypropylene, nitrile, Viton and Teflon materials.

The other feature of an FFV is that this vehicle operates with equal efficiency on petrol and ethanol, and needs only a single fuel tank. Any blend of fuel can be used, from 100% petrol to E85 (85% ethanol, 15% petrol). The car is provided with a sensor that measures the conductivity in the fuel, and thus determines the ratio of the blend. The signals are later sent to a powerful computer that controls injection, ignition time and quantity of air. The capacity of injectors is increased and substituted with resistant material to enable large quantities of fuel to be injected. Thus, the fuel consumption increases by about 30% as the energy content per liter of ethanol is lower than that of petrol but this is offset by the fact that the FFV is about 7% more powerful than a pure petrol engine, and the energy is utilized much more effectively. Therefore, in practice, a motor vehicle will experience only a 5% to 12% decline in fuel mileage per liter of E85 ethanol fuel.

Because ethanol has a lower vapor pressure than petrol at low temperatures, this makes cold starts more difficult. It is one of the reasons 15% to 25% petrol is added to the anhydrous ethanol fuel. In addition, the fuel is heated as it enters the combustion chamber, and fuel pressure is also increased. Studies are underway to increase the ethanol content even more than 85%, with 100% ethanol fuel being the ultimate goal of some.

The FFVs Powertrain Control Module means that ethanol cars can be on the roads even before a complete tanking station network has been set up. In the U.S. about 3 million FFVs are sold as standard equipment, with virtually no "cost of production" price premium over comparable models. Several models are available and are covered under the same warranty, service and maintenance conditions as their gasoline-powered counterparts. According to the U.S. E85 data center, most operating problems with dedicated ethanol vehicles and FFVs have been traced to contaminated fuel. Consequently choosing the right materials for fuel storage and dispensing systems and following proper handling procedures are crucial for successful vehicle operation. [7.27]

Sweden has a few thousand FFVs and the results of emissions tests on a 1996 model Ford Taurus FFV during the approval certification using E85 petrol, were a 6 mass% reduction in NOx, 27% reduction in CO and a 49% decrease in hydrocarbon emissions.[7.25]

In the U.S., a study was conducted in 1998 by the National Renewable Energy laboratory (NREL) Ohio, where operating data was collected from ten Ford Taurus model year 1996 FFVs operating on reformulated gasoline (RFG) with 2.7 wt% oxygen content, and with E85. This data was compared with that from three petrol vehicles of the same make and model year operating on RFG. The results of the study were different in some aspects from the Swedish results, but did show an overall decrease in CO, NOx, and carbon dioxide (CO_2) emissions compared to the standard gasoline vehicles using RFG. The test results are in Table 1.

Table 1: FFVs and Standard Gasoline Vehicles Emissions Comparison from Ohio Study [7.15]
(Grams per kilometer except fuel economy in liters /100 km)

EMISSIONS	FFV USING E85 FUEL	FFV USING RFG	STANDARD GASOLINE VEHICLE USING RFG	EPA TIER 1 EMISSIONS STANDARD
Regulated Emissions				
NMHC	0.09	0.06	0.07	0.16
THC	0.12	0.07	0.08	0.25
CO	0.81	0.62	0.87	2.11
NOx	0.06	0.05	0.14	0.25
Greenhouse gases				
CO_2	242	255	252	n/a
Methane	0.03	0.01	0.01	n/a
Aldehydes				
Formaldehyde	$1.4X10^{-3}$	$0.6X10^{-3}$	$0.8X10^{-3}$	n/a
Acetaldehyde	$8.1X10^{-3}$	$0.2X10^{-3}$	$0.2X10^{-3}$	n/a
Fuel Economy				
L/100 km (actual)	14.9	11.1	11.0	n/a
L/100 km (gasoline equivalent basis)	11.0			

NOTE: NMHC = non-methane hydrocarbons; THC=total hydrocarbons including evaporative emissions; CO_2 emissions are for vehicles only. n/a=no standard for this pollutant.

Source: International Energy Agency: "Biofuels for Transport – An International Perspective," April 2004

2.3 HYDROUS ETHANOL IN PETROL ENGINES

In Brazil, pure or "hydrous" ethanol, which is a mixture of greater than 93 vol% ethanol and water, has been used in especially designed engines since the oil crisis of the late 1970s. These engines have been protected against corrosion and used in dedicated ethanol vehicles re-designed to take full advantage of ethanol's very high octane. In Brazil, some engine manufacturers have reportedly increased vehicle compression to 12:1, compared with the typical 9:1 ratios of conventional petrol vehicles.

Soft loans by the government funded the introduction of alcohol vehicles fuelled with hydrated ethanol. In addition, tax reductions made the ethanol option highly attractive to consumers. By 1985, about 17% of the country's fleet was operating on pure hydrated ethanol (i.e. about 93 vol% to 95 vol% ethanol). The sharp decrease in oil prices in the mid-1980s greatly increased the relative cost of fuel ethanol production and the pure hydrous ethanol vehicle sales reduced to less than 1% by the mid-1990s. However, during 2003, major Brazilian manufacturers produced Brazil's first FFVs. These vehicles operate on a mixture of petrol and ethanol, or pure hydrous ethanol. Volkswagen's "Totalflex" vehicle can use petrol, ethanol or compressed natural gas. Ethanol producers are eagerly awaiting the consumer's acceptance of the flexible fuel concept to accommodate ethanol production and international market variations.

2.4 HYDROUS ETHANOL IN DIESEL ENGINES

Blends of ethanol in diesel were investigated in the late 1970s and early 1980s in a number of countries including the U.S., Germany, Brazil, Denmark, Sweden and South Africa. About 10,000 hours of field test results were accumulated in South Africa on various diesel farm tractors operating under normal field conditions.[7.3] These tests concluded that with certain precautions and careful management, it was feasible to use a 15% ethanol-diesel blend in unmodified agricultural tractors. Studies in the U.S. in 1980 by the Illinois University Department of Agricultural Engineering showed satisfactory engine performance with a small increase in engine efficiency and a reduction in emissions. The U.S. study concluded that blends of 10% aqueous ethanol in diesel with a surfactant added would be of practical interest during periods of petroleum shortages, but economic factors prevailing at the time limited commercial use.

Since ethanol is not naturally miscible with diesel fuel, an emulsion is produced, typically containing 15% hydrous ethanol, and special additive emulsifiers (surfactants). In addition, the cetane number of the blend is low, making it difficult to burn by the compression ignition technology employed in diesel engines. As a result, a lot of the research has been carried out. New additives to improve ethanol solubility in diesel, as well as to improve cetane have made ethanol in diesel an interesting and potentially viable option

The other challenge facing widespread commercialization of ethanol-diesel blends is that unlike petrol, the vapor phase above the ethanol-diesel blend is stoichiometrically equivalent to the mixture in the tank for a range of ambient temperatures tested between about 10^0C (50^0F) and 40^0C (104^0F) regardless of the percentage of ethanol present. If it ignites the entire fuel tank will ignite. With modern day fuel dispensers that have vapor recovery systems and seal onto the tank to reduce emissions, the economic feasibility of providing a safe environment for ethanol-diesel fuel has been greatly enhanced.

In Curitiba, Brazil, a group sponsored by the Alcohol and Sugar producers Association of Paraná tested anhydrous ethanol in diesel in urban buses.[7.1] The blend was about 86 vol% diesel, 11 vol% anhydrous alcohol and 3% of an additive AEP-102. A reduction in smoke emissions, fuel consumption as well as an increase in cetane rating, was observed. The only problems experienced were with rotating injection pumps, which are in the minority in the Brazilian bus fleet. Lubrizol Corporation has been conducting extensive studies that include the more sensitive rotary, or distributor type pumps that rely solely on the fuel for lubrication, and promising results have been reported.[7.19]

Since the 1990s a different approach has been taken of modifying diesel engines and adjusting their fuel auto-ignition characteristics to allow them to perform on very high ethanol blends. In 1992 in the U.S., Archer Daniels Midland Corporation (ADM) put into service the first fleet of ethanol powered heavy duty test trucks.

In Thailand, Lubrizol was jointly involved in an ethanol-diesel test program with Ford Motor Company, the Petroleum Authority of Thailand, the National Science and Technology Development Agency and Bosch Japan. The work demonstrated the successful use and durability of ethanol-diesel blends used in Ford trucks in Thailand. Lubrizol produces the “Purinox” additive, which has shown promising results in ethanol-diesel blends.

Another pilot project started in Thailand 3 years ago. Thailand’s Oil & Gas company (PTT) Research & Technology Institute (PTT R&T) is responsible for evaluation of fuel properties whilst Thailand’s National Metal and Materials Technology Center (MTEC) is the project administrator. The Pollution Control department (PCD) will test emission data. E-diesel is diesel splash blended with anhydrous ethanol including Beraid ED10 additive from Akzo Nobel. MTEC is looking to publish a report on the findings of the study mid 2004. SCANIA assisted in developing the Akzo Nobel blending agent “Beraid,” which is undergoing approval testing in the EU.

Table 2 : E-diesel fuel data from Thailand field trials

Typical Data	Ultra Low Sulfur Diesel	Ethanol + diesel (E-diesel)
Viscosity, 40 ^{0}C, cst	2.7	2.3
Flash point, ^{0}C	59	<23
Sulfur content, ppm	47	<47
Cold Filter Plugging Point (CFPP), ^{0}C	-20	-20
Cloud Point, ^{0}C	-3	-2
Cetane Number	54	52
HFRR (lubricity) micron WSD	374	313

Source: Akzo Nobel

AKZO Nobel also claimed E-diesel reduced 5% of NOx, 28% of CO and 31% of PM but increased HCs by 13% when tested in a SCANIA truck in Denmark.

The Swedish ethanol-diesel program is arguably the world's largest and is ongoing. Sweden has at least 400 ethanol-powered buses, 250 of which operate in central Stockholm. Successful trials have also been conducted using ethanol-powered heavy trucks and refuse disposal vehicles. Measured environmental benefits compared with Euro 2 diesel are reported to be a 44 mass% reduction in NOx, 98% reduction in CO, 91% reduction in HCs and 73% reduction in particulate emissions.[7,25] Sweden's Sekab sales specification for ETAMAX D is shown in table 3.

Table 3 : Sekab Sales Specification for ETAMAX D

PROPERTY	SPECIFICATION	TEST METHOD
Appearance	Clear, without particles	ASTM D 2090
pH min-max	5.2 – 9.0	AMSE 1131
Water max %mass	6.20	SS-ISO 760
Density g/ml	0.820 – 0.840	SS-ISO 758
Fuel composition		
Ethanol 95%, %mass	90.2	
Ignition Improver, %mass	7.0	
MTBE, %mass	2.3	
Isobutanol, %mass	0.5	
Corrosion Inhibitor, ppm	90	
Color	red	

Source: Sekab

The ETAMAX-D product for diesel is produced from Sekab's 95% ethanol. The 95% ethanol specification is essentially the same as the anhydrous 99,5% specification for petrol blending in all respects except ethanol and water content. Other parameters adjusted to accommodate the slightly different physical properties of a higher water content are: maximum density is 0,8084 compared with 0.790; distillation drypoint is a maximum of 79 ^{0}C compared with 81 ^{0}C; and refractive Index is 1,3630 compared with 1,3618.

Several E-diesel trials have been conducted in Australia and the details are included in the recently published position paper on setting an E-diesel standard from the Australian Department of Environment and Heritage (DEH).

3. ETHANOL MANUFACTURE

3.1 COMMERCIAL PRODUCTION OF ETHANOL

Ethanol can be produced from any source containing appreciable amounts of sugar or materials such as starch and cellulose that can be converted into sugar. It has been suggested that if advanced technology and farming methods are used to produce ethanol, then the resulting ethanol/petrol blend has lifecycle CO_2 emissions substantially lower that those of neat petrol. Even greater CO_2 reductions are estimated from the use of cellulosed biomass as an ethanol feedstock, though the technology for such production is not yet widely used on a commercial scale.

Ethanol can be manufactured:

- by the fermentation of sugar derived from grain starches(wheat & corn), sugar beets or sugar crops using microorganisms;
- surplus wine ethanol;
- by the fermentation of the non-sugar lignocellulosic fractions of crops (grasses & trees);
- using waste biomass such as crop residue, forestry waste, municipal waste and food processing waste;
- synthetically through direct hydration of ethylene (derived from petroleum), or the high temperature conversion of coal to liquid fuels by the Fischer Tropsch process in South Africa where mainly ethanol, but also propanol to pentanol are produced as co-products.

3.1.1 Ethanol from Sugar

Enzymes produced from yeast are used to ferment the sugar in sugar cane and sugar beets to produce ethanol. Six carbon sugars (mainly glucose) found in sugar cane and sugar beets are fermented directly to ethanol, making these ideal feedstocks for ethanol production.

The chemical reaction to produce ethanol from sugar is as follows:

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{(fermentation)}} \underset{\text{Ethanol}}{2\ CH_3CH_2OH} + 2\ CO_2 + \text{heat}$$

The sugar crops are first processed to remove the sugar by crushing, soaking, and sometimes using chemical treatment. The resultant molasses is then fermented to ethanol using enzymes produced from yeast. A final step purifies the ethanol by distillation to the azeotropic form of ethanol, which is about 93% to 95% ethanol, water and other components. To remove the water and soluble components, specialized azeotropic distillation using a solvent such as cyclohexane is required. Alternatively, molecular sieves may be used to produce anhydrous ethanol.

The crushed stalk of the sugar cane, known as bagasse, contains cellulose and lignin and is often burnt as fuel in the ethanol manufacturing process. The amino acids naturally present in molasses undergo reductive deamination thereby forming a mixture of alcohols, collectively known as fusel oil, as a by-product. The major alcohols formed are isoamyl alcohol, 2-methylbutanol, n-propanol and phenylethanol, all of which are important natural raw materials for the flavour industry.

3.1.2 Ethanol from Grains

In conventional grain-to-ethanol processes, only the starch component of grain crops, such as corn, wheat and barley, are used. The starch is concentrated mainly in the kernels, representing a fairly small percentage of the total plant mass. Considerable quantities of fibrous remains such as the husks and stalks of these plants are left behind. Research is on-going to use these waste cellulosic materials to create fermentable sugars, ultimately leading to more efficient production of ethanol from grains.

The grain-to-ethanol process starts with the separation, cleaning and milling of the starchy feedstock. Before processing, sulfur dioxide (SO_2) can be used to prevent the formation of mildew. Milling can be wet or dry. The key differences in the processes are the required capital investment and the range of products produced. In wet milling, the grain is soaked and broken down further before the starch is converted to sugar. In dry milling, the grain is broken down during the conversion of starch to sugar. In both cases, the starch is converted to sugar using a high-temperature enzyme process. A typical enzyme used for starch conversion is Alpha amylase, requiring a pH of about 6. Glucoamylase is often used for saccharification (i.e. conversion to sugar) and requires a pH of 4.5. Small amounts of strong acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl) or phosphoric acid (H_2PO_4) are sometimes added. The phosphorus serves an additional purpose as a nutrient source for the microbes.

Once sugar has been produced, the process is similar to that for sugar crops, where the sugars are fermented to ethanol using yeasts and other microorganisms, followed by distillation and drying. The grain to ethanol process also yields several by-products such as protein rich animal feed, and small amounts of fusel oil.

3.1.3 Ethanol from Cellulosic Biomass

Cellulosic biomass is a complex mixture of carbohydrate polymers known as cellulose, hemi-cellulose, lignin and a small amount of compounds referred to as extractives. Examples of cellulosic biomass include agricultural and forestry residues, wastes from pulp/paper processes, municipal solid waste, and herbaceous and woody plants. Agricultural wastes include crop residues such as wheat straw, corn leaves, stalks and cobs, rice straw and sugar cane bagasse. Forestry wastes include under-utilized wood and logging residues, rotten and dead wood, and excess small trees. Crops grown specifically for fuel include fast-growing trees, shrubs and grasses such as hybrid poplars, willows and switchgrass. The cellulose and hemi-cellulose components of these materials can range from 30% to 70%.

Cellulose is composed of glucose molecules bonded together in long chains that form a crystalline structure, and it is a tough, fibrous, water-insoluble substance. Hemi-cellulose, a mixture of polymers made up from xylose, mannose, galactose or arabinose, is also not soluble in water. Hemi-cellulose is much less stable than cellulose. Lignin is a complex aromatic polymer of phenylpropane building blocks that are resistant to biological degradation.

To produce ethanol, the cellulosic feedstock is pretreated to convert hemi- cellulose into soluble sugars such as xylose sugars. Acids or enzymes to produce glucose hydrolyze the cellulose fraction. The soluble xylose and glucose sugars are subsequently fermented to ethanol. Lignin, which cannot be fermented into ethanol, can be used as fuel to produce heat or electricity. Pathways to produce ethanol using cellulosic feedstock include enzymatic hydrolysis, dilute acid hydrolysis and concentrated acid hydrolysis. Considerable research is being invested in the development of biological enzymes that can break down cellulose and hemi-cellulose. Dilute acid hydrolysis uses low concentration acids and high temperatures to process the biomass. Concentrated acid hydrolysis uses strong acids such as 40 mass% hydrochloric acid, 60 mass% sulfuric acid or 90 mass% hydrofluoric acid. Hydrochloric acid is reportedly the only concentrated acid hydrolysis process to have reached commercialization. [7.7]

The production of ethanol from sugar and corn is mature technology and therefore unlikely to see any substantial reduction in costs. However, the potential for cellulosic biomass as a renewable energy source is huge, since the feedstock is primarily waste materials, at significantly reduced value. A number of countries are involved in research in this area, but large scale commercialization is not yet a reality.

3.1.4 Synthetic Ethanol

Ethanol is commercially prepared from ethylene by the direct reaction of extremely pure water with ethylene gas. This process, called direct hydration, is generally considered environmentally and technically the best commercial method for obtaining a consistently high quality ethanol product. The primary chemical reaction for this process occurs when water vapor and ethylene are combined at elevated pressure and temperature and are passed over the surface of a catalyst support impregnated with phosphoric acid.

The chemical reaction to produce ethanol from ethylene is as follows:

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + \underset{\text{water}}{H_2O} \xrightarrow{\text{(catalyst)}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

The main reaction yields a dilute crude ethanol. This ethanol is then separated from unreacted ethylene, which is recycled, and is concentrated and purified through a series of distillation towers. The ethanol stream then undergoes hydrogenation to convert unsaturated components into a form in which they may more readily be removed. Water not removed during the distillation process typically is in a molecular sieve dehydration unit to produce high purity anhydrous ethanol.

Through the high temperature Fischer Tropsch process used by Sasol in South Africa, ethanol is produced as a by-product, in addition to higher alcohols such as propanol, butanol and pentanol. Most of the petrol marketed in the interior region of South Africa since 1981 (typical altitude 1500 m above sea level) contained 10 +/- 2 vol% fuel ethanol but this has been phased out recently in favour of higher value chemical market applications for the ethanol. The effect of synthetic 95 vol% ethanol/ 5 vol% higher alcohols (C_3+ alcohols) on octane response and fuel performance of petrol alcohol mixtures was compared with that of fermented ethanol of 99.9% purity sourced from California. Pure ethanol (99.99%) was used as the reference. It was concluded that the 95/5 Sasol fuel alcohol compared very favourably to the other alcohols, and is therefore a feasible alternative to the fermented alcohol in use elsewhere in the world.[7.17]

At present the primary manufacturers of synthetic ethanol (Sabic in the Middle East, BP in the United Kingdom, Sasol and PetroSA in South Africa, Equistar in the U.S.) supply their ethanol into high value chemical markets such as solvents, pharmaceuticals, and the food and cosmetic industry. Value added derivatives are produced. In times of fuel ethanol shortage such as occurred in Brazil in the 1980s for example, these alcohols have been used in fuel markets. Provided the synthetic ethanol is of high purity and meets the anhydrous fuel ethanol standard, to date there is no known technical reason why it should not be used in fuel.

3.2 THE POTENTIAL FOR GENETICALLY MODIFIED FEEDSTOCKS

Mendel published his research in plant hybridization in 1865 and sent it to several prominent scientists worldwide. However, it was not appreciated at the time. It was only in 1900 that three European scientists independently confirmed his results.

Genetically engineered or modified crops (GM) have genes from other species inserted in their DNA (i.e. their genetic blueprint). This gives the plant different characteristics very quickly, such as major increases in yields, reductions in fertilizer requirements and improvements in pest-resistance. Worldwide research into plant “genomics” (the study of genes) reportedly amounts to several hundred million dollars per year, with the majority of the funding and activity occurring in the private sector. With the necessary genes available in the gene pools of crops, genetic engineering could also be used to produce new co-products. The greatest barriers to GMs are the social concerns regarding their safety in the food chain. For this reason, the real potential for this technology may lie in dedicated energy crops such as switchgrass, which are not consumed by humans.

Corn husks and stalks, and switchgrass are closely related to rice, corn and sugar cane. Genetic engineering methods will be available from major biotechnology companies as a result of their work on maize and rice. Tree species like poplar and willow have no close relatives under genomic study, but they do have small genomes, which simplifies gene identification and mapping.

The future fuel potential for genetic engineering is that it does not only result in high yields of crops, but these in turn can be modified to contain a higher percentage of usable cellulose/hemicellulose and lower lignin content. Bioenergy crops could also be engineered to produce large quantities of cellulytic enzymes, which could be used directly for feedstock processing, thereby reducing the cost of Cellulase currently required for feedstock conversion to ethanol and co-products.

During the course of this study, no evidence of likely commercial ethanol production from GM feedstocks was encountered, and it appears to be more of a concept for the future than a reality at this time.

3.3 CHARACTERISTICS OF FUEL ETHANOL MANUFACTURED IN AUSTRALIA

At the present time, there are two manufacturers of ethanol in Australia. The Manildra Group is primarily a wheat flour processor. Starch and gluten are extracted from the flour to produce glucose syrups. The waste starch liquid, supplemented by physically extracted grain starch, is used to manufacture ethanol. CSR Distilleries produce ethanol by fermentation of the sugars in molasses. Both companies produce high purity anhydrous ethanol fuel grades.

3.3.1 Manildra Group

Manildra uses enzymes to break down the starch to form sugars (see Section 3.1.2). Small amounts of hydrochloric acid (HCl) could be added to adjust pH during the saccharification process. Because Manildra produces fuel ethanol from waste starch streams, the percentage of ethanol in the fermented product is less than 8 vol%. This ethanol is recovered in one of two distillation plants (next to each other, with one using Speichim and the other Katzen technology), followed by dehydration in molecular sieves.

The fuel ethanol produced by Manildra typically contains 99.8 vol% ethanol, measured using an alcohol hydrometer. At present it is sold in Manildra's own distribution system to petrol stations located primarily in the Sydney area. Manildra's fuel grade ethanol specification is based on the U.S. ASTM D 4806 anhydrous fuel ethanol specification.

Table 4: Manildra Group SMS 100 F21 (Fuel Grade Ethanol)

Property	Typical Analysis
Appearance	Clear liquid, free of any foreign matter
Alcohol strength % v/v @ 20 ^{0}C [1]	99.25 minimum
Acidity (as acetic acid) % mass, max	0.007
Water content % mass, max	1.25
Fuel content of denatured ethanol % volume unleaded petrol , min	1.0

Notes: 1. Prior to denaturing
2. Contains corrosion inhibitor DCI 11 (Octel)

Source: Manildra Group, issue date 26 February 2003

Although not reported in the above product data sheet, samples are drawn from the fuel ethanol tanks on a daily basis and tested for other components such as methanol, higher alcohols and fusel oils. Other parameters tested on an occasional basis (because they are always extremely low) are non-volatile residue, inorganic chloride and copper (there is no copper equipment in the plant). Tests not presently carried out are those for aldehydes, phosphorus content and solvent washed gum.

The pHe of the ethanol is tested routinely after addition of denaturant and corrosion inhibitor, and has a typical value close to 7 (neutral). Manildra has equipment on site capable of measuring most of the fuel parameters for ethanol discussed in Chapter 5.

3.3.2 CSR Distilleries

CSR Distilleries (CSR) produce ethanol by fermentation of the sugars in molasses, using yeast. (see Section 3.1.1). No adjustment of pH by addition of strong acids is required. The fermentation and primary distillation is carried out at CSR's Sarnia distillery in North Queensland. The dehydration and purification is carried out at CSR's Yaraville distillery using azeotropic distillation with cyclohexane as solvent. High purity ethanol with a minimum ethanol content of 99.4 vol%, and a typical ethanol content of 99.8 vol% at 20^0C is produced. The ethanol purity is measured using an alcohol hydrometer.

British Pharmacopoeia Standards (BPS) and test methods are used as CSR's primary business is pharmaceutical applications and toiletries. BPS is a widely accepted standard in the United Kingdom, Europe and Australia for therapeutic (TGA) goods. CSR has sold anhydrous ethanol into fuel in the past and has sporadic sales into fuel, but this is not regular business at this time.

Table 5: CSR Distilleries Product Specification Sheet: Ethanol 100 Fuel Grade
with Corrosion Inhibitor

Property	Specification limit	Test Method
Description	Clear, colorless, volatile liquid, hygroscopic, miscible with water and with methylene chloride, free from matter in suspension and apart from water, consisting essentially of ethanol	BP 2002
Strength vol% min @ 20^0C	99.4	BP 2002
Relative Density, max	0.793	CSR AP-03
Water content %mass, max	1.0	CSR AP-27
Alkalinity	Alkalinity to Phenolphthalein - nil	BP2002
Acidity, max	1 ml of 0.01 N NaOH	BP 2002
Clarity of Solution	Dilution of 1 ml sample to 20 ml water should remain clear and colorless after 5 minutes	BP 2002
Aldehydes & ketones, max	100 ppm as Acetaldehyde	BP1973
Reducing substances, min	30 minutes	BP1973
Non-volatile matter, mg/100 ml, max	2.5	BP2002
Volatile Impurities	Passes test	BP2002
PHe [1]	6.5 – 9.0	ASTM D6423

Notes: 1. After the addition of denaturants
2. Denaturant is 1 vol% of unleaded petrol of maximum specific gravity of 0.793 @ 20^0C.
3. Corrosion Inhibitor (DCI-11) is added at nominal concentration of 86 mg/liter.
4. Tests are carried out in accordance with the requirements of British Pharmacopoeia 2002 with additional tests carried over from British Pharmacopoeia 1973, prior to the addition of denaturants

CSR has purchased the probe required to make ASTM D 6423 pHe measurements. To date they have not purchased other equipment required for fuel applications testing. The company has instead used a contract laboratory in Melbourne. The anhydrous fuel ethanol produced is of a high quality, and no problems were experienced with other components. The copper content was, however, on the U.S. ASTM D 4806 limit of 0.1 mg/kg. It is suspected that this may be because CSR's distillation columns are made of copper, which is common practice in the food and beverage industry since copper assists with odor removal from the ethanol.

4. INTERNATIONAL QUALITY SPECIFICATIONS FOR FUEL ETHANOL

4.1 UNITED STATES OF AMERICA (U.S.)

Ethanol has been added to petrol in the U.S. since the 1970s, when the Arab oil embargo triggered research on substitutes for petroleum-based fuels. Ethanol's properties as a fuel more closely suited petrol engine applications, resulting in the introduction of "gasohol" in the U.S. There are 73 ethanol production facilities in operation, and these plants have a listed nameplate capacity of more than 3 billion gallons/year (11 billion liters/year). Until the late 1980s, ethanol's primary role in the fuels market was that of octane enhancer, and it was viewed as an environmentally sound alternative to the use of lead in petrol. In the late 1980s some states began to use ethanol and other oxygenates in mandatory oxygenated fuels programs. A blend of about 7.7 vol% ethanol will achieve compliance with the 2.7 weight percent (wt%) wintertime average oxygenate requirement. Ethanol is more frequently blended at 10 vol% to take maximum advantage of available tax credits.[7.23]

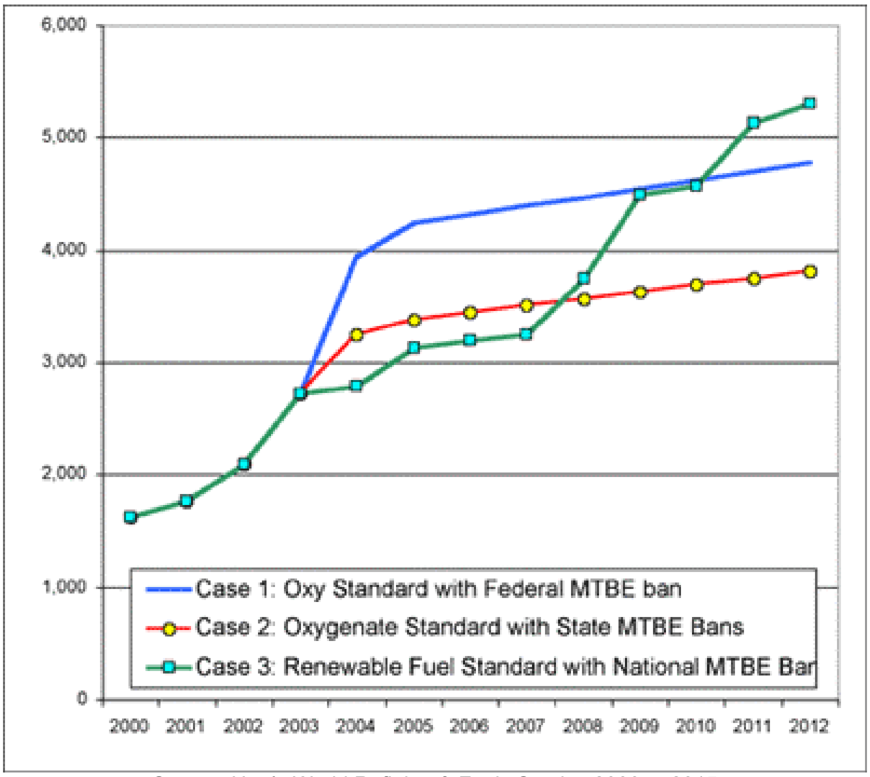
U.S. ethanol production is primarily from corn and the vast majority of ethanol plants in the U.S. utilize a dry-milling process to make their product. However, the wet-mill facilities tend to be larger and actually account for a larger share of total production capacity. Of the 73-ethanol plants in operation, seven are wet milling operations and represent about 33% of U.S. ethanol capacity.

Automobiles sold in the U.S. are designed with full warranty protection to operate with ethanol-blended petrol at a concentration of up to 10 vol% ethanol, without further engine modification. During the past few years, several major automobile manufacturers have developed FFVs that can run on either petrol or E85 fuel (85% ethanol by volume), or any blend of ethanol and petrol from 0% to 85% ethanol. In the U.S., there has been an increase in the sale of FFVs to more than 3 million vehicles. E85 availability also increased. Early in 2003, it was estimated that E85 was sold at 154 stations in 22 states. By May 2004, the number of E85 refueling stations had reportedly risen to 188 across 27 states.[7.28]

Ethanol-blended diesel is an experimental fuel in the U.S. With the increasingly more stringent U.S. Environmental Protection Agency (EPA) regulations restricting emissions from both on-road and off-road vehicles, the government's desire to reduce the imports of crude oil and petrol, and a Renewable Fuels Standard being discussed as part of a U.S. Energy policy, ethanol-diesel has the potential to become a future renewable alternative fuel for unmodified diesel engines.

Depending on a number of scenarios, Hart's *World Refining & Fuels' Service 2000 – 2015* predicts ethanol demand in the U.S. could increase to between 3.8 billion gallons and 5.3 billion gallons (14.4 billion and 20 billion liters respectively) by 2012 (Graph 1). The ethanol industry in the U.S. has risen to its current levels through strong public policy support. Virtually every candidate for U.S. presidency has supported ethanol, and its federal tax incentive. In addition, the U.S. Senate has traditionally been a pro-ethanol body. This support is expected to continue through the foreseeable future, particularly in light of energy security and growing dependence on foreign energy, and the need for improved air quality. It has been estimated that 60% of Americans live in areas where levels of one or more air pollutants are high enough to affect public health and/or the environment.

Graph 1: Projected U.S. Ethanol Demand Cases



Source: Hart's World Refining & Fuels Service 2000 to 2015

4.1.1 Fuel Ethanol Specifications

While the state of California regulates the quality of fuel ethanol, the U.S. federal government does not. However, the Renewable Fuels Association (RFA), which is the national trade organization for the U.S. fuel ethanol industry, recommends adherence to the ASTM specifications and guidelines.

The U.S. industry standard for ethanol is "ASTM D 4806 Standard Specification for Denatured Fuel Ethanol for Blending with Petrol for Use as Automotive Spark Ignition Engine Fuel."[7.4] The purpose of the ASTM specification is to provide parameters so petrol and petrol oxygenate blends will perform satisfactorily in as wide a range of consumer vehicles as possible. The ASTM has followed the premise that the only ethanol to be used in the marketplace as a gasoline extender will be denatured, and hence the specification D 4806 is for denatured fuel ethanol.

A separate ASTM specification[7.5] D 5798 "Specification for Fuel Ethanol (Ed75-Ed85) for Automotive Spark-Ignition Engine Fuel" is for fuel ethanol to be used in specially designated vehicles as a petrol substitute. This Ed75-Ed85 fuel ethanol is produced from ethanol complying with the ASTM D 4806 standard, and contains additional specifications for parameters applicable to vehicles designed to operate with high percentages of ethanol in their fuel. Additional parameters specified include hydrocarbon volume (as opposed to small amounts of hydrocarbon denaturant in the ethanol standard), vapor pressure, lead, phosphorus, sulfur, and total and inorganic chloride. The limits of several of the parameters are different than the ethanol standard, which is understandable since the fuel is comprised of up to 30 vol% of hydrocarbons.

The quality specifications contained in ASTM D 4806 and ASTM D 5798 are shown in the Tables below.

Table 6: ASTM D 4806 Standard Specification for Denatured Fuel Ethanol

Property	Specification	ASTM Test Method
Ethanol, vol%. Min	92.1	D 5501
Methanol, vol% max.	0.5	
Solvent-washed gum, mg/100 ml max	5.0	D 381
Water content, vol% max.	1.0	E 203
Denaturant content, Vol% min Vol% max	 1.96 4.76	
Inorganic Chloride content, mass ppm (mg/L) max	40	D 512
Copper content, mg/kg max.	0.1	D 1688
Acidity (as acetic acid CH_3COOH), mass% max	0.007	D 1613
pHe	6.5 – 9.0	D 6423
Appearance	Visibly free of suspended or precipitated contaminants (Bright & Clear)	

Table 7: ASTM D 5798 Standard Specification for Fuel Ethanol (Ed75–Ed85)

Property	Specification	ASTM Test Method
Ethanol + higher alcohols vol% minimum	70 – 79 [1]	D 5501
Hydrocarbon vol% [2]	17-30 [1]	D 4815
Vapor Pressure, kPa	38-83 [1]	D4953 / 5190 / 5191
Lead, max, mg/l	2.6-3.9 [1]	D 5059
Phosphorus, max, mg/l	0.2-0.4 [1]	D 3231
Sulfur, mg/kg , max [4]	210-300 [1]	D 1266 / 2622 / 3120 / 5453
Methanol, vol%, max	0.5	D 4815
Higher Alcohols (C_3-C_8) vol%, max	2	D 4815
Acidity (as acetic acid), mass% (mg/l), max	0.005 (40)	D 1613
Solvent-washed gum Content mg/100 ml, max	5	D 381
pHe	6.5 – 9.0	D 6423
Unwashed gum content, mg/100 ml, max	20	D 381
Total chlorine as chlorides, mg/kg, max	2	D 4929 B
Inorganic chloride, mg/kg, max	1	D 512 / 2988
Copper, mg/l, max	0.07	D 1688 modified
Water, mass%, max	1.0	E 203 / E 1064
Appearance @ higher of ambient temperature or 21^{0}C	Visibly free of suspended or precipitated contaminants (clear & bright)	

1. Three vapor pressure classes are provided for varied seasonal and climatic changes per geographical location.
2. The hydrocarbons may contain aliphatic ethers as blending components that are customarily used for automotive spark-ignition engine fuel.
3. The denaturant for the denatured fuel ethanol used in making fuel ethanol (Ed75-Ed85) shall meet the requirements of ASTM specification D 4806
4. Superseded 1 January 2004 by Federal specification of 30 ppm max.

The 15% petrol (and 25% petrol during winter) in the D 5798 Standard Specification for Fuel Ethanol are required to increase the fuel volatility and prevent engine cold-start difficulties. Safety is an additional benefit, since ethanol burns with a colorless blue flame making it more difficult to detect a fire in the engine system, whereas the presence of hydrocarbons would result in a clearly visible flame.

Since D 4806 denatured ethanol is used to prepare the D 5798 ethanol fuel, the discussion below focuses on D 4806.

The Bureau of Alcohol, Tobacco and firearms (BATF) requires fuel grade ethanol be denatured to render it un-potable and thereby avoid payment of the beverage alcohol tax. The BATF permits using several denaturants and specifies the volume range of denaturant to be added. However, certain denaturants permitted by BATF may not be suitable for fuel grade ethanol from the standpoint of fuel quality. For example, the BATF permits ketones such as 4-methyl pentanone (methyl isobutyl ketone) but these tend to degrade fuel stability. Kerosene could contribute to piston scuffing. Because of the above, the ASTM D 4806 permits only hydrocarbons in the petrol boiling range to be used as denaturants, and lists certain materials that are not permitted as denaturants under any circumstance.

U.S. Refiners are faced with the need to reduce the sulfur content of their petrol to comply with federal and state regulations that came into effect on 1 January, 2004. As of this date, the federal government has adopted a requirement that denatured ethanol used in conventional or reformulated petrol contain no more than 30 ppm sulfur. The process of amending ASTM D 4806 and D 5798 accordingly is underway. The State of California has adopted requirements that are more stringent and require an even lower sulfur level, and that place limits on other compounds. These requirements are summarized in Table 8.

Table 8: California Denatured Ethanol Standards (in addition to ASTM D4806)

Property	Specification	ASTM Test Method
Sulfur, ppm max	10	D 5453-93
Benzene, vol% max	0.06 [1]	D5580-95 [2]
Olefins, vol% max	0.5 [1]	D6550-00 (modified) [2]
Aromatics, vol% max	1.7 [1]	D5580-95 [2]

Source: RFA

1. Exceptions may apply, as outlined in ASTM D4806. Higher amounts of these components may be used if the supplier can assure that the denaturant will be used at less than 4.76 vol% max specified in ASTM, and that the specified limits for denatured fuel ethanol are still met.
2. Test results of a sample of the denaturant multiplied by 0.0476

In addition, California places limits on the denaturants used in ethanol, as specified in Table 9.

Table 9: California Ethanol Denaturant Standards

Property	Specification	ASTM Test Method
Benzene, vol% max	1.1	D5580-95
Olefins, vol% max	10	D6550-00 (modified)
Aromatics, vol% max	35	D5580-95

Ethanol is routinely commingled in storage, making it difficult to segregate ethanol destined for California from other destinations. In July 2002, the RFA board of directors adopted a recommendation that all ethanol distributed for fuel use in the U.S. meet the more stringent California specifications as set forth in the above tables.

In addition, the RFA recommends:

- **Filtering of Ethanol Product**: The product delivery system dispensing denatured ethanol from plant storage tanks should be equipped with a final filter sized no larger than a maximum of 10 microns absolute to control any suspended particulates or precipitates.
- **Corrosion Inhibitors**: The RFA recommends that corrosion inhibitors be added to fuel grade ethanol at a treat rate sufficient to provide corrosion protection comparable to that of other available motor fuels. While the RFA

does not endorse a specific corrosion inhibitor, they have established criteria for what the additive should achieve. Specifically their guideline calls for ethanol to be added to an E rated petrol (National Association of Corrosion Engineers (NACE) Standard test Method TM-01-77). The additive, when blended at the recommended treat rate, must raise the NACE rating to B+ or better.

Table 10: Corrosion Inhibitors Recommended for Fuel Grade Ethanol

ADDITIVE	**TREAT RATE** *in* **PTBE (** ***pounds per thousand barrels of ethanol)***
Octel DCI-11	20
Petrolite Tolad 3222	20
Petrolite Tolad 3224	13
Nalco 5403	30
ENDCOR FE-9730 (formerly Betz ACN13)	20
MidContinental MCC5011E	20
MidContinental MCC5011EW	27

Source: RFA Publication # 960501 Revised December 2003

Corrosion inhibitors adjust the pHe (and hence corrosion potential by strong acids) of the ethanol. The pHe specification in both ASTM D 4606 and ASTM D 5798 is performed on denatured fuel ethanol.

4.2 EUROPEAN UNION (EU)

It is important to distinguish between the U.S. and the EU in terms of their focus on different biofuel streams. The U.S. has always addressed biofuels in the form of ethanol primarily due to its large petrol market. By comparison, biodiesel has received greater attention in Europe due to the oversupply of petrol and continued diesel demand growth.

The feedstocks used in the EU to produce ethanol are cereals, sugar beets, potatoes, co-products of the agro-industry and surplus wine. At present, there are two main applications for ethanol in Europe:

- Direct blending of ethanol with petrol (Sweden, Poland and Spain in very small quantities)
- Conversion of ethanol into ETBE for blending into petrol (France, Poland, Spain, Italy)

Table 11: Existing European Ethanol and ETBE production; 2000

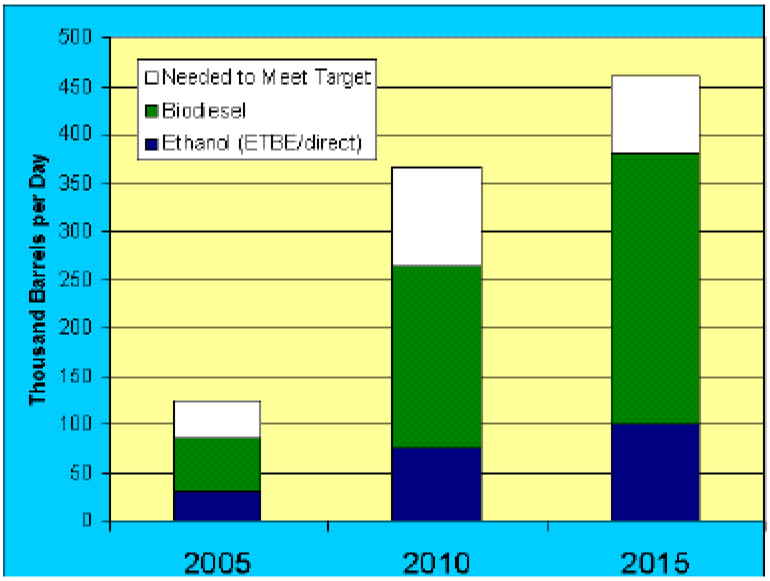
Country	Ethanol (tons/yr)	ETBE (tons/yr)
France	91,000	193,000
Spain	80,000	170,000
Sweden	20,000	-
Total	191,000	363,000

Source: EuroObserver April 2002

European automakers, policy makers and refiners have tended to be more reticent towards the use of greater than 5 vol% ethanol petrol blends due to a variety of reasons, including the fact that refiners are already faced with a European market that is long in petrol and short in diesel.

The goal for biofuels in the EU is a transportation fuel market penetration of 2 vol% by 2005, 6 vol% by 2010 and 7 vol% by 2015, with the percentages based on energy content, not liquid volumes. So far, there is no binding legislation to enforce the goal and the biofuel targets remain indicative rather than mandatory. However, there is some movement to make the targets mandatory if the voluntary levels are not met. Growth predictions for a 2 vol% biofuels market penetration could amount to approximately 7.2 million tons of ethanol and biodiesel. This estimate is based on EU total automotive fuel demand of 270 million tons in 2005. In 2010, a target of 5.75 vol% could amount to approximately 21.4 million tons ethanol and biodiesel (see Graph 2). Of that amount, almost two-thirds will be from the use of biodiesel.

Graph 2: EU Renewable Fuel Use & Targets



Note: Amount needed to meet EU Biofuels targets assumes the fuel split between petrol remains constant and that ethanol enters the Pool primarily as feedstock for ETBE.

Source: Hart's Renewable Fuel News

4.2.1 Fuel Ethanol Specifications

The European Union does not currently have a fuel ethanol specification, which is harmonized across the existing 15 EU member states (Austria, Belgium, Denmark Finland, France, Germany, Greece, Italy, Ireland, Luxembourg, Portugal, Spain, Sweden, The Netherlands, United Kingdom) and new members (Cyprus, Czech republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovenia, Slovakia).

European Directive 98/70/EC (amended by 2003/17/EC), which regulates the quality of petrol and diesel fuels, officially authorizes petrol that contains no more than 5 vol% anhydrous ethanol for sale at the pump. To date, splash blended 5 vol% anhydrous ethanol blends have been limited to only a few European markets including Spain, Sweden and Poland. The European Commission recognizes that an ethanol standard and monitoring (enforcement) standard will be necessary, and a Center for European Normalization (CEN) TC 19 Ethanol Task Force is in the process of drafting an ethanol standard for blends up to 5 vol% anhydrous ethanol.

According to present EU legislation, high percentage ethanol fuel such as E85 is not covered by the current Fuels Standards. Therefore an E85 working group has been established to address issues related to E85 and to decide whether an EU standard is necessary for Europe. This group is run by Ford Motor Company and is comprised of bio-ethanol producers, oil refiners and car manufacturers who are already involved in the CEN/TC 19 Ethanol Task Force. The envisaged Workshop Agreement has a small direct market impact, as there are only limited numbers of European cars running on E85 at the moment. E85 is produced in Europe by Sekab (Sweden) and supplied to restricted fleets of vehicles. In Sweden 6 000 FFVs have been sold since 2001. Sales of vehicles commenced in Spain in 2003 and next the German and United Kingdom markets are under consideration. The techniques to produce and use this type of fuel are known and other car manufacturers may well intend to start production of FFVs. Once the CEN report is published the market can be more readily opened to other areas that would like to introduce E85 as a fuel for use in captive fleets or restricted areas.

Ethanol activities in EU member countries are as follows:

Finland

Fortum Oil launched a pilot project to produce Futura 98 octane with a maximum of 5 vol% ethanol until the end of 2003. The first batch of 3,000 cubic meters of ethanol was imported from Italy, and the delivery of the first batch of Futura 98 was trucked from Fortum's Porvoo refinery to Helsinki and South East Finland. For the time being, the ethanol used in the manufacture of the new bio-petrol will be procured from the EU's surplus stocks of wine alcohol. Other procurement sources will be needed in the future.

France

France is the country with the most advanced fuel alcohol production in Europe. France currently uses 70% sugar beet and 30% cereals as the feedstock for its bio-ethanol. In 1987, a law was passed allowing the blending of 3-15 vol% of organic oxygenated compounds into petrol (3 vol% for pure ethanol and 15 vol% for ethers such as ETBE). In November 1996, the French parliament approved a draft law on clean air that made the use of oxygenated components in fuel mandatory by year 2000. The government has yet to decide upon the exact blend composition, but the farming sector is lobbying heavily for a 2 vol% ethanol-petrol mixture.

Italy

Bio-ethanol production in Italy has been based on a European surplus of wine ethanol, which was originally intended for export to Brazil, but is increasingly used for national ETBE production. However, Italy is now planning to use other ethanol feedstocks (such as wheat) in a new 115,000 liter/day fuel ethanol plant to be constructed in Salerno.

Spain

Barley is the feedstock used at the 100 million liter Ecocarburantes Espanoles ethanol plant owned by Abengoa, which was commissioned in October 1999. A co-generation plant is connected to the alcohol plant to provide energy for the alcohol plant and the neighboring community.

4.2.2 SWEDEN

Sweden started to consider ethanol in 1985 because of the environmental benefits, mainly in the form of reduced climatic impact. In Sweden, ethanol is derived from both grain and timber, for example from the Modo company's sulphite plant in Örnsköldsvik. Annual production capacity is 12,000 m^3. That is enough to power more than 8,000 midsize cars for a year. A new Agroetanol plant in Östergötland province, running on corn, is expected to produce 50,000 m^3 of ethanol a year, using the utilities of a close by biofuel power plant. At present however, about two-thirds of ethanol is still an imported commodity, mainly from Spain and Brazil. For it to become a significant source of fuel, it will have to be more effectively extracted from timber.

Sweden's ethanol plant supplied the Stokholm Norrkòping area anhydrous alcohol in a 5 vol% mixture into premium petrol. In 2003, Sweden decided to increase its use of ethanol substantially and now 80% of the petrol pool contains 5 vol% ethanol, which meets the EN228 petrol specification. This equates to about 240,000 m^3 of ethanol. There are 110 filling stations at which 5% ethanol blends are offered.

In addition, there are at least eight E85 fuelling stations in Stockholm, and over 50 more sites nationwide. Swedish weather requires that ethanol have a 15% petrol mix to help cold starts. Previously only one ethanol-powered car model existed in Sweden – the Ford Taurus Flexible Fuel Vehicle (FFV). The number of FFVs in Sweden is growing, and additional models have been introduced into the market. The city of Stockholm operates Europe's largest fleet of FFVs.

After successful research with ethanol-fuelled buses since the eighties, pure ethanol with ignition improver has become an established bus fuel.

4.2.2.1 Fuel Ethanol Specification

Svensk Etanolkemi AB, or Sekab, supplies biological ethanol for a number of different applications from Sweden's Domsjö Fabriker, which manufactures ethanol from forestry raw materials. Sweden does not have a national standard for fuel ethanol at the time of writing this report. The Sekab sales specification for anhydrous ethanol 99,5% is serving as the industry standard at the moment, pending the outcome of the EU CEN/TC19 task force.

Table 12: Sekab 99,5% Ethanol specification

Property	Specification	Test method
Ethanol content, % volume	99.8 %minimum	AMSE 1112
Density, g/ml	0.790 max	SS-ISO 758
Appearance	Clear, without particles	ASTM D 2090
Color, Hazen	5 max	AMSE 1102
Water, % weight	0,3 max	SS-ISO 760
Aldehydes (as acetaldehyde), % weight	0.0025 max	AMSE 1118
Acidity (as acetic acid), % weight	0.0025 max	AMSE 1114

In addition, the seller guarantees the following properties although they are not tested on each delivery:

Distillation Interval: - Starting point ^0C - Drypoint ^0C	 Min 77 Max 81	ASTM D 1078
Flashpoint ^0C	+12	SS-EN 22719
Fusel Oil mg/l	Max 50	AMSE 1136, GC-method
Methanol mg/l	Max 20	AMSE 1135, GC-method
Explosion limits, % by volume in air	3,5 - 15	Accepted from literature
Refractive Index n_D20	1,3618	Accepted from literature
Evaporation residue mg/l	Max 10	AMSE 1124

The guaranteed but not regularly tested specifications are selected by the supplier and not discussed by the industry, but some such as methanol and fusel oil may be included in a future EU standard.

Sweden is in favor of a high purity ethanol of 99.8% minimum to ensure the correct degree of purity for use in automobiles. The remaining 0.2% is mainly water and methanol.

East/Central Europe and Russia

At present the Russian ethanol market is geared towards beverage alcohol. However, the potential for non-food production of ethanol is quite high and, if an ethanol fuels market develops, and the Russian government's ethanol policy gets finalized, Russian ethanol production for transport purposes could increase substantially.

Although Russia dominates the ethanol market, other Eastern and Central European countries as well as the Baltic States have taken an interest in ethanol production for fuel purposes. **Poland** is well ahead of the pack and has already invested in ethanol production for fuel purposes. In addition to Poland, **Hungary**, the **Czech Republic** and **Estonia** are very interested in investing in ethanol production but no concrete projects have materialized yet.

4.2.3 POLAND

Poland has stipulated ethyl alcohol use as a leaded and unleaded petrol component (ethanol 4.5% - 5%) by lowering the excise tax. Due to this initiative, the market share of petrol containing ethanol is now almost 30%, as shown in table below. This policy was mainly intended to support the farming community.

Table 13: Poland's use of bio-ethanol in petrol

Year	1995	1996	1997	1998	1999	2000	2001	2002
Bioethanol production [m3]	63000	100900	110000	99800	83226	51449	71899	82 800
Bioethanol production [t]	49 707	79 610	86 790	78 742	65 665	40 593	56 728	65 329
% of ethanol in total production of petrol in Poland	0,91	1,70	1,72	1,55	1,11	0,78	1,13	1,45
% petrol with min 4.5% bioethanol on market acc. EN228	20,22	37,70	38,13	34,51	24,71	17,43	22,6	29,0

4.2.3.1 Fuel Ethanol Specification

The Polish Bioethanol Standard PN-A-79521 for anhydrous ethanol used in fuel is based on the U.S. ASTM D 4806 standard. It is not a mandated standard at this time, and will be replaced once the European standard has been finalized.

Table 14: Fuel Ethanol Specifications in Poland and Ukraine

Property	Poland	Ukraine
Ethanol, vol% min	99.6	99.3
Water, mass% max	0.4	0.2
Density @ 20 ^{0}C, Kg/m^3 max	-	791
Refractive Index, R2^0, min	-	1.3626
Chloride mg/l (ppm) max	40	-
Copper content, mg/kg, max	0.1	-
Methanol, vol% max	0.2	-
Acids as Acetic Acid, g/l max	0.03	0.02
Aldehydes & ketones , g/l max	0.2	-
Fusel oil/ Amyl Alcohol % vol	2	-
Bitrex g/100 liters ethanol	0.1	
Cyclohexane, vol% max	-	0.5
C_3-C_5 alcohols, ppm max	-	12,000
Non-volatile matter, g/100 ml, max	-	0.005

The Polish regulation allows up to 5 vol% maximum of unleaded gasoline to be added to the 99.6% purity ethanol, and this blend may be sold as fuel ethanol. Corrosion inhibitors are typically added to finished petrol and not to the fuel ethanol itself.

"Bitrex" is the brand name of an extremely bitter, inert and odorless substance. Only tiny amounts are needed to make products taste unpalatable. Since children are particularly sensitive to bitter tastes, Bitrex is a powerful deterrent to accidental swallowing. Macfarlan Smith Ltd, now a wholly owned subsidiary of Johnson Matthey plc, first discovered Bitrex in 1958 with representation in several countries including

Australia. Bitrex was first used in denaturing alcohol to make it legally unfit for human consumption, and it is now added to a wide range of household cleaners, pesticides, and automotive products.

4.3 BRAZIL

Ethanol has been added into petrol in Brazil since the 1930s. It was a “relief valve” of surplus ethanol production when the sugar market was in recession. At that time, vehicles were not tuned to run on the mixture, and they had poor performance and higher fuel consumption, and Brazilian petrol developed a negative image to consumers. However, during the World Oil Crisis in the 1970s, ethanol attained a new role as a fuel extender in Brazil. The PROÁLCOOL program was established in 1975 to promote petrol replacement by ethanol. In 1979, petrol C was created, which was petrol plus 20 vol% maximum anhydrous ethanol. In addition, petrol vehicles were converted to run with pure hydrated ethanol, and the petrol price was increased artificially to force ethanol use, while the price of ethanol itself was artificially reduced through subsidies. The first hydrated ethanol (~93% ethanol, 7% water) only fueled vehicle was produced in 1979, and the government fleet renovation had to be with pure ethanol vehicles. The first ethanol specification was adapted from pharmaceutical use.

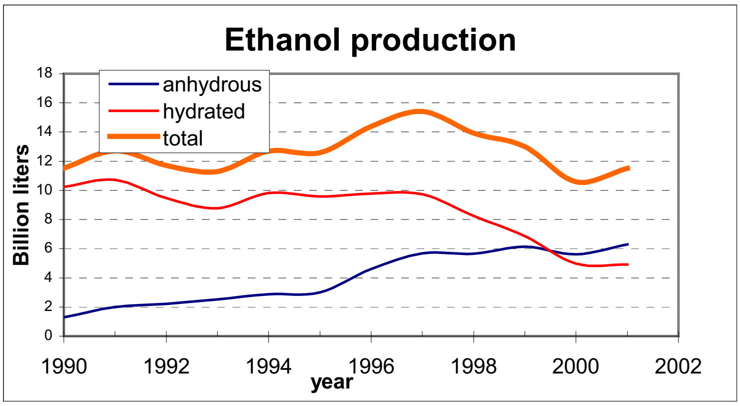
In 1982, the anhydrous ethanol content in petrol in Brazil was increased to 22-vol% due to high ethanol production and limited exports. Fuel economy and drivability were the main concern during this period. Then in 1988, due to an increase in sugar prices in the international market, Brazil suffered a shortage of ethanol. A mixture of ethanol, methanol and petrol was used to fuel the pure ethanol vehicles, and the anhydrous ethanol content in petrol was reduced to 18%. The result of these changes was an increase in spark plug fouling, and high CO and HC emissions due to alcohol/fuel enrichment in the pure ethanol vehicles. Consumers lost confidence in the PROÁLCOOL program and sales of pure ethanol vehicles dropped dramatically.

In 1993 the PROCONVE (exhaust emissions legislation in force since 1986) was the reason for enacting a law regulating ethanol addition to petrol. This law established that automotive petrol must contain 22 vol% of anhydrous ethanol. The result is that imported vehicles have to be recalibrated to run with Brazilian petrol and Brazilian manufacturers need to have a separate assembly line for exported vehicles.

Since 2002, the Brazilian government began reviving the PROÁLCOOL program, and anhydrous ethanol addition to petrol has been fixed at between 20 vol% and 25 vol%, depending on ethanol production. During the years of low world sugar prices and high ethanol production, producers and traders requested the government to increase ethanol addition in petrol to 30 vol%. But the Brazilian automotive industry does not accept higher that 25 vol% anhydrous ethanol content in petrol. In addition, sales of hydrous ethanol vehicles have shown some increase. Behind the government’s program is a 10-year deal with Germany, where the latter will purchase carbon credits as part of it’s commitments to the Kyoto Protocol, and these funds will in turn help the Brazilian government to subsidize fleets operating on pure, hydrous ethanol.[7.15]

Ethanol production capacity in Brazil is of the order of 16 billion liters/year (see Graph 3). The primary feedstock is sugar.

Graph 3: Ethanol Production in Brazil



Source: Hart's WFC Petrobras presentation March 2004

During 2003, Brazil's first flexible fuel vehicles were produced by major Brazilian manufacturers. These vehicles operate on a mixture of petrol and ethanol, or pure ethanol. Volkswagen's "Totalflex" can use petrol, ethanol or compressed natural gas. Ethanol producers are eagerly awaiting the consumer's acceptance of the flexible fuel concept to accommodate all ethanol production and international market variations.

With PROÁLCOOL, the internal gasoline consumption in Brazil was drastically reduced, but the refining level could not be reduced accordingly since diesel oil consumption was high and sufficient diesel had to be produced. Actions to increase the ethanol market included ethanol addition to diesel. To date the addition of ethanol to diesel fuel, even in small amounts such as 3 vol%, has not been implemented because tests have shown a high premature wear of rotary fuel pumps and evidence of it in in-line fuel pumps. Participants in the test program included Maxim, Cummins, Daimler Chrysler, Bosch and Petrobras.[7.1]

4.3.1 Fuel Ethanol Specifications

The National Petroleum Agency (ANP) set specifications for both hydrous and anhydrous fuel ethanol.[7.6] The current specifications, dated 15 January 2002, and re-published on 2nd August 2002, are presented in Table 15 below.

The test methods specified are from the Brazilian Association of Technical Standards (NBR) and American Society for Testing and Materials (ASTM).

Table 15: Brazilian Fuel Ethanol specifications

Property	min/ max	Anhydrous Ethanol	Hydrated Ethanol	NBR test Method	ASTM test Method
Appearance		Clear & free of suspended impurities	Clear & free of suspended impurities	Visual	Visual
Color		Colorless or yellow	Colorless or yellow	Visual	Visual
Total Acidity as acetic acid, mg/l	max	30	30	9866	D 1613
Electrical conductivity, MicroS/m	max	500	500	10547	D 1125
Density@ 20 0C kg/m3	max	791.5	807,6– 811,0 [1]	5992	D 4052
Alcohol content ^{0}INPM	min	99,3	92,6 – 93.8 [2]	5992	_
pH		-	6 - 8	10891	-
Evaporative Residue 3 mg/100 ml	max	-	5	8644	-
Hydrocarbon content % vol [3]	max	3,0	3,0	13993	
Chlorides mg/kg [3]	max	-	1	10894/10895	D 512
Ethanol content % vol	min	99,3	92,6	-	D 5501
Sulphate, mg/kg	max	-	4	10894/12120	-
Fe mg/kg	max	-	5	11331	-
Na mg/kg	max	-	2	10422	-
Copper mg/kg	max	0,07	-	10893	-

1. For importation and distribution the density limits are 805.0-811.0
2. For importation and distribution the alcohol limits are 92.6-94.7
3. Importation and distribution specification

A committee of stakeholders that included corrosion experts from the automotive industry set Brazil's fuel ethanol standards. They decided it was unnecessary to limit other components (except copper and water content) in the anhydrous ethanol specification as the ethanol content was so high that these other components would have been removed during the dehydration process.

Brazil imported mixtures of fuel alcohols during the ethanol shortages, and corrosion problems were experienced. Acids such as HCl formed by chloride ions in water were suspected, and this led to a more stringent Chloride specification of 1 mg/kg max for hydrated ethanol – substantially more stringent than the 40 ppm max in place for anhydrous ethanol in most countries. Even low levels of chloride ions are corrosive to many metals. The Brazilian distilleries cannot use hydrochloric acid (HCl) during the manufacturing process as they use stainless steel equipment, and hence they have to use sulfuric acid (H_2S0_4). Therefore they have no problem meeting the Chloride specification. The Chloride specification and the pHe specification applicable to hydrated ethanol ensure that the presence of strong acids is within acceptable limits.

A sodium (Na) specification for hydrated ethanol is used to prevent too much addition of sodium hydroxide (NaOH) to adjust acidity when the pHe is off-specification. Carryover of strong acids from the manufacturing process could cause the pHe to be too low. Na accumulates in the vehicle combustion chamber and causes corrosion. Iron (Fe), Cu and sulphates (present as SO_3 and SO_4) form a gum with petrol, and result in scale in engine pipes, and hence these parameters are also limited.

The pHe and acidity specification are two different methods of measuring acidity. The former measures strong acids, and the latter detects the presence of weak acids. Water content and other components affect the conductivity. Thus a conductivity specification is an additional control to check that there have not been problems in the distillation process and carryover of salts to the ethanol.

Sometimes two different test results do not correlate well with each other. After storage in the tank for 3 to 4 months, sometimes the pHe of the ethanol drops and NaOH is added to correct this. It would be expected that the conductivity would increase, but this does not always happen. It is thought that the practice of adding NaOH to correct acidity results in a precipitation in the tank. It is recommended that Brazilian fuel stations install filters, however, many do not have these.

4.4 ASIAN OVERVIEW

4.4.1 CHINA

China has become the third-largest ethanol producer in the world, with annual production of around three billion liters. Corn is the primary feedstock, but distilleries are also experimenting with cassava, sweet potato and sugar cane. Analysts estimate that in the next two to three years, as much as 25% to 30% of the country will use corn-based ethanol blended fuels. The regulated gasohol specification (GB18351-2001) limits the amount of ethanol added to conventional petrol to 10±2 vol%, and was implemented on 1 July 2003. China does not currently have a standard for fuel grade ethanol.

Various trials are taking place in corn producing provinces:

- In Henan province 8 vol% to 12 vol% ethanol-petrol blends have been used in a trial, with no negative response so far. The next step is to possibly use ethanol permanently in the province. The original aim of the trial was to promote ethanol based petrol in the whole Henan province by the end of 2002.
- China has recently decided to expand its gasohol trial to nine provinces: Heilongjiang, Jilin, Liaoning, Henan and Anhui as well as parts of the provinces of Hubei, Shandong, Hebei and Jiangsu.

There have been discussions between the Chinese and Brazilian governments on the possibility of dedicated ethanol vehicles in China.

4.4.2 INDIA

India initiated the use of ethanol as an automotive fuel a few years ago. The introduction (and mandate) of a maximum of 5 vol% ethanol blended into petrol (gasohol) in all of the first stage areas (8 States and 3 contiguous Union Territories (UT)) is supposed to be in effect by early 2004. States of Tamil Nadu as well as UT of Pondicherry and Uttaranchal and Madhya Pradesh are the last to be included in the first stage. The second stage will expand this mandate to the rest of the country.

There has been a steady increase in the production of ethanol in India, with estimated production rising from 887.2 million liters in 1992-93 to nearly 1,654 million liters in 1999-2000. Surplus alcohol leads to depressed prices for both alcohol and molasses. According to the “alcohol task force,” the projected alcohol production in the country will increase from 1869.7 million liters in 2002-03 to 2,300.4 million liters in 2006-07. Thus the surplus alcohol available in the country is expected to go up from 527.7 million liters in 2002-03 to 822.8 million liters in 2006-07.

Utilization of molasses for the production of ethanol in India will not only provide value-addition to the byproduct, but also ensure better price stability for the sugar mills. This will improve the viability of the sugar mills, which will in turn benefit cane growers. With petrol demand expected to increase from 7.9 million tones in 2001-02 to 11.6 million tones in 2006-07, the requirement of ethanol at 5 vol% in the blend is expected to rise from 465 million liters to 682 million liters.

Following is a table showing the ethanol blend coverage in Indian States and districts as at December 2003:

Table 16: Indian states blending ethanol: December 2003

Sl. No.	State/UT	Districts	Districts Covered
1	Uttar Pradesh	71	71
2	Haryana	19	19
3	Punjab	17	17
4	Chandigarh	1	1
5	Maharashtra	35	35
6	Gujarat	25	25
7	Goa	2	2
8	Daman & Diu	2	2
9	Dadra & Nagar Haveli	1	1
10	Karnataka	27	27
11	Andhra Pradesh	23	9
	TOTAL	223	209

Envisioning the third phase of this project (originally planned to start in October 2003), the Indian government is considering three pilot projects in 2004 with up to 10 vol% ethanol-petrol blends. Two of the three locations were named. These are Maharahtra and Uttar Pradesh, both sugar cane producing states.

Diesohol (ethanol blended with diesel) R&D studies have also been started, which is the fourth phase of the introduction of ethanol into the conventional fuel pool.

Timing has been a problem (deadline for 5 vo% ethanol mandate has been postponed many times), and currently there is not enough ethanol produced to cover a mandate of 10 vol% blends in the whole of the country.

4.4.2.1 Fuel Ethanol Specification

Table 17 below shows the Indian standard "IS 15464:2004 for Anhydrous Ethanol for Use in Automotive Fuel – Specification."[7.14] The standard below prescribes requirements, methods of sampling and test for anhydrous ethanol, which is used either as such or more usually in a blend with gasoline and diesel as a fuel for automobile engines.

The term "anhydrous ethanol" can be applied loosely and alike to absolute ethanol that is later denatured, ethanol after denaturant has been added, and a blend obtained from this denatured ethanol by mixing it with other fuels such as petrol. An attempt has been made in this standard to confine the name anhydrous ethanol to be denatured ethyl alcohol only and to keep it distinct from the blends that may be produced from it by a mixture of this anhydrous ethanol and automobile fuel.

Ethyl Alcohol (Absolute Alcohol) is defined in the standard as a clear, colourless and homogeneous liquid consisting essentially of ethanol with not more than 0.5 vol% of water. Anhydrous ethanol is defined as essentially ethyl alcohol, which is denatured and is meant for use as fuel in automobile engines.

Table 17: Indian Ethanol Specification – Indian Standards IS 15464:2004
Requirements of Anhydrous Ethanol for use in Automotive Fuel

Absolute (Anhydrous) Alcohol	Special Grade	Test method [1]
Relative Density @ 15.6/15.6 °C, max	0.7961	A
Ethanol content @ 15.6 °C, vol%, min (excluding denaturant)	99.5	B
Miscibility with water	Miscible	C
Alkalinity	Nil	D
Acidity (CH3COOH), mg/l, max	30	D
Residue on evaporation, wt%, max	0.005	E
Aldehydes, as (CH3CHO), mg/l, max	60	F
Copper, mg/kg, max	0.1	G
Conductivity, microS/m, max	300	H
Methyl alcohol, mg/liter, max	300	J
Appearance	Clear and bright	visual

Note: 1. For test methods, reference should be made to the Bureau of Indian Standards IS 15464:2004
2. The denaturant to be mixed with ethanol in a proportion which is to be prescribed by law from time to time.

The Indian Standard makes specific mention of a list of prohibited denaturants, which it states have extremely adverse effects on fuel stability, automotive engines and fuel systems. These materials may not be used as denaturants for anhydrous ethanol for use in automotive fuels in any circumstances. They are as follows: methanol, pyrroles, turpentine, ketones and tars (high molecular weight pyrolysis products of fossil or non-fossil vegetable matter). It further states that unless a denaturant such as higher aliphatic alcohol or ether is known to have no adverse effect on a gasoline-ethanol blend, or on automotive engines or fuel systems, it shall not be used.

Subject to the effect of the added denaturant, anhydrous ethanol is required to comply with the requirements for general purposes prescribed for ethyl alcohol above.

4.4.3 THAILAND

The push for ethanol in petrol (gasohol) and biofuels is not a recent development in Thailand; it has been encouraged for the past 20 to 30 years by previous governments. This encouragement has led to a pilot scale ethanol distillery and continuous Research and Development (R&D) of gasohol, ethanol in diesel (diesohol) and more recently biodiesel as well. Also, several governments and research institutes have conducted R&D programs, which provided the base for the launch of an ethanol policy in Thailand in the year 2000.

Biofuels and gasohol are a means not only to allow Thailand to ease reliance on imported crude products, but moreover, to provide Thailand the possibility of using excess food commodities (tapioca, sugar cane, rice, coconut, palm and other edible crops) as raw material for ethanol production and simultaneously improve the living standards for several millions of farmers in rural Thailand, as well as improving environmental conditions (water and air quality). For ethanol production, there is an annual capacity of more than 20 million tons of cassava, 50 million tons of sugar cane and 2.5 million tons of molasses available.

Hydrous ethanol in Thailand is normally produced from sugar cane, molasses or cassava root. In 2000, Thailand produced 19 million tons of cassava and 49 million tons of sugar cane. There is currently only one plant producing ethanol in Thailand: Pornvilai International of Ayuddhaya with a capacity of 9.1 million liters/year. By June or July another plant in Nakornpathom is expected to come on line with another 73 million liters/year. By the end of this year two more plants are expected to be commissioned. At this stage the production capacity may reach around 183 million liters/year – a conservative estimate. Up to six others are being planned, and combined with the existing plant, will see a total capacity of over 490 million liters/year. The Japanese Marubeni Corporation is working with the Thai company Tsukishima Kikai to complete a commercial plant in Thailand in 2005, using sugar cane wastes and tapioca as feedstock, and genetically modified bacteria. The plant is expected to produce 30 million liters/year of ethanol, some of which could be exported to Japan

Thailand will begin replacing MTBE in petrol with up to 1 million liters/day (264,172 gallons/day) ethanol during 2004-2006, according to a representative from PTT, Thailand's only fully integrated gas company with a dominant position in oil marketing and trading. Replacing MTBE with ethanol is part of the government’s effort to promote gasohol (10 vol% ethanol petrol blend) and has been ongoing for many years. This plan was first announced on 9 December 2003, after a Thai Cabinet resolution. In the initial stages, only 95 RON petrol will be blended with ethanol. Once ethanol capacity reaches an expected 3 million liters/day (792,516 gallons/day) by 2011, blending in both 95 RON and 91 RON petrol to replace the use of MTBE is planned. At this stage, a mandated ban of MTBE is not expected.

4.4.3.1 Fuel Ethanol Specification

According to PTT, there is currently no specification for fuel ethanol grade in Thailand. An “Absolute Ethanol Industrial Standard” is set up for distillery plants and this ethanol can be used as fuel ethanol after it has been denatured. See Table 18 for the specifications for “Absolute Ethanol:”

Table 18: Specifications of Absolute Ethanol

Absolute (Anhydrous) Ethanol	Specification	Test Method
Ethanol @ 20°C, vol%, min	99.5 (*)	B.S. 507
Acidity (as acetic acid), wt%, max	0.002	GC
Ketone (as acetic acid), wt%, max	0.001	GC
Isoamyl alcohol, wt%, max	0.05	GC
Furfuraldehyde, wt%, max	0.001	GC
Propan-2-ol, wt%, max	0.002	GC
Methanol, wt%, max	0.010	GC
Non-volatile matter, wt%, max	0.001	USP (1985)

Note: (*) In case used for alcoholic beverage, spec is min 95 vol% (B.S. 506).
Fuel ethanol specification that is agreed between commercial ethanol plant and each oil company will be different from the above specification. It may apply to absolute or denatured ethanol.

4.4.4 JAPAN

Japan plans to introduce gasoline containing 3 vol% ethanol in 2004, as part of its commitment to meet the targets set in the Kyoto protocol. The petrol standard has already been amended to allow 3 vol% ethanol to be added to petrol. The government has plans for 10 vol% ethanol blends by 2008. The Ministry of Environment has urged the automobile industry to produce models that can be warrantied for petrol containing 10 vol% anhydrous ethanol. It is estimated that if Japan were to implement ethanol blending at 10 vol%, the potential market for anhydrous ethanol in Japan could be as much as 6 billion liters/year. Since Japan has no surplus agricultural production and limited useable land, most of the ethanol will have to be imported.

5. ASSESSMENT OF KEY PARAMETERS OF FUEL ETHANOL THAT IMPACT VEHICLE EMISSIONS & PERFORMANCE

5.1 KEY PARAMETERS OF FUEL ETHANOL

In this section, the key parameters of anhydrous fuel ethanol that are regulated in the countries surveyed as well as by Australia's Manildra Group and CSR Distilleries, are discussed. If the parameters of anhydrous fuel ethanol need to differ for use in the higher concentrations than permitted by non-conventional vehicle technology, such as found in dedicated ethanol vehicles, or in FFVs, this will be highlighted.

Sweden does not have a national ethanol standard. The Svensk Etanolkemi AB (Sekab) specification has become a de facto standard. In the discussion below, when reference is made to Sweden, the specification actually being referred to is the Sekab specification.

When Brazil's hydrous ethanol specification is quoted, as opposed to anhydrous ethanol, this is noted in the tables below the country title.

1) Ethanol Content

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Volume % min	92.1 [1]	99.8 (99.7 mass%)	99.6	99.5	99.3	99.25	99.4
Test method	ASTM D 5501	AMSE 1112		B	ASTM D 5501		BP2002

1) After denaturing

Specifying the minimum ethanol content is essential to minimize the presence of other components that may have a detrimental effect on vehicles or fuel performance. Ethanol content may also affect the lubricating properties of the fuel, it's water tolerance and ability to meet cold area volatility requirements.

The U.S. specification equates to a minimum undenatured ethanol content of approximately 95 vol%. In the U.S., the minimum ethanol content of denatured ethanol plus the minimum denaturant make up at least 97% of the total volume, thereby limiting other components to under approximately 3%. Other components typically found in commercially produced fuel ethanol include water, methanol, and fusel oils such as amyl and iso-amyl alcohols. Discussions have been held within ASTM to increase the minimum ethanol content to be more in line with international norms. However the ethanol producers extract fusel alcohol from chemical grade ethanol during the drying step, and have argued that they require the outlet for this product into fuel grade ethanol, particularly during summer months. Since no evidence of detrimental fuel performance as a result of this activity has been identified to date, the minimum ethanol content has not been increased in the U.S.

In dedicated ethanol vehicles, the air to fuel ratio is set, and as consistent an ethanol content as possible will facilitate optimum vehicle operation. This is much less important for FFVs where the onboard computer measures the conductivity of the fuel and automatically adjusts the air to fuel ratio accordingly.

Since both Australian producers currently meet a specification in excess of 99 vol%, a minimum ethanol content specification of 99 vol% should not cause any hardship.

2) Methanol content

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Volume % max	0.5 [1]	20 ppm (0.002%)	0.2	300 ppm (0.03 %)			
Test method	Methanol standard ASTM D 1152	AMSE 1135, GC method		J			

1. After denaturing

Methanol is toxic, and is naturally present in small quantities in industrially produced ethanol. According to ASTM, any significant amount of methanol will lower the water tolerance and increase the vapor pressure of an ethanol-petrol blend, but these effects become more serious when methanol is present at more than 2.5 parts by volume per 100 parts by volume of fuel ethanol. In addition, lower purity methanol can contain turpentine and tars, which increase the tendency of the fuel ethanol blend to corrode metals or attack elastomers. The ASTM D 4806 and the ASTM D 5798 recommend a maximum of 0.5 vol% of methanol that meets ASTM specification D 1152 " Standard Specification for methanol (methyl alcohol)" 99.85% grade.

Although the EU allows up to 3 vol% methanol in petrol under the EN228 petrol specification, Poland and Sweden do not allow methanol. This is in accordance with the World-wide Fuel Charter 2002, which does not permit methanol in fuel.

The U.S. ASTM specification is higher than both Sweden and Poland, but since the U.S. allows a higher concentration of heavier fusel alcohols which will act as a co-solvent to methanol, thereby enhancing it's solubility in gasoline in the presence of water, and it requires high purity methanol to be used, this limit seems reasonable.

With a minimum ethanol purity specification as high as 99 vol%, the need for a methanol specification is debatable, and will likely be a consensus decision between Australian stakeholders. The British Pharmacopoeia (BPS) specification on methanol for food and cosmetic applications is 0.02 vol% maximum. Currently Manildra tests fuel ethanol tank samples daily, and reports typical results well below 0.1 vol%. CSR typically measures less than 0.005 vol% methanol in their fuel ethanol. The contract laboratory reportedly measured levels of 0.045 vol% methanol in CSR fuel ethanol samples.

3) Solvent-washed gum

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
mg/100 ml max	5.0 [1]						
Test method	ASTM D 381						

1.After denaturing

The ASTM test measures the amount of residue after the evaporation of the fuel and following a heptane wash. The heptane wash removes the non-volatile materials such as additives, carrier oils used with additives, and diesel fuels. According to ASTM, solvent-washed gum can contribute to deposits on the surface of carburetors, fuel injectors and intake manifolds, as well as ports, valves and valve guides. However, ASTM also states that the impact of solvent washed gum from pure alcohols such as ethanol on malfunction of modern engines is not known, and the test is used primarily to detect the presence of high boiling, heptane-insoluble impurities. Since carburetors are no longer found in modern engines, this test is considered by many to be antiquated and of little practical use, particularly in an undenatured fuel ethanol standard.

4) Involatile matter

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Mg/100 ml max		1 (10 mg/l)		0.005 mass%	5 (hydrous)		2.5
Test method		AMSE 1124		E	NBR 8644		BP2002

1. After denaturing

Involatile matter is an alternative measurement to solvent washed gum, and is also used to detect components in ethanol that are associated with the blocking of fuel filters and deposits on the engine systems. Sweden chose involatile matter as they claim the measurement is more accurate than solvent washed gums. In addition, solvent washed gum is included in the EN228 gasoline specification, so they believe that it is unnecessary in the ethanol standard as well.

It is likely unnecessary to specify both solvent washed gum and involatile matter. In Australia, neither Manildra nor CSR test solvent washed gum. However both test non-volatile matter, and that is the parameter most widely used in the world. The CSR specification is derived from the BPS standard of 0.0025%, or 2.5 mg/100 ml maximum. Both Manildra and CSR claim to have results well within this limit.

5) Water content

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Volume % max	1 [1]	0.3 % by weight (~0.2 vol %)	0.4 % by weight	0.5 (~0.6 mass%		1.25% by weight	1% by weight
Test method	ASTM E 203	SS-ISO 760					CSR-AP27

1. After denaturing

This parameter is more important in low ethanol content petrol blends.

Because ethanol is hygroscopic, and easily picks up water from ambient air and from the distribution system, the water content of the denatured fuel ethanol must be limited when it is blended with gasoline to reduce the risk of phase separation. Phase separation is a phenomenon that occurs because of the solubility behaviour of gasoline-alcohol-water tertiary systems. The solubility will vary with the ethanol content (higher ethanol blend has higher water tolerance), the temperature of the blend (at higher temperature has higher water tolerance), and the aromaticity of the base gasoline (higher aromatic levels generally result in higher blend water tolerance). At low temperatures, even small quantities of water present in an ethanol gasoline blend can lead to direct hydrogen bonding between ethanol and water, and phase separation occurs. The upper phase is rich in gasoline, and the lower phase is composed of water, ethanol and the aromatic components of gasoline soluble in ethanol. This phase separation can cause serious operating problems for normal spark-ignition engines.

The ASTM standard in the U.S. is set at 1 vol% maximum, but ASTM recommends that particularly in colder climates, the reduced water content measured at the time of delivery is agreed upon between the buyer and seller. U.S. experience has shown that the water pick-up in distributing ethanol is typically 0.35 vol %, and believes that having a 1 vol% specification, but with lower production specification agreed between buyer and seller, avoids water pick-up disputes. However, as a result of the reduced aromatic content of U.S. gasoline following Tier 2 gasoline reduced sulfur specifications, the maximum water content of 1 vol% is currently under review by the responsible ASTM committee.

Sweden and Poland have much lower water limits of 0.3 mass% and 0.4 mass% respectively. In both countries, a maximum of 5 vol% ethanol is blended in gasoline as opposed to the 10 vol% in the U.S., and since both experience cold climates, the water content needs to be lower than in the U.S. India has chosen a limit of 0.5 vol% (~ 0.6 mass%).

Whether a vol% or a mass% specification is used appears to be arbitrary. The use of a mass% specification is in line with the beverage industry specifications, and therefore considered by some countries to be more convenient. With Sweden and Poland both having mass% specifications, it is likely that the EU will adopt a mass% specification.

Presently both Australian ethanol producers report that they are well below the U.S. specification of maximum 1 vol% (~1.25 mass%), with typical measured water contents of up to 0.3 vol%.

In setting a maximum water content for Australian ethanol, the percentage of ethanol blended in petrol, the aromaticity level (which tends to be a function of sulfur content as deep desulfurization processes typically destroy aromatics) and the distribution system need to be considered. Australia, like the U.S., allows 10 vol% ethanol in petrol. The Australian petrol pool contains 42% aromatics on average, with a cap of 45% from 2005. Directionally this should mean that the ethanol-petrol blend is at least as water tolerant as in California with its 35% cap on aromatics in petrol. It should also be noted that the U.S. allows a relatively high content of fusel alcohol (discussed below at point 12), which will improve the water tolerance of the ethanol-petrol blend.

A consensus decision will need to be taken by Australian stakeholders as to whether to set a water specification of 1 vol% maximum (or 1.25 mass% maximum) as in the ASTM D 4806, with the recommendation that buyer and seller agree to a lower level (which is typically 0.6 vol% in the U.S.), or whether a lower limit should be set in the ethanol standard itself.

6) Denaturant content

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Volume % min Volume % max	1.96 [1] 4.76		0.1 g Bitrex per 100 liters of ethanol	As prescribed by law from time to time	 3.0	1.0	1.0 % nominal
Test method					NBR 13993		

1.After denaturing

Denaturing is usually a requirement of Government's Custom and Excise departments to differentiate industrial ethanol from its potable beverage counterpart, to which high levels of taxation are often applied in most countries. A number of chemical substances are allowed for this purpose, but several could be harmful to engine operation. The ASTM specifications as well as the Indian specification lists substances that are acceptable to Excise departments, but which may not be used to denature ethanol for fuel applications.

The U.S. specifies hydrocarbons in the petrol boiling range to be used as denaturants. Since the ethanol will be blended with petrol, this specification ensures vehicle compatibility. Brazil and India recommend that gasoline be used. In Sweden, iso-butanol is used in combination with unleaded gasoline or ethers (such as MTBE or ETBE) for fuel ethanol denaturing purposes, and in Poland, trace amounts of Bitrex are used in addition to unleaded petrol.

In Australia, both Manildra and CSR use unleaded petrol and corrosion inhibitor as denaturants. Since Manildra has it's own petrol distribution network, there would be no advantage to using Bitrex as a denaturant. The unleaded gasoline denaturant is in the petrol tankers that are loaded with fuel ethanol. In the case of CSR Distilleries where petrol is not regular business for them, drums of unleaded gasoline have to be used for denaturing purposes. Since Bitrex is used routinely in some of their other products, replacing unleaded petrol with Bitrex for ethanol fuel applications would be attractive provided that the economics made sense, and the relevant Customs and Excise legislation was amended.

In specifying the denaturant, it is important to ensure that only substances that are known to not be harmful to engines are allowed, and that flexibility is built into the national standard to allow exports of ethanol that comply with other countries denaturing standards and requirements.

7) Inorganic Chloride

	U.S.	Sweden	Poland	India	Brazil (hydrous)	Manildra	CSR
Mass ppm maximum	40 [1] (32 mg/l)		40		1		
Test method	ASTM D 512				ASTM D 512		

1.After denaturing

The source of Chloride in ethanol appears to be related to the feedstock used to produce the ethanol, and in some cases it may come from hydrochloric acid (HCl) if it is used in the process.

Even very low concentrations of chloride ions are corrosive to metals typically contained in vehicles, such as stainless steel exhaust systems and fuel injection equipment. In the presence of water, hydrochloric acid (HCl) is formed. Sweden does not currently limit this parameter, but is of the opinion that it will likely be included in the future EU fuel ethanol standard. The U.S. allows 40 ppm, or 32 mg/l, but automakers and equipment manufacturers are arguing for a lower limit. In Brazilian hydrous ethanol, the limit is set at 1 ppm, a limit that is strongly supported by engine and equipment manufacturers.

Brazil does not specify inorganic chloride in its anhydrous fuel ethanol standard, and India has also chosen not to specify this parameter in their standard. With the high minimum ethanol content specified in their anhydrous ethanol standards, they believe that other components such as inorganic chloride will be minimal and hence do not need to be specified.

In Australia, Manildra produces ethanol from starch, and as described in section 3.1.2, they sometimes use small amounts of HCl in their process. However, if the pHe specification is adopted then it is debatable whether the Chloride specification is required as well, particularly if the minimum ethanol content is set above 99 vol%. Having both parameters specified does prevent the masking of the Chloride content by the correction of the pHe result using NaOH, as reportedly occurs in Brazil from time to time (see Section 4.3.1). Australian stakeholders will need to reach consensus about the importance of this parameter.

8) Copper content

	U.S.	**Sweden**	**Poland**	**India**	**Brazil**	**Manildra**	**CSR**
Mg/kg max	0.1 [1]		0.1	0.1	0.07		
Test method	ASTM D 1688			G	NBR 10893		

1.After denaturing

Copper is a very active catalyst for the low-temperature oxidation of hydrocarbons, significantly increasing the rate of gum formation. ASTM[7.4] states, “experimental work has shown that copper concentrations higher than 0.012 mass ppm in commercial gasolines may significantly increase the rate of gum formation.”

At the present time, neither Manildra nor CSR include a copper specification, but it is advisable that at least the ASTM limit of 0.1 mg/kg should be included in the fuel ethanol standard, particularly since CSR uses some copper equipment in the ethanol manufacturing process.

9) Acidity

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
% mass maximum	0.007 [1]	0.0025	30 ppm (0.03 g/l)	30 ppm (30 mg/l)	30 ppm	0.007	1 ml of 0.01N NaOH max
Test method	ASTM D 1613	AMSE 1114		D	ASTM D 1613		BP2002

1.After denaturing

Very dilute aqueous solutions of low molecular weight organic acids such as acetic acid are corrosive to a wide range of metals and alloys. It is therefore necessary to keep such acids at a very low level, and every country surveyed includes an acidity specification.

The specification varies from the lowest of 0.0025 mass% (Sweden) to the highest of 0.007 mass% (U.S.), with Poland, India and Brazil all at 30 ppm (~ 0.004 mass%).

In the EU, the gasoline specification EN228 requires an acidity limit of 0.007% (m/m as acetic acid) for ethanol as blend stock up to 5 vol%, and therefore one can speculate that an acidity limit will also be included in the future EU standard for fuel ethanol. It is recommended that Australia adopt this acidity limit for weak acids in the fuel ethanol standard.

10) pHe test

	U.S.	Sweden	Poland	India	Brazil (hydrated)	Manildra	CSR
pHe	6.5-9.0 [1]				6-8		6.5-9.0 [1]
Test method	ASTM D 6423				NBR 10891		ASTM D 6423

1.After denaturing

H_2SO_4, HCl and H_2PO_4 are strong acids used by several producers in the ethanol manufacturing process. Sulphur dioxide (SO_2) gas is also sometimes used to prevent mildew formation on the raw materials, and could carryover in the process and form corrosive acids.

In the U.S., General Motors Corporation originally developed the pH test procedure for ethanol. ASTM later adopted a modification of the test procedure and a pHe standard. General Motors experienced corrosion of aluminium parts in low acidity (as acetic acid) ethanol fuel. They found that very low levels of strong acids (like H_2SO_4, HCl or H_2PO_4) might not always be detected by other test procedures such as the acidity by acetic acid. Fuel grade ethanol with a pHe below 6.5 may contribute to failure in fuel pumps and fuel injectors due to corrosive wear. If the pHe is above 9.0, it may negatively impact plastic parts in the fuel system. The effects are more pronounced in high level blends such as E75 and E85.

The problem with the pHe test is that pH of a denatured fuel ethanol is hard to measure as it is not an aqueous solution. The probe starts to dehydrate and drift occurs in the results measured. However provided that ASTM method D6423 is used, which specifies rehydration of the probe between readings, ASTM claims the repeatability (same operator, same apparatus, identical test material) would exceed 0.29 in 1 case in 20 (a 90% confidence factor), and with a reproducibility (same material, different apparatus and operator) of 0.52.

The pHe test is usually done after denaturing and addition of corrosion inhibitors. Both Australian producers have the equipment necessary to carry out this test, and it is advisable to include pHe in the Australian fuel ethanol standard, in addition to the acidity by acetic acid parameter.

11) Appearance

U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Visibly free of suspended or precipitated contaminants (clear & bright)	Clear, without particles		Clear & bright	Clear & free of suspended impurities	Clear liquid free of any foreign matter	Clear, colorless volatile liquid, hygroscopic, miscible with water and with methylene chloride, free from matter in suspension and apart from water, consisting essentially of ethanol
Visual at ambient temperature	ASTM D 2090		Visual	Visual		BP 2002

Suspended or precipitated contaminants would have a detrimental effect on engines, increasing wear and causing blockage. This test is intended to ensure that the ethanol is free of such contaminants.

CSR includes a “clarity of solution” specification in addition to appearance. It detects suspended or precipitated contaminants after 5 minutes in a 1 ml sample of ethanol diluted with 20 ml of water.

12) Fusel Alcohol (Amyl alcohol)

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
Mg/l max		50	2 vol % max				
Test method		AMSE 1136, GC method					

1.After denaturing

Particularly when molasses is used as a source of fermentable sugar, the amino acids naturally present undergo reductive deamination thereby forming a mixture of alcohols collectively known as fusel oil. The major alcohols formed are amyl and isoamyl alcohol, and 2-methylbutanol, n-propanol and also phenylethanol are formed, all of which are important natural raw materials for the flavour industry. For the producers of potable alcohol, fusel oil must normally be removed during the distillation process.

The ASTM D 4806 specification in the U.S. does not include a limit for fusel oil. However the minimum ethanol content of denatured ethanol plus the minimum denaturant make up at least 97% of the total volume, thereby limiting other components to under approximately 3%. Other components are mostly fusel oil, methanol and water, and since the maximum limits on the latter are 1.5 vol%, fusel oil in U.S. ethanol can vary between about 1.5% and 3%.

There is much debate globally about whether a fusel oil specification is required or not. The C_3-C_5 alcohols in fusel oil should actually enhance the quality of the ethanol blend, and any potentially harmful heavier components of fusel oil should be taken care of by the involatile matter specification. If fusel oil is to be allowed in the fuel ethanol, then certainly a lower ethanol content specification is required to make allowance for it, and levels such as allowed in U.S. ethanol should not present any technical problems. In fact, the converse may be true. A paper produced by Istanbul Technical University in Turkey in April 1996 [7.11]shows fusel oil as highly effective in reducing the phase separation temperatures and increasing the water tolerances of the azeotropic ethanol-unleaded gasoline blends.

There are typically not a lot of fusel oils in grain ethanol such as that produced by Manildra. Ethanol from sugar such as produced by CSR could contain higher levels of fusel oils, but since their involatile matter specification is 2.5 mg/100 ml maximum (0.0025%), any fusel oils present will likely be less than this, and hence almost negligible.

13) Density

	U.S.	Sweden	Poland	India	Brazil	Manildra	CSR
g/ml Maximum		0.790 (D 20/4)		0.7961 @ 15.6 ^{0}C	0.7915 @ 20 ^{0}C		0.793
Test method		SS-ISO 758		A	ASTM D 4052		CSR AP-03

Density is not included in the U.S. specification, but it is included in the specifications of Brazil, Sweden, and India. Density is a natural characteristic of ethanol. It is probably not necessary for high purity ethanol that is undenatured and contains little water. However, density measurement is usually an uncomplicated and quick test that can be used to identify contamination, and to this end it may be considered a useful parameter to include for field quality monitoring purposes.

Both Australian producers measure density using an alcohol hydrometer, from which the ethanol purity at 20^{0}C is determined from Spirit Tables. Including a density limit in the Australian ethanol standard would not require additional measurement on the part of producers, and is advisable for quick fuel ethanol quality monitoring purposes.

5.2 OTHER PARAMETERS

14) Aldehydes (as acetaldehyde)

Most modern vehicles are equipped with exhaust catalysts that control the emissions of aldehydes (formaldehyde and acetaldehyde). Poland, Sweden and India include this specification. It is an important limit for ethanol used in ETBE synthesis. Whether Australia should include this parameter is a matter for debate between Australian stakeholders.

15) Sulfur

Not many ethanol specifications include a sulfur limit at this time. However this is expected to change with decreasing sulfur in future gasoline specifications. In the U.S., California requires ethanol to meet a maximum sulfur specification of 10 ppm, and the U.S. federal gasoline specification that came into effect on 1 January 2004, requires fuel ethanol to meet a 30 ppm maximum sulfur specification. The ASTM is currently reviewing the D 4806 fuel ethanol specification to include a sulfur specification. It is expected that the EU fuel ethanol standard will also contain a sulfur limit.

16) Phosphorus

More recent gasoline and diesel specifications often prohibit the inclusion of phosphorus containing compounds in unleaded gasoline in order to protect vehicle exhaust catalyst systems from deactivating. The source of phosphorus is usually from certain performance additives, or it can be from the fermentation process if H_2PO_4 is used. H_2PO_4 is the catalyst used in the manufacture of synthetic ethanol from ethylene, and therefore if synthetic ethanol in fuel is envisaged, the parameter should be considered.

With emissions limits becoming more stringent globally, phosphorus is certainly an important parameter to consider, but it is debatable whether a specification is required for a fuel ethanol standard, or whether it is sufficient to include this limit in finished fuel standards. The U.S. includes a phosphorus limit of 0.2-0.4 mg/l maximum in its ASTM D 5798 specification for Ed75-Ed85 automotive fuel.

17) Refractive Index

The refractive index indicates ethanol purity. It is used by Poland and Sweden, but they both suggest it will be unlikely to be included in the future EU specification as the other more important parameters specified above already cover ethanol purity.

18) Color

This parameter is specified by Brazil and Sweden, and is considered an easy and quick way to identify the product. The U.S. ASTM notes that this parameter can be agreed between the buyer and seller of ethanol if considered by the buyer or seller to be important.

19) Explosion limits / Electrical Conductivity

Sweden includes an explosive limit specification, and Brazil includes a conductivity specification. Ethanol and ethanol blends conduct electricity. Gasoline by contrast is an electrical insulator. This parameter is specified in the context of reduced fire risk when high percentages of ethanol are pumped, and corrosion inhibitors may be present. It is probably not required in an anhydrous ethanol standard for low percentage blending into petrol, but is a more important consideration for a fuel specification for higher content ethanol, such as E75 and E85 fuels. However, the U.S. ASTM D 5798 standard specification for these fuels does not include a conductivity or explosive limit specification.

6. RECOMMENDATIONS

It is important when setting the standard, to define the ethanol, and whether the specification refers to denatured fuel ethanol or not.

A decision needs to be taken as to whether the specification is going to be for denatured fuel ethanol – the approach taken by the U.S., or for fuel ethanol before denaturing. The rationale of the U.S. is sound in that the fuel ethanol will be sold in the marketplace denatured. The permitted denaturant is pretty much confined to unleaded gasoline. However, since 7 May 2004, an International Fuel Ethanol Futures Contract has been opened on the New York stock exchange. This paves the way for fuel ethanol to become a globally tradable commodity. Different countries have varying denaturing requirements dependant on tax exemption and other issues in their marketplace. Therefore an ethanol standard for undenatured fuel ethanol provides more flexibility. It is recommended to include a list of denaturants suitable for use that should be added. These include gasoline, or any gasoline compatible components such as ethers (MTBE, ETBE, TAME). Poland has specified Bitrex, which is a bitter substance first used to make alcohol unpalatable, and now used in a wide range of potentially dangerous products such as household cleaners and pesticides, to combat accidental swallowing.

Some countries such as the U.S. use vol% as the unit of measurement, and others starting out from the regulations used for alcoholic beverages for convenience, use mass%. It is probably advisable to select either vol% or mass% for the major parameters in the standard in order to avoid confusion. It should also be made clear when ppm specifications are used as to whether they are mass per volume or mass per mass measurements.

For ethanol to be used in ethanol-diesel blends that are hydrated, a high level of water can be tolerated. Industrial bio-ethanol production typically yields an azeotroph that is 93% to 95% ethanol and water by volume. A further step (and therefore additional cost) is required to produce anhydrous ethanol, as discussed in Chapter 3. Sweden's Sekab has taken the approach of having a 95% ethanol specification that differs from the 99.5% ethanol for petrol standard with respect to water content. A few other non-critical parameters are adjusted to match the changed physical properties of 95% hydrous ethanol. Particularly if the ethanol is to be splash blended with diesel, it is important to have a separate specification for the ethanol itself, or an addendum to the anhydrous ethanol specification, to ensure that with 95% ethanol, the remaining 5% does not contain other components as opposed to water, which could be harmful to the engine.

During the test phase and in the absence of a standard for the finished ethanol-diesel fuel, most countries recommend that high purity anhydrous ethanol be used as the ethanol source for the diesel blend.

Since it is technically possible to use synthetic ethanol that meets the anhydrous ethanol standard in automotive engines without adverse effects, but these ethanol's typically do not qualify for renewable energy tax incentives, consideration needs to

be given to methods of differentiating synthetic ethanol from its biological counterpart, such as the use of marker chemicals.
It is advisable to use corrosion inhibitors in gasoline that is blended with ethanol. The inhibitors can either be specified in the ethanol itself, or in the finished fuel.

The test methods in use around the world have been reported where possible. However they have not been compared and evaluated as this is considered beyond the scope of this project. It is recommended that a group of test method experts review the various methods in use, and select those where the precision with respect to ethanol is consistent with the proposed specifications.

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