# SETTING NATIONAL FUEL QUALITY STANDARDS

## Paper 2A

## Proposed Management of Petrol Octane Enhancing Additives/Products

Prepared by


Environment Australia

Department of the Environment and Heritage


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# TABLE OF CONTENTS

# 1 INTRODUCTION

## 1.1 Objective of the paper

An assessment of the additives and products used to increase octane in petrol is necessary before any national management strategies for their use can be adopted.

To assist in this process, Environment Australia commissioned an independent literature review and analysis of available octane enhancing petrol additives and products (octane enhancers). This study, completed by *Duncan Seddon and Associates Pty Ltd* Ltd, was designed to review and analyse chemical additives and products that may be added to petrol to increase octane. It did not consider refinery processes that can be adopted to increase octane levels.

This paper presents a Commonwealth response to the results/recommendations of the literature review and analysis, and outlines the preliminary Commonwealth proposal for the management of these additives/products.

## 1.2 Structure of the paper

The information in this paper is presented in two parts.

The first part is the Commonwealth's response to the literature review and analysis and includes the preliminary Commonwealth position for the management of octane enhancers.

The second part (Appendix A) is the full report of the literature review and analysis completed by *Duncan Seddon and Associates Pty Ltd*.

## 1.3 Call for public submissions

This discussion paper is Paper 2A in a series of papers produced by the Commonwealth for the purposes of public consultation on the development of national fuel quality standards. Details of this process and copies of the discussion papers can be obtained from the Environment Australia Internet address www.environment.gov.au/epg/fuel, or by contacting the Air Quality Section on telephone 02 6274 1693 or e-mail airquality@ea.gov.au.

In particular, this discussion paper should be read in conjunction with Paper 2, *Proposed Standards for Fuel Parameters (Petrol and Diesel) May 2000* (Environment Australia, 2000a), and the revised Commonwealth position September 2000 (Environment Australia, 2000b).

In order to ensure that the most appropriate strategies are put in place to manage the use of octane enhancers in Australian petrol, comment on the Commonwealth Government's preliminary position put forward in this discussion paper is sought from all interested stakeholders and the community.

While comments are welcome on any matter discussed in this paper, particular attention should be directed to the proposed management positions identified as boxed text.

All submissions will be treated as public documents and should be sent to:

Mr Sean Lane
Air Quality Section
Environment Australia
GPO Box 787
CANBERRA ACT 2601

Phone (02) 6274 1872
Fax (02) 6274 1172
E-mail airquality@ea.gov.au

and are requested by **12 January 2001**.

# 2 BACKGROUND

## 2.1 National fuel quality standards setting process

The current national fuel quality standards setting process (as it applies to petrol and diesel) has the aim of harmonising Australian fuel quality parameters with European (Euro) standards.

The principal driver for change to fuel quality standards in Australia is an environmental one - the need to provide fuels that facilitate the adoption of emerging vehicle engine and emission control technologies, a key strategy in managing air pollution and greenhouse gas emissions. This is supported by the need to better manage those fuel parameters that do not impact directly on vehicle technology, but nevertheless contribute to ambient levels of pollutants identified as posing health or environmental problems.

The Commonwealth Government has an ongoing program of introducing new vehicle emission standards to ensure that the environmental benefits of evolving emission control and fuel efficiency technologies are realised in Australia. New vehicle emission standards are established as Australian Design Rules (ADRs) under the *Motor Vehicles Standards Act 1989* and are subject to complete review on a 10 year cycle.

## 2.2 Predicted increase in petrol octane requirements

Currently, premium unleaded petrol sales in Australia are very small (approximately 4.2% of total petrol sales). The vast majority (approximately 76.3%) of petrol sales are regular unleaded petrol, with the balance made up of leaded and lead replacement petrol sales. (DISR, 2000)

As outlined in Paper 2, a key component of the Commonwealth's move to harmonise Australian fuel quality parameters with Euro standards is the expanded supply of high octane (95 RON) petrol, known as PULP (Environment Australia, 2000a).

It is considered that the increased availability of PULP to the market will encourage the motor vehicle industry to supply more advanced technology engines that reduce tailpipe emissions and deliver improved fuel economy (and therefore reduced greenhouse emissions). It is likely that the engines used to comply with Euro 3 emission standards will be high compression engines with a requirement for increased octane levels (DoTRS, 1999).

The demand for higher octane unleaded petrol will also be strengthened as 96 RON leaded petrol is phased out nationally prior to 1 January 2002. Leaded petrol will be replaced by lead replacement petrol (LRP), essentially high-octane unleaded petrol with an anti-valve seat recession (AVSR) additive.

LRP performs the same function as leaded petrol, offering the same octane performance and providing lubrication to prevent wear on the exhaust valve seats.

As the increasing demand is coupled with the fact that other octane enhancing properties of petrol (such as benzene, aromatic and olefin content) will be reduced or capped under national fuel quality standards, Australian petrol refiners and importers may consider it necessary to introduce additives to petrol to increase its octane.

## 2.3 Options for increasing octane

The literature review and analysis describes octane as a measure of a fuels tendency to knock in a test engine when compared to other fuels. Knocking occurs when the fuel/air mixture explodes on the compression stroke of the engine cycle before the application of the spark. This creates a loud knocking noise within the engine that can result in engine damage.

For the purpose of ranking, fuels are compared to isooctane (2,2,4-trimethylpentane) which has a low tendency to knock and given an octane number of 100, and normal heptane (n-heptane) which has a great tendency to knock and assigned an octane rating of zero. The octane number of a fuel is that value which will give the same knocking tendency of a proportional mixture of isooctane and n-heptane.

There are many possibilities for refineries to increase the octane number of the petrol pool.

Refinery processes are employed for converting low octane components into higher octane ones by chemical reaction (RMIT, 1994). Australian refineries use (in some cases a combination of) three in-house plant processes to boost octane; isomerisation[1], alkylation[2] and reforming. However, the literature review and analysis suggests that as the ability to use isomerisation and alkylation is limited, it is likely that Australian refiners will increasingly rely on the use of reforming, ie increase in the level of aromatics, to lift octane to the target levels.

Octane enhancers may also be used to assist in the production of greater quantities of premium (high octane) unleaded petrol.

The use of chemical additives and products to boost octane in petrol presents a number of issues, in particular potential impacts on public health, the environment and vehicle (emission reduction) technologies.

## 2.4 Review of octane enhancing additives and products

In 1994, the then Commonwealth Environment Protection Agency commissioned the Royal Melbourne Institute of Technology (RMIT) to undertake a review of octane enhancers, as part of the national Lead Abatement Strategy. This Strategy included the reduction of lead levels in leaded petrol.

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[1] Isomerisation practiced at Caltex Lytton and Kurnell, BP Kwinana, Mobil Port Stanvac and Shell Geelong.

[2] Only Mobil Port Stanvac has no alkylate producing facility.

RMIT provided a desktop assessment of chemical products and/or refinery processes available to substitute for the reduced use of lead in petrol, considering technical, environmental, health, cost and availability issues.

To update this earlier work and provide advice on which octane enhancers are suitable for use in Australian petrol (including informing national policy on their management), Environment Australia commissioned *Duncan Seddon and Associates Pty Ltd* to investigate the use of these additives and products.

The (summarised) objectives of the review were:

1. Identify chemical additives/products that may be added to lead replacement petrol and/or unleaded petrol to increase its octane number.

2. Identify their potential effects on petrol characteristics, engine efficiency and performance, compatibility with current and future motor vehicle emission reduction technologies, other vehicle and engine components and the vehicle's tailpipe and evaporative emissions profile.

3. Compare the financial costs of their use.

4. Provide details on, and advise on the significance of, their environmental and health effects.

5. Identify impediments to Australia's objective to harmonise with Euro petrol quality standards due to their use.

6. Provide recommendations on octane enhancers that could be suitable for use in petrol in Australia, for both unleaded petrol and lead replacement petrol.

The complete report (including the complete set of study objectives) is reproduced at APPENDIX A.

# 3 GENERAL PRINCIPLES AND POLICY REQUIREMENTS

As noted above, the principal driver for changes to fuel quality specifications is an environmental one – that is, the need to provide fuels which facilitate the adoption of emerging vehicle engine and emission control technologies.

The decision to harmonise Australian vehicle emission standards with UN ECE emission standards (as best representing international standards – see box below) effectively gives rise to a starting premise that Australian fuel specifications should be harmonised with UN ECE fuel specifications.

Recent changes to UN ECE fuel specifications have been driven by vehicle emission requirements and by engine emission control technologies, with new emission control standards coupled with mandated quality and compositional requirements for petrol and diesel fuel.

**International standards**

Under the World Trade Organisation rules to which Australia is a signatory, only the regulations developed by the UN ECE meet the definition of an 'international' standard in the vehicle standards field (as opposed to national standards such as the Japanese or US).

The UN ECE vehicle emission standards were therefore selected for adoption in Australia to give effect to the goal of 'harmonisation with international vehicle emission standards'. The Japanese Government has also made a commitment to harmonisation with UN ECE vehicle standards. Most other Asian countries, and indeed the majority of countries in the world, are moving to adopt UN ECE regulations on emission standards.

The terms 'Euro 2', 'Euro 3' and 'Euro 4' are common terminology used to describe the progressively more stringent versions of the UN ECE standards (DoTRS, 1999).

It is recognised, however, that recent changes to the UN ECE fuel specifications have also been designed to address a number of other issues, some of which are specific to European Union member countries. While the standards include technology-enabling fuel specifications (sulfur levels being a typical example), they are also designed to contribute directly to the management of air pollutants identified as posing significant health or environmental problems within the European Union.

While there are similarities between Europe and Australia in terms of public exposure to air pollutants of concern, there are also some significant differences. The most recent Australian State of the Environment Report (SOE Advisory Committee, 1996) found that in general, annual mean concentrations of common pollutants within major Australian airsheds are low by world standards.

The starting premise - harmonisation with European fuel specifications - is therefore subject to a number of qualifications. The first of these is the suite of environmental and industry policy decisions previously announced by the Government. These establish a number of criteria, and pre-determine a number of issues, in relation to the development of national fuel quality standards. These are then further qualified by the need to take into account a number of more general, but equally important Commonwealth Government principles, such as those addressing legislative/regulatory approaches and competition policy.

A key issue is Government policy with respect to harmonisation, trade facilitation and efficiency. The development of fuel quality standards has therefore been based on the following general guiding principles and specific Government policy decisions.

## 3.1 General principles

1. Fuel standards are intended to manage those fuel qualities/parameters that are known to have the potential to impact adversely on the environment.

2. Fuel standards should be compatible with relevant international or internationally accepted standards in order not to impede competition and trade.

3. Fuel standards are intended to be mandated and implemented on a national basis. In particular, fuel standards that are technology enabling must apply nationally. Local environmental circumstances may, however, dictate variation within the national standard to achieve environmental outcomes. (DISR, 1999)

   – Consideration will be given to State by State establishment of fuel standards that address airshed specific environmental conditions, however, in such cases a national standard will be determined as a default.

4. Fuel standards will apply to, and be enforced equally in respect of, imports as well as domestically produced petroleum fuels. (DISR, 1999)

   – Fuel standards must not impede competition, either between Australian refiners, or with imported refined product.

5. Fuel standards that directly address environmental or health issues will be determined on the basis of Australian-specific requirements. In such instances, harmonisation with European specifications may be neither necessary nor desirable.

6. The timetable for the introduction of new fuel standards will be based on Australian requirements. Harmonisation, in terms of timing, will not be based on European or any other regional timetable, except where there is a previous policy decision to this effect or the standard is technology enabling and the need for such harmonisation is clearly demonstrated.

7. Consideration will be given to setting standards that provide, as far as possible, flexibility in terms of compliance.

   – Flexibility provisions must not impede competition or trade; and

   – Flexibility provisions must not add significantly to legislative/regulatory complexity or implementation/enforcement costs to Government.

## 3.2 Policy context

The following Commonwealth policy decisions have been identified as directly influencing the requirement for higher octane unleaded petrol. The full set of policy decisions influencing the fuel standards development process is listed in Paper 2 (Environment Australia, 2000).

### 3.2.1 Vehicles – general

- *A 15% or better improvement over business-as-usual in the fuel efficiency target for passenger vehicles by 2010 within the National Average Fuel Consumption (NAFC) framework.*
  - Safeguarding the Future: Australia's Response to Climate Change, Statement by the Prime Minister of Australia, 20 November 1997. (Howard, 1997)

The Commonwealth Government is seeking to expand the supply of high octane (95 RON) petrol, as it considers it will encourage the motor vehicle industry to supply more advanced technology engines which deliver improved fuel economy (and therefore reduced greenhouse emissions). The Commonwealth is currently negotiating with the motor vehicle industry on NAFC targets for 2005 and 2010.

### 3.2.2 Vehicles – petrol

- *Introduction of Euro 3 petrol vehicle emission standards for all new vehicles in 2005 and for continuing models in 2006.*
  - Safeguarding the Future: Australia's Response to Climate Change, Statement by the Prime Minister of Australia, 20 November 1997. (Howard, 1997)

This decision has been given effect through the gazettal of ADR 79/01.

Consistently low sulfur levels are required to ensure proper functioning of the on-board diagnostic (OBD) systems required to meet Euro 3 emission standards. The maximum acceptable sulfur level for Euro 3 vehicles is 150ppm. As it is likely that the engines used to comply with Euro 3 standards will also be high compression engines, there will also be a requirement for increased octane levels. (DoTRS, 1999, p72)

### 3.2.3 Fuel – petrol

- *A move to higher octane rating and lower sulfur for petrol products.*
  - Measures for a Better Environment, Prime Minister, May 1999. (Howard, 1999)

While MBE does not set out any explicit specifications for petrol, it notes that the new emission standards timetable for petrol vehicles will require a move to higher octane and lower sulfur levels for Australian petrol.

- *Bringing forward the phase out of leaded petrol, taking equity considerations into account.*
  - Safeguarding the Future: Australia's Response to Climate Change, Statement by the Prime Minister of Australia, 20 November 1997. (Howard, 1997)

During the December quarter 1999, leaded petrol accounted for 22% by volume of total petrol sales and its market share is continuing to decline. On 15 March 2000, the Commonwealth Government announced that 1 January 2002 would be the national phase out date for leaded petrol.

# 4 THE COMMONWEALTH PROPOSAL FOR DISCUSSION

The Commonwealth's approach to managing petrol octane enhancers has been strongly influenced by the decision to harmonise, within the framework of the previously identified guiding principles and Government policy decisions, Australian fuel quality requirements with UN ECE (Euro) fuel specifications.

The premise of this approach has been used as a starting point for the literature review and analysis of octane enhancers and the development of the Commonwealth's proposal to manage the use of octane enhancers in Australian petrol.

## 4.1 The management of octane enhancers

The management of fuel quality, including octane enhancers, has in the past been the responsibility of the States and Territories. This has resulted in varied levels of fuel quality control with different regulations governing octane enhancer use within Australia.

For example, Queensland has recently introduced regulations that prohibit the use of the octane enhancers MTBE, ETBE and TAME from petrol distributed in that State[3]. Western Australia has also introduced similar regulations prohibiting the use of MTBE[4]. A number of other States and Territories are looking at regulating these and other octane enhancers, eg MMT.

The implementation of national fuel quality standards legislation by the Commonwealth will give Australia, for the first time, the opportunity to set nationally consistent specifications for fuel quality. The *Fuel Quality Standards Bill 2000* is currently before the Commonwealth Parliament and can be viewed by following the links from www.aph.gov.au/legis.htm.

The Bill sets out a framework for making, monitoring and enforcing fuel quality standards. The first standards made following passage of the new legislation will regulate petrol and diesel quality. There are two avenues currently available in the Bill to regulate the use of an octane enhancer:

1. enter the octane enhancer on the Register of Prohibited Fuel Additives; or

2. list the octane enhancer as a specification in the fuel standards, thereby managing the permissible amount in petrol as a specification

## 4.2 Identification of octane enhancers

Octane enhancers have been a part of the fuel supply chain since the mass production of the motor vehicle. The efficacy of lead was identified early and lead based additives quickly became the universal octane enhancer.

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[3] The *Environment Protection Amendment Regulation (No 3) 2000* (Qld) limits the concentration to 0.5% by volume.

[4] The *Environmental Protection (Diesel and Petrol) Regulations 1999* (WA) regulation limits the concentration to 0.10% v/v

However, during the 1970s the US identified motor vehicles as a major source of urban air pollution. The prime technology to reduce their emissions was the introduction of catalytic converters. As the catalysts are irrevocably damaged by lead, unleaded petrol was introduced. Unleaded petrol was first introduced into Australia in 1985.

Concomitant with this was the recognition that lead poses a significant health risk, with lead emissions from motor vehicles contributing to significant quantities of airborne lead in urban areas. These issues lead to the international movement away from leaded petrol and will lead to its eventual phase out. Leaded petrol will be phased out in Australia by 1 January 2002.

In order to maintain the level of octane in petrol while removing lead, there has been a significant amount of research into octane enhancers. The research undertaken includes the effects the additives have on engine technology, the properties of the fuel and the emissions profile of the vehicle, and the additive's environmental and health effects. This work has identified a number of alcohols, ethers and some organometallics with octane boosting properties.

To assist in determining the appropriate strategy for the management of octane enhancers in Australian petrol, the Commonwealth commissioned *Duncan Seddon and Associates* to undertake the independent literature review and analysis of octane enhancing petrol additives/products. The octane enhancing additives/products considered by the review are listed in Table 1 below.

**Table 1 Octane enhancing additives/products considered in the literature review and analysis.**

| Grouping | Short Chemical Name | Full Chemical Name | CAS No |
|---|---|---|---|
| **Alcohols** | **Methanol** | Methyl alcohol | **67-56-1** |
| | Ethanol | Ethyl alcohol | 64-17-5 |
| | TBA | Tertiary butyl alcohol | 75-65-0 |
| | IPA | Iso propyl alcohol | 67-63-0 |
| | n-propanol | 1-Propanol | 71-23-8 |
| | Isobutanol | 2-Methyl-1-Propanol | 78-83-1 |
| | sec-Butanol | 2-Butanol | 78-92-2 |
| | n-Butanol | 1-Butanol | 71-36-3 |
| Ethers | MTBE | Methyl tertiary-butyl ether | 1634-04-4 |
| | DIPE | Di-isopropropyl ether | 108-20-3 |
| | ETBE | Ethyl tertiary-butyl ether | 637-92-3 |
| | TAME | Tertiary amyl methyl ether | 994-05-8 |
| | **ETAE** | Ethyl tertiary amyl ether | 919-94-8 |
| Organometallics | MMT | Methylcyclopentadienyl manganese tricarbonyl | 12108-05-8 |
| | Ferrocene | Dicyclopentadienyl iron | 102-54-5 |

## 4.3 The Commonwealth proposal

The Commonwealth has considered a range of issues to determine management options for each octane enhancing additive/product.

It should be noted that the aromatics are not considered here as the Commonwealth intends to manage these by setting maximum permissible limits for aromatics in the fuel quality specifications for petrol.

### 4.3.1 Methanol

#### *Use*

Methanol as an octane enhancer has had limited use in commercial supplies of petrol in Australia. Methanol is a clean burning fuel and can be used as a high octane fuel in its own right. Its use is permitted under the US EPA rules for the production of reformulated gasoline (RFG) and Brazil has occasionally used methanol when the supply of ethanol is insufficient.

The main driver for the use of methanol is that it is made from natural gas and is easily transported as a liquid.

#### *Environmental and health issues*

Methanol is completely miscible with water, biodegrades in soil and does not bioconcentrate or adsorb to sediment. Methanol is reported to have a relatively short half-life in water should it be released to this compartment (ie ground and surface water) and due to its high vapour pressure, it will evaporate quickly from spills.

The use of methanol in fuel used in non-catalyst equipped vehicles results in higher formaldehyde emissions (RMIT, 1994).

#### *Vehicle operability issues*

Vehicles fuelled by methanol are specifically made for this purpose as the use of methanol in traditional fuels may damage vehicles in the general vehicle fleet. The main concern is that the additive can act as a solvent. It is also known to corrode certain metals high in the electrochemical series (zinc, aluminium and in particular titanium). Any component containing these elements would potentially be attacked by methanol.

Due to these concerns, the literature review and analysis concluded "*of the alcohols, methanol is to be avoided*".

#### *Effect on fuel specifications*

The RMIT study (1994) reported that splash blending of methanol is not appropriate and refinery blending requires a very low volatility blendstock (40 kPa) to make a 72.4 kPa fuel blend. To achieve this a considerable amount of light components would have to be backed-out of the petrol blendstock.

Of additional concern to petrol refiners is that traces of water in petrol will cause methanol to separate. Distribution systems must therefore be kept dry to prevent phase separation.

The WorldWide Fuel Charter (WWFC) does not recommend the use of methanol and a number of petroleum industry stakeholders have indicated that they would not use methanol because of safety, blending and corrosion issues.

#### *Proposed management*

Based on the concerns surrounding the use of methanol, in particular its solvent properties and corrosive nature, the Commonwealth proposes to prohibit its use in all grades of Australian petrol.

### 4.3.2 Ethanol

#### *Use*

Ethanol has a long history of use as a petrol extender, octane enhancer and alternative fuel. Ethanol can be produced by petrochemical processes or from biomass. The normal practice is to use 10% ethanol as an extender to the petrol (E10 blends).

The momentum for using ethanol has been helped by the fact that it can be produced from a wide variety of agricultural sources. It can be considered a renewable fuel when produced from these sources and there is a potential for greenhouse gas emissions abatement. Whether this potential is realised however, depends on the production process, especially the nature of energy inputs used in distillation and other phases.

The world's largest use of ethanol is in Brazil, where it must be used in all petrol at 24%. The largest promoters for ethanol use are the so called 'corn states' of the US. This has resulted in tax breaks for the use of ethanol produced from corn, making it cost competitive with MTBE in the US market. With the likely phase out of MTBE in the US, ethanol usage in petrol there is likely to become more widespread.

In December 1998, addressing concerns about the use of MTBE in gasoline in California, the Air Resources Board approved the use of ethanol in gasoline up to 10% by volume (increased from 6.5%). This move was designed to increase options for the use of non-MTBE gasoline. (Air Resources Board, 1998)

There is also growing support for the use of ethanol in petrol from the Australian sugar industry. Ethanol produced from biomass currently has an excise free status in Australia (equivalent to a tax benefit of about 38 cents/litre). Without this status, ethanol would probably be uncompetitive against low cost crude oil products and other chemical octane enhancers.

### *Environmental and health issues*

With the expected increase in ethanol use in the US (due to the anticipated MTBE phase-out), there has been concern expressed about water supplies being contaminated by ethanol from petrol as it is also completely miscible with water. However, similar conclusions are likely to be expressed in relation to all octane enhancing products if they were widely used. Nonetheless, should ethanol be released to groundwater (eg from leaking underground fuel storage tanks) or surface water it expected to biodegrade rapidly with a half life of 4.1 days (unlike MTBE with a half life of >120 days). Ethanol does not bioconcentrate or adsorb to sediments.

Vehicle emission profiles vary markedly between different ethanol petrol blends. (Ontario Round Table on Environment and Economics, 1995) The results from several studies that have been conducted throughout the world on exhaust emissions from ethanol blended fuels are often contradictory.

Emission test results from the US using E10 blends generally show reductions in carbon monoxide and hydrocarbons, and about the same $NO_X$ emissions as petrol. (Ontario Round Table on Environment and Economics, 1995)

However, another US study reports that at 10% ethanol by volume added to conventional gasoline results in statistically significant decreases in emissions of CO (13%), VOCs (6%) and benzene (11%), and increases in $NO_X$ (5%) and acetaldehyde (159%) as well as increases in evaporative emissions. (Keller, Froines, Koshland, Reuter, Suffet & Last, 1998)

The California Energy Commission (1999) reports that preliminary results from vehicle testing show that gasoline blends of 10% ethanol would cause major increases in hydrocarbon and benzene emissions. While these increases are all mostly due to excess evaporative emissions, higher exhaust emissions of nitrogen oxides would also be expected.

In the Australian context, while the use of E10 blends results in decreased emissions of carbon monoxide, it can result in increased emission of acetaldehyde and nitrogen oxides. (RMIT, 1994) More recent studies have found E10 blends result in reductions of carbon monoxide and hydrocarbons, with an increase in acetaldehyde and formaldehyde, and a slight (1%) increase in $NO_X$. (ERDC, 1998)

There are some concerns about ethanol’s tendency to evaporate more readily than other fuel components. It is also possible that ethanol’s propensity to be tightly held by activated carbon and attract water may decrease the working capacity of the carbon canisters used to control evaporative emissions, resulting in increased diurnal emissions. (Rice and Cannon, 1999)

It is also reported that ethanol may increase the solubility of the benzene, toluene, ethylbenzene and xylene (BTEX) components of petrol, and that this action could result in BTEX groundwater plumes. This may even be enhanced by ethanol’s ability to hinder the biodegradation of BTEX. However, there are significant knowledge gaps regarding the anticipated environmental behaviour of petrol containing ethanol (Rice and Cannon, 1999).

Ethanol is known to have developmental and neurotoxic effects, but the risk at the levels anticipated in the environment from its use as a fuel additive is unclear. (Keller et al, 1998)

#### *Vehicle operability issues*

Local Australian petrol distributors have had some experience in using an E10 blend of petrol. The Federal Chamber of Automotive Industries (FCAI) has acknowledged that use of E10 blends could be tolerated by the current Australian vehicle fleet, however noted that ethanol at higher concentrations (>20%) had detrimental effects on paints and finishes of some vehicles.

#### *Effect on fuel specifications*

There are concerns about the ability of ethanol-petrol blends to meet the proposed summer vapour pressure specifications for Australian petrol, especially at concentrations of greater than 10%. The addition of ethanol to petrol blends must be carefully managed so that RVP limits are not exceeded.

Ethanol, like methanol, also suffers from fungibility problems. However, ethanol/petrol blends have a higher water tolerance than methanol/petrol blends (RMIT, 1994).

Refiners have outlined their concerns that ethanol may be inadequate for lifting MON while still maintaining final petrol sensitivity within specification.

#### *Proposed management*

Based on the information at hand, the Commonwealth proposes to manage the use of ethanol in all grades of Australian petrol by setting a maximum content limit of 10%. The use of ethanol at these levels is acceptable provided that the other specifications for petrol, in particular RVP limits, are not exceeded.

Due to the potential greenhouse benefits associated with the use of ethanol-petrol blends, the use of fuel blends with higher ethanol concentrations will be given further consideration in the proposed future development of biofuel standards.

### 4.3.3 TBA (Tertiary butyl alcohol)

#### *Use*

TBA has the closest physical properties to petrol. However, a mixture of TBA12 (a 12% TBA/petrol blend) gives only a small increase in RON, ie 1.2 RON. (RMIT, 1994)

Worldwide TBA production is small, mainly confined to the US and Europe, and its availability is limited. Australian Petroleum Industry members have shown no enthusiasm for using TBA, with lack of infrastructure a particular problem.

TBA is a primary metabolite of MTBE and is often a contaminant of commercial MTBE supplies. The fungibility problems with methanol and ethanol can be ameliorated by the addition of higher alcohols such as TBA.

#### *Environmental and health issues*

As TBA is miscible with water and difficult to biodegrade, it's widespread use in Australian petrol may result in groundwater contamination (similar concerns surround MTBE use). The RMIT (1994) study reported that it does not bioaccumulate.

The California Energy Commission (1999) reports that TBA is comparable in air quality impacts to MTBE.

The RMIT (1994) study reported that TBA has low toxicity. However, while not recognised as a human carcinogen, the US National Toxicology Program suspects TBA as being a development toxicant, kidney toxicant and neurotoxicant.

TBA is on the current candidate list for potential assessment as a priority existing chemical by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS).

#### *Vehicle operability issues*

Studies have not established any evidence of material component damage due to TBA/petrol blends (RMIT, 1994).

#### *Effect on fuel specifications*

TBA is more tolerant to water in petrol than ethanol and methanol (RMIT, 1994)

#### *Proposed management*

The potential for TBA to contaminate groundwater is of concern. However, its use in Australia is likely to be small due to its limited availability. Based on the information at hand, the Commonwealth proposes not to regulate the use of TBA in Australian petrol at this time.

### 4.3.4 IPA (Iso propyl alcohol)

#### *Use*

Over 2 million tonnes of IPA are produced annually, mainly in the US, Europe and Japan. Refineries can produce considerable quantities of propylene and this can be the immediate precursor to the production of IPA.

IPA is identified as an acceptable additive for Euro-3 and Euro-4 fuel specifications.

Modelling in the literature review and analysis report identified ethanol and IPA (at 10%) as the best alcohols for approaching the 95 RON target. There has been no visible interest expressed by Australian Petroleum Industry members to use IPA, with “lack of infrastructure” a particular problem.

#### *Environmental and health issues*

While IPA is suspected as having a range of health effects, no pertinent data on the fate of IPA in the environment is available. However, as a secondary alcohol IPA is likely to degrade more slowly than ethanol (a primary alcohol) but faster than TBA (a tertiary alcohol).

Spectrum Laboratories Inc reports that IPA would not be very long lived in natural waters, and if released to this environment would volatilise (estimated half-life approximately 5.4 days) and biodegrade. IPA would not be expected to adsorb to sediment or bioconcentrate.

#### *Vehicle operability issues*

No data presented.

#### *Effect on fuel specifications*

No data presented.

#### *Proposed management*

| |
|---|
| Based on the information at hand, the Commonwealth proposes not to regulate the use of IPA in Australian petrol. |

### 4.3.5 Other alcohols

These include

- n-propanol
- n-butanol
- sec-Butanol
- isobutanol

#### *Use*

It is likely that the use of higher alcohols (propanols, butanols) in Australian petrol will be constrained by supply. However, they may make an occasional contribution in selected instances.

#### *Environmental and health issues*

The literature review and analysis found no pertinent data available on the environmental fate of these chemicals. However, if released to soil they would be expected to leach to groundwater or to biodegrade. Volatilisation from the soil surface may also occur.

None of these alcohols are expected to bind strongly to soil and would be expected to move into the water compartment where they would biodegrade.
As linear alcohols, n-propanol and n-butanol are likely to degrade quickly. Isobutanol and sec-butanol are expected to degrade more slowly than ethanol but faster than TBA.

Bioconcentration is not expected to be significant.

### *Vehicle operability issues*

No data presented.

### *Effect on fuel specifications*

No data presented.

### *Proposed management*

Based on the information at hand, the Commonwealth proposes not to regulate the use of these alcohols in Australian petrol.

## 4.3.6 MTBE (Methyl tertiary-butyl ether)

### *Use*

MTBE is the principle oxygenate and octane enhancer used by refineries worldwide due to its compatible blending properties and lower cost. It is described as an oxygenate – an oxygen-bearing additive used to reduce engine knocking and assist gasoline burn more cleanly.

World production capacity of MTBE is 21 Mt per annum, with a further 7 Mt per annum of capacity in construction or in planning. It is widely used in Europe, the US and the Far East. Australian domestic refineries do not use MTBE, however it may be present in occasional batches of imported petrol.

MTBE has been prohibited in petrol supplied in Western Australia and Queensland due to potential water contamination concerns (see below).

#### Experience in the US

The US Clean Air Act Amendments, introduced in 1990, attempted to reduce air pollution from the transport fleet by mandating the specifications of gasoline, called 'reformulated gasoline' (RFG). Among other things, this managed the oxygen content of gasoline (at 2%) in areas with severe air pollution. The addition of MTBE to gasoline at approximately 10-15% was identified as being able to assist in meeting this specification, which resulted in an enormous increase in demand for the product.

After the introduction of RFG, MTBE started to be detected in ground water in several states (eg California and Maine), with the primary source of contamination from leaks or illegal drainage from underground gasoline storage tanks and distribution pipes. Surface water was also contaminated through older recreational watercraft operating on lakes and waterways.

While the majority of MTBE water contamination in the US was detected below the levels for public health concern, MTBE can be detected by taste and odour at extremely low levels, ie less than 20 parts per billion (ppb). It is reported that water authorities in the US are even likely to shut down contaminated water sources at the 5 ppm level (Keller et al, 1998).

In response, the US EPA appointed the Blue Ribbon Panel in November 1998 to investigate air and water quality issues relating to the use of MTBE. The final report was issued in September 1999, with the following pertinent recommendations:

- that MTBE should be substantially phased out of gasoline in the US; and
- in order to facilitate the phase out, the 2% limit on oxygenate level in RFG should be waived.

Following findings and recommendations of an MTBE assessment performed by the University of California, MTBE was declared as "an environmental risk to California" in March 1999. At that time, Californian agencies were directed to take steps towards eliminating its use in gasoline in California by 31 December 2002. (Air Resources Board, 2000)

Activity is continuing in the US with the US Executive promoting bills in Congress that would lead to MTBE being phased out nationally.

### *Environmental and health issues*

MTBE is known to be soluble in water and is not adsorbed readily on soil particles. MTBE is very slow to biodegrade, with a half life in surface water, estimated to be between 28 and 180 days for aerobic degradation, and in ground water between 112 to 720 days for anaerobic degradation. (RMIT, 1994) MTBE is not expected to bioaccumulate (RMIT, 1994; Spectrum Laboratories Inc).

The literature review and analysis report argues that the controversy surrounding the use of MTBE is a consequence of the failure to properly control petrol transport and storage, and that all oxygenates (including ethanol) are likely to suffer a similar level of concern if they were widely used. However, MTBE degrades significantly more slowly than other octane enhancers.

In addition, the use of petrol containing MTBE in motor boats, in particular those using older 2-stroke engines can result in contamination of surface water (Keller et al, 1998).

MTBE is on the current candidate list for potential assessment as a priority existing chemical by the NICNAS, and some stakeholders have expressed concerns about the potential carcinogenicity of MTBE. However, for the general population, the risk of exposure to MTBE through the ingestion of contaminated water or inhalation is low (Keller et al, 1998).

The use of MTBE in petrol results in decreased vehicle emissions of hydrocarbons and carbon monoxide, with little changes in nitrogen oxides (RMIT, 1994). However, recent research completed by the University of California (Keller et al, 1998) found that MTBE and other oxygenates had no significant effect on exhaust emissions in advanced technology vehicles. Further, there were no significant additional air quality benefits to the use of oxygenates such as MTBE in US RFG relative to alternative non-oxygenated RFG formulations.

### *Vehicle operability issues*

The WWFC considers the use of MTBE acceptable. Ether/petrol blends have no significant effect on vehicle performance (RMIT, 1994).

### *Effect on fuel specifications*

MTBE is compatible with the gasoline blend streams and can be blended along with the other streams within the refinery.

To date, there has been no move to phase out the use of MTBE in Europe with the literature review and analysis report claiming that it is doubtful Europe could adopt the new Euro-3 and 4 standards for aromatics and 95 RON petrol without its use.

The Australian Petroleum Industry members have also expressed some concern that the European standards were developed within a framework of the widespread use of MTBE (at about 10%). However, the literature review and analysis also reports that these members do not favour the use of MTBE in Australia (and have a similar position on TAME and ETBE).

The use of ether additives does not lead to an increase in RVP levels, unlike alcohol additives.

### *Proposed management*

Based on the concerns surrounding the use of MTBE, in particular its potential to contaminate surface and ground water supplies, the Commonwealth proposes to prohibit its use in all grades of Australian petrol.

A maximum content level in petrol of 0.10% v/v will be set for MTBE to cater for contamination of petrol by residual amounts of MTBE blended petrol remaining in storage facilities and/or distribution systems.

While it is accepted that the current controversy surrounding the use of MTBE is generally a consequence of the failure to properly control petrol transport and storage systems, the use of MTBE in Australia poses an unacceptable risk due to the extremely low levels at which it taints ground and surface water supplies.

Environment Australia will review the use of MTBE in Australian petrol if it is assessed as a priority existing chemical by NICNAS.

## 4.3.7 DIPE (Di-isoproprropyl ether)

### *Use*

The world production capacity of DIPE is unknown but likely to be small. It is a permitted additive under US Federal reformulated gasoline regulations, and the Euro-3 and proposed Euro-4 standards.

It is likely that a MTBE ban in the US would have a major impact on the trade in other additives, in particular, TAME, ETBE and DIPE. The supply of these additives would be interrupted because of their similarity to MTBE.

There is little data available on DIPE.

#### *Environmental and health issues*

DIPE is reported as a suspected neurotoxicant.

#### *Vehicle operability issues*

Ether/petrol blends have no significant effect on vehicle performance (RMIT, 1994). It is also reported that ether/petrol blends do not have detrimental effects on vehicle materials.

#### *Effect on fuel specifications*

The use of ether additives does not lead to an increase in RVP levels, unlike alcohol additives.

#### *Proposed management*

DIPE is expected to have similar properties to MTBE and therefore raise similar concerns. The Commonwealth proposes to prohibit the use of DIPE in all grades of Australian petrol.

A maximum content level in petrol of 0.10% v/v will be set for DIPE to cater for contamination of petrol by residual amounts of DIPE blended petrol remaining in storage facilities and/or distribution systems.

### 4.3.8 Other Ethers

These include:

- ETBE (Ethyl tertiary-butyl ether)
- TAME (Tertiary amyl methyl ether)
- ETAE (Ethyl tertiary amyl ether)

ETBE, TAME and ETAE are not currently listed on the *Australian Inventory of Chemical Substances* (AICS). Subsequently, until these chemicals are notified and assessed by NICNAS, they are **not** permitted to be used in Australia. This includes their use in domestically produced and imported petrol blends.

ETBE and TAME are prohibited in petrol supplied in Queensland due to potential water contamination concerns.

#### *Use*

ETBE, TAME and ETAE are all permitted for use under US Federal RFG rules.

ETBE is an ethanol variant of MTBE, and is widely used as an additive in the US and Europe (including Sweden). When the ethanol is produced from agricultural sources, there is a potential for achieving greenhouse benefits (see discussion on ethanol use above)

TAME is used extensively as a supplement to MTBE in the US for RFG and as an octane booster in Europe. ETAE is an ethanol variant of TAME.

#### *Environmental and health issues*

These ethers are likely to have similar properties to MTBE, ie be highly soluble in water, poorly adsorbed by soil and have low biodegradation rates.

The California Energy Department (1999) reports that, as with MTBE, compounds such as ETBE and TAME are able to mix with water, are difficult to remove from contaminated water and cause water to taste and smell unpleasant even at very small concentrations.

ETBE in petrol results in a decrease of carbon monoxide emissions but may increase aldehyde emissions. The California Energy Commission (1999) reports that ETBE and TAME are comparable in air quality impacts to MTBE.

#### *Vehicle operability issues*

Ether/petrol blends have no significant effect on vehicle performance (RMIT, 1994). It is also reported that ether/petrol blends do not have detrimental effects on vehicle materials.

#### *Effect on fuel specifications*

The use of ether additives does not lead to an increase in RVP levels, unlike alcohol additives.

#### *Proposed management*

ETBE, TAME and ETAE are expected to have similar properties to MTBE and therefore raise similar concerns. The Commonwealth proposes to prohibit their use in all grades of Australian petrol.

A maximum content level in petrol of 0.10% v/v will be set for these additives to cater for contamination of petrol by residual amounts of ETBE/TAME/ETAE blended petrol remaining in storage facilities and/or distribution systems.

### 4.3.9 MMT (Methylcyclopentadienyl manganese tricarbonyl)

#### *Use*

The use of the manganese additive MMT is highly controversial but has growing acceptance in the refining industry. It is in widespread use overseas in both unleaded petrol and lead replacement petrol, and is permitted in Canada and the US (see below), Europe, Asia, and Central and South America.

The use of MMT as an octane booster has been studied extensively for 30 years with about 20 years of "on road" experience.

### Experience in Canada[5]

MMT has been used in Canadian petrol since 1976.

In June 1997, trade in MMT was restricted under the *Manganese-based Fuel Additives Act*. The legislation was challenged by the Government of Alberta, joined by the Governments of Quebec, Saskatchewan and Nova Scotia, and the Ethyl Corporation.

In June 1998, an independent panel established under the Agreement on Internal Trade (AIT) dispute settlement procedures found that the MMT restrictions were inconsistent with the Canadian Federal Government's obligations under the AIT.

The panel noted that the Government's legislation was based on representations by the Canadian automobile industry. This industry maintained that MMT adversely affected automobile on-board diagnostic systems (OBDs). A malfunctioning OBD could fail to detect that a car is emitting higher levels of pollutants into the air.

The panel reported that the current scientific information fails to demonstrate that MMT impairs the proper functioning of OBDs. Furthermore, there is no new evidence to modify the conclusions drawn by Health Canada in 1994 that MMT posed no health risk.

In response to this finding, the Canadian Government lifted its restrictions on the inter-provincial trade and import of MMT in July 1998.

### Experience in the US

MMT is now permitted for use in unleaded and leaded petrol.

MMT was prohibited from use in unleaded petrol in 1977 because it was found to increase hydrocarbon emissions and block the type of catalytic converters in use at that time.

Ethyl Corporation (the principle manufacturer of MMT in North America) applied to the US EPA in 1977, 1981 and 1992 for MMT to be allowed to be used in unleaded gasoline. These requests were all denied on the basis that MMT increased hydrocarbon emissions and blocked catalytic converters. (Health Canada, 1994)

The US Court of Appeals accepted a petition for review of the 1992 denial decision. After submission by Ethyl Corporation of extensive emission data, the US EPA concluded in November 1993 that MMT did not contribute significantly to increases in hydrocarbon emissions or failure of catalysts. (Health Canada, 1994)

In July 1994, the US EPA announced that it would deny Ethyl Corporation's waiver application on the grounds that there remained unresolved concerns regarding the health

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[5] Environment Canada, 1998.

impact of manganese emissions produced by MMT use. (Health Canada, 1994; Oge, 1999) In 1996 however, the courts rejected the US EPA's argument that public health impacts of 'fuel additives' should be fully evaluated prior to broad use, permitting MMT's use. The US EPA claims that more data is required "proving MMT is not a threat". (Browner, 1996)

In January 1999 the US EPA notified Ethyl Corporation under their *Clean Air Act* that it required additional health effects test data to assist in the identification and evaluation of any adverse effects on human health (Oge, 1999). The US EPA notification requires that Ethyl Corporation study the short term health effects of MMT's combustion products by undertaking tests "for sub-chronic systematic and organic toxicity, as well as the assessment of specific health effect endpoints" (Bureau of National Affairs, 2000).

The US EPA is aiming to determine whether or not manganese can have any cumulative effect (similar to lead) by building up in the bloodstream, and whether there is any need for future regulatory action.

### *Environmental and health issues*

Emissions test data have shown that the use of MMT results in a reduction in tail pipe emissions of $NO_X$, $N_2O$, hydrocarbons, CO and some other toxic gases (formaldehyde, acetaldehyde and benzene). MMT can also result in greenhouse gas emission reductions by facilitating improved refinery efficiency ($CO_2$ emissions reduced by up to 3%) and reducing tail pipe emissions of $N_2O$ by 15-20%.

The literature review and analysis reports that MMT oxidises very quickly in ambient air to manganese oxides, and of itself MMT does not pose a risk.

Recent data indicates that actual emissions of manganese from exhaust tailpipes are approximately 12-16%, with the manganese being present as the more inert manganese phosphates or silicates.

For cities in Canada with no major manganese emitting industries, MMT was found not to be entering the environment at a rate that would cause concern (Health Canada, 1994). There was no correlation between levels of respirable manganese ($PM_{10}$ or $PM_{2.5}$) and MMT sales or uses, and all analyses indicates that the combustion products of MMT in gasoline do not represent an added health risk to the Canadian population. (Health Canada, 1994)

RMIT (1994) reported that MMT undergoes rapid photolysis in sunlight, with a half life of less than 2 minutes. The hydrophobicity of MMT suggests a strong tendency to sorb to soil or sediment particles, and its high density will cause it to sink if spilled in surface waters.

In Australia, NICNAS has recently advised that they will be assessing the use of MMT as an anti-valve seat recession (AVSR) additive as part of the priority existing chemical program.

#### *Vehicle operability issues*

The automotive industry (including the Federal Chamber of Automotive Industries) opposes the use of metal-based fuel additives such as MMT. This position is reflected in the WWFC that specifically excludes manganese additives. In essence the WWFC expresses the opinion that ash-forming additives, such as MMT and ferrocene, are to be avoided because of perceived detrimental effects on the engine and ancillary systems, in particular automobile on-board diagnostic systems (OBDs).

However, Ethyl Corporation disputes these claims, providing data refuting the WWFC position. Authorities in the US and Canada have also concluded that the current scientific information fails to demonstrate that MMT impairs the proper functioning of OBDs or leads to catalyst damage. (Health Canada, 1994; Environment Canada, 1998)

#### *Effect on fuel specifications*

MMT is used at relatively low concentrations, and while it is unlikely to be used to raise the octane of Australian petrol to the Euro-3 level (95 RON) by itself, it could have a role in trimming gasoline blends to ensure a minimum 95 RON with lower aromatic levels.

Ethyl Corporation have also advised that higher than normal use of MMT (>0.018 mg Mn/L) provides protection from wear of soft exhaust valve seats (valve seat recession). As such, MMT is gaining widespread acceptance from the refining industry for formulating lead replacement petrol (LRP). The U.K. and French governments have approved MMT for AVSR applications, and it is also used in California for this purpose.

#### *Proposed management*

Based on the information at hand, including the in-principle support given for MMT in the literature review and analysis report, the Commonwealth proposes not to regulate the use of MMT in Australian petrol at this time.

Environment Australia will review the use of MMT in Australian petrol when either:
1. the US EPA's evaluation of the health effects of MMT is completed; or
2. a priority existing chemical assessment on MMT has been completed by NICNAS.

Given the continuing concerns that the automobile industry has with metal-based fuel additives such as MMT, the Commonwealth is specifically seeking stakeholder comment on the use of MMT in petrol. Submissions on this matter should be accompanied by supporting technical information.

### 4.3.10 Ferrocene

#### *Use*

There is an increasing interest in ferrocene. The depth of analysis and availability of public data however, is much less than that for MMT.

### *Environmental and health issues*

Ferrocene used in petrol is expected to be emitted in the exhaust as iron oxide. The literature review and analysis reports that iron oxide emissions would be expected from normal engine wear and ferrocene use at the recommended levels may not add significantly to the total levels of iron emitted.

Octel (the principle manufacturer) has provided exhaust emission toxicological data on vehicles using petrol containing ferrocene. None of the studies identified differences in the toxicity of the exhausts derived from fuels with (at 30 ppm) and without ferrocene.

### *Vehicle operability issues*

The literature review and analysis report states that the ferrocene additive has struggled to gain industry acceptance. This situation appears to be based on the perceived erosive nature of the combustion products. However, the technical data provided by Octel refutes this claim, with test data revealing no detrimental damage to any engine part. The claim of widespread damage to vehicle cylinders and valves in China appears to be the result of excessive concentrations of the additive used.

The automotive industry (Federal Chamber of Automotive Industries) opposes the use of metal-based fuel additives such as ferrocene. This position is also reflected in the WWFC, which expresses the opinion that ash-forming additives, such as ferrocene, are to be avoided because of perceived detrimental effects on the engine and ancillary systems, in particular automobile on-board diagnostic systems (OBDs).

These claims are disputed by the manufacturer who has provided data that demonstrates the product has no impact on or reduction in the efficiency of vehicle catalysts or sensors, and as with MMT, vehicle catalyst efficiency is maintained.

### *Effect on fuel specifications*

No data presented.

### *Proposed management*

Based on the information at hand, including the in-principle support given for MMT in the literature review and analysis report, the Commonwealth proposes not to regulate the use of ferrocene in Australian petrol.

Given the continuing concerns that the automobile industry has with metal-based fuel additives such as ferrocene, the Commonwealth is seeking stakeholder comment on the use of ferrocene in petrol. Submissions on this matter should be accompanied by supporting technical information.

# 5 CONCLUSION

The principle objective for the management of the use of octane enhancers in Australian petrol is to ensure that their use does not have significant adverse impacts on public health or the environment, and that their use does not impede the adoption of emerging vehicle engine and emission control technologies.

To meet this objective, the Commonwealth proposes to prohibit the use of the following octane enhancers in <u>all</u> grades of Australian petrol:

- Methanol
- MTBE (Methyl tertiary-butyl ether)#
- DIPE (Di-isoproprопyl ether)#
- ETBE (Ethyl tertiary-butyl ether)*#
- TAME (Tertiary amyl methyl ether)*#
- ETAE (Ethyl tertiary amyl ether)*#

* The use in Australia of these additives is not permitted until they have been notified and assessed by NICNAS.

\# A maximum content level in petrol of 0.10% v/v will be set for these additives to cater for contamination of petrol by residual amounts remaining in storage facilities and/or distribution systems.

The Commonwealth proposes not to manage/regulate the use of the following octane enhancers in any grade of Australian petrol:

- TBA (Tertiary butyl alcohol)
- IPA (Iso propyl alcohol)
- n-propanol
- n-butanol
- sec-butanol
- isobutanol
- MMT (Methylcyclopentadienyl manganese tricarbonyl)
- Ferrocene

The Commonwealth proposes to limit the use of ethanol in all grades of petrol to a maximum content limit of 10%. At greater than 10%, its blends will be treated as a separate fuel and be regulated as such.

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# 7 APPENDIX A

Octane Enhancing Petrol Additives/Products: Literature Review and Analysis, 10 August 2000. Completed by *Duncan Seddon and Associates Pty Ltd* on behalf of Environment Australia.

The views expressed in this report do not necessarily represent the views or reflect the policies of the Commonwealth Government or Environment Australia.