## **12. Premium Unleaded Petrol**

## 12.1 Introduction

The study brief requires an examination of premium unleaded petrol (PULP) (95 RON) meeting either the Euro2 specification for unleaded petrol or the fuel specifications for PULP proposed by the Commonwealth for implementation in 2002. It is assumed that this fuel does not contain ethanol and that it is used in light vehicles as defined in ADR 79/00 and 79/01. The emission limits specified in these ADRs may be found at:

http://www.dotrs.gov.au/land/environment/emissionrequirements.pdf

Our analysis is thus based on a hypothetical vehicle that satisfies Euro2 tailpipe emissions. PULP will thus be used as a reference fuel with which to compare emissions from the use of anhydrous ethanol in PULP.

## 12.2 Full Fuel-Cycle Analysis

### 12.2.1 Tailpipe emissions

We take tailpipe emissions for the hypothetical vehicle to be those of a Euro2 vehicle as given by http://www.dotrs.gov.au/land/environment/emissionrequirements.pdf:

CO 2.2 g/km HC 0.28 g/km NOx 0.22 g/km PM 0.08 g/km,

with an additional requirement that there be less than 2 g/km evaporative emissions.

Further, we follow Louis (2001) and take these values as appropriate to a Mercedes A-class 1.6 L reference vehicle. The fuel consumption of this vehicle is 7.5 L per 100 km (13.33 km/L), which corresponds to a fuel energy use of 2.42 MJ/km. According to Louis (2001) this corresponds to 172 g/km emissions of greenhouse gases from such a vehicle when using petrol.

### 12.2.2 Upstream

### Production of ULP and PULP

Petrol is manufactured using a number of refinery product streams derived from crude oil. The blending process is generally determined by three major factors: specification requirements, availability of specific process units within particular refinery configuration, and the properties of the crude oil used.

There are two grades of unleaded petrol manufactured in Australia for use in vehicles – regular unleaded (ULP) and premium unleaded (PULP). The most important parameters for both grades are summarised in Table 12.1.

Petrol grade	Property	Minimum	Maximum
Regular	MON	82	N/a
0	RON	91	93
	FVI	80	106
	Sulfur	N/a	500 ppm
Premium	MON	82	N/a
	RON	95	N/a
	FVI	80	106
	Sulfur	N/a	500 ppm

Table 12.1Unleaded petrol specifications

Both grades have the same requirement for motor octane number (MON). Research octane number (RON) requirement is higher for PULP. The determination of both the RON and the MON is done using standard test engines under strict conditions defined in the relevant specifications. RON test reflects anti-knock properties at lighter load, while MON is determined under conditions resembling high power demand under heavy load.

Flexible volatility index (FVI) is related to vapour pressure of petrol at various temperatures. Variations in FVI are seasonal – FVI requirement changes every month and this variation is a reflection of the average ambient temperatures within different geographic regions at different times of the year. Sulfur content is generally limited to 500 ppm (w/w), with excursions of up to 1000 ppm allowable under specific conditions.

Hydrocarbons constituting petrol can be broadly broken into three categories: paraffins, naphthenes and aromatics. Generally the octane rating of those increases with increasing chain branching, unsaturation and aromaticity. Variation of octane rating and volatility between different hydrocarbon types is the basis for the blending process. The objective is to produce petrol up to the specification while maximising efficiency of the refining process and feedstock utilisation.

An example of crude oil processing is presented in the chapter describing diesel fuel production. The first stage of crude oil processing is atmospheric pressure distillation. Fraction boiling between 90°C and 220°C, called straight run naphtha (gasoline), is the basic feedstock used in petrol production. It consists of predominantly straight chain aliphatic hydrocarbons. Its octane rating is generally below specification and needs to be adjusted by further processing. The first processing step is usually hydrotreating, which lowers sulfur contents and reduces unsaturation.

A number of processes are used to produce blending components. These typically include:

- Reforming thermal catalytic isomerisation and aromatisation of paraffins and naphthenes, which increases octane rating.
- Isomerisation conversion of paraffins to isoparaffins in the presence of hydrogen and the catalyst.
- Cracking thermal catalytic breaking of heavy fractions which produces a broad range of highly aromatic fractions.
- Alkylation/polymerisation catalytic oligomerisation of light olefines producing isoparaffins.

The difference between ULP and PULP is determined by differences in octane rating. PULP blend typically contains a larger proportion of high octane streams, i.e those containing aromatics, isoparaffins and naphthenes.

Upstream emissions in petrol production arise from oil recovery, transportation and processing. Further emissions derive from the distribution through the retail network.

### 12.3 Results

The upstream emissions results are based on the energies involved in typical refining operations (as evaluated for low sulfur diesel).

#### 12.3.1 Emissions per unit energy

Table 12.2Exbodied emissions per MJ for PULP

Full Lifecycle	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.0888
HC total	g HC	0.170
HC urban	g HC	0.141
NOx total	g NOx	0.185
NOx urban	g NOx	0.129
CO total	g CO	0.930
CO urban	g CO	0.920
PM10 total	mg PM10	38.2
PM10 urban Energy embodied	mg PM10 MJ LHV	36.9 1.14

Table 12.3Precombustion emissions per MJ for PULP

Precombustion	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.0177
HC total	g HC	0.0543
HC urban	g HC	0.026
NOx total	g NOx	0.094
NOx urban	g NOx	0.038
CO total	g CO	0.021
CO urban	g CO	0.011
PM10 total	mg PM10	5.19
PM10 urban Energy embodied	mg PM10 MJ LHV	3.8 1.14

Combustion	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.071
HC total	g HC	0.116
HC urban	g HC	0.116
NOx total	g NOx	0.091
NOx urban	g NOx	0.091
CO total	g CO	0.909
CO urban	g CO	0.909
PM10 total	mg PM10	33.06
PM10 urban Energy embodied	mg PM10 MJ LHV	33.06 0

Table 12.4Combustion emissions per MJ for PULP

 Table 12.5

 Summary of exbodied emissions per MJ for PULP

		PULP
Greenhouse kg	Precombustion	0.0177
Greenhouse kg	Combustion	0.0711
HC total g	Precombustion	0.0543
HC total g	Combustion	0.1157
HC urban g	Precombustion	0.0257
HC urban g	Combustion	0.1157
NOx total g	Precombustion	0.0937
NOx total g	Combustion	0.091
NOx urban g	Precombustion	0.038
NOx urban g	Combustion	0.091
CO total g	Precombustion	0.0212
CO total g	Combustion	0.9091
CO urban g	Precombustion	0.0113
CO urban g	Combustion	0.9091
PM10 total mg	Precombustion	5.19
PM10 total mg	Combustion	33.06
PM10 urban mg	Precombustion	3.80
PM10 urban mg	Combustion	33.06
Energy embodied MJ	Precombustion	1.14

### 12.3.2 Emissions per unit distance

Table 12.6Exbodied emissions per km for PULP

Full Lifecycle	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.2148
HC total	g HC	0.412
HC urban	g HC	0.342
NOx total	g NOx	0.447
NOx urban	g NOx	0.313
CO total	g CO	2.251
CO urban	g CO	2.227
PM10 total	mg PM10	92.5
PM10 urban	mg PM10	89.2
Energy embodied	MJ LHV	2.75

Table 12.7Precombustion emissions per km for PULP

Precombustion	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.0428
HC total	g HC	0.132
HC urban	g HC	0.062
NOx total	g NOx	0.227
NOx urban	g NOx	0.093
CO total	g CO	0.051
CO urban	g CO	0.027
PM10 total	mg PM10	12.5
PM10 urban	mg PM10	9.19
Energy embodied	MJ LHV	2.75

Table 12.8Tailpipe emissions per km for PULP

Combustion	Units	PULP
Greenhouse	kg CO <sub>2</sub>	0.172
HC total	g HC	0.280
HC urban	g HC	0.280
NOx total	g NOx	0.220
NOx urban	g NOx	0.220
CO total	g CO	2.200
CO urban	g CO	2.200
PM10 total	mg PM10	80.00
PM10 urban	mg PM10	80.00
Energy embodied	MJ LHV	0

		PULP
Greenhouse kg	Precombustion	0.0428
Greenhouse kg	Combustion	0.1720
HC total g	Precombustion	0.1320
HC total g	Combustion	0.2800
HC urban g	Precombustion	0.0622
HC urban g	Combustion	0.2800
NOx total g	Precombustion	0.2270
NOx total g	Combustion	0.220
NOx urban g	Precombustion	0.093
NOx urban g	Combustion	0.220
CO total g	Precombustion	0.0513
CO total g	Combustion	2.2000
CO urban g	Precombustion	0.0272
CO urban g	Combustion	2.2000
PM10 total mg	Precombustion	12.50
PM10 total mg	Combustion	80.00
PM10 urban mg	Precombustion	9.19
PM10 urban mg	Combustion	80.00
Energy embodied MJ	Precombustion	2.75
Greenhouse kg	Combustion	0

 Table 12.9

 Summary of exbodied emissions per km for PULP

### 12.3.3 Uncertainties

We will assume that the uncertainties are the same as those associated with low sulfur diesel.



Figure 12.1 Exbodied greenhouse gases emissions (kg CO<sub>2</sub>eq) from PULP production and processing and use in vehicle



Figure 12.2 Exbodied particulate matter (mg - urban) from PULP production and processing and use in vehicle

## 12.4 Viability and Functionality

Petrol is the most common automotive fuel, and unleaded petrol has been in use in Australia since 1986. Manufacturers produce premium unleaded petrol and its use does not cause warranty problems. Vehicle operational range depends on the size of the fuel tank, but typical values for a four or six cylinder car range from 400 to 600 km.

During consultation with stakeholders we were informed that there are considerable benefits arising from the widespread use of Euro4 quality RON petrol over 91 RON petrol. The improvement in fuel efficiency available for cars tuned for 95 octane is of the order of 2 to 4% over engines tuned for 91 octane. There is thus scope for smaller engines using 95 RON to have similar performance to engines tuned for 91 RON fuel.

All forms of petrol are considered hazardous according to Worksafe Australia criteria; more so than diesel fuel. Petrol has an extreme flammability rating and extreme chronic effect rating. It has moderate toxicity and body contact ratings.

PULP properties (Louis, 2001) are a density of 749 g/L and a LHV 43.1 MJ/kg.

## 12.5 Health Issues

Petrol is flammable, carcinogenic, and potentially addictive when inhaled (petrol sniffing). A typical material data safety sheet notes that unleaded petrol is:

- Highly flammable.
- Harmful by inhalation, in contact with skin and if swallowed.
- May cause cancer.
- Danger of serious damage to health by prolonged exposure.
- Harmful-petrol may cause lung damage if swallowed.
- May produce discomfort of the eyes and respiratory tract\*.
- Repeated exposure potentially causes skin dryness and cracking\*.
- Vapours potentially cause drowsiness and dizziness\*.

Substance	Unit	PULP
Benzene (tailpipe)	mg	0.0768
Benzene (sea)	μg	0.268
Formaldehyde	mg	0.0148
Formaldehyde (sea)	μg	9.6
PAH (total)	μg	0.511
PAH (sea)	μg	0.0948
PAH (tailpipe)	μg	0.0071
Toluene (total)	mg	0.386
toluene (sea)	μg	0.467
Xylenes (total)	mg	0.153

Table 12.10Summary of air toxics emissions of PULP per km

### 12.5.1 Production and transport

#### Particulate matter

The LCA estimate for PULP urban precombustion (car) PM10 emissions is 9 mg/km.

#### Air toxics

The LCA estimate for PULP urban precombustion (car) HC emissions is 0.062 g/km. The public health effects of air toxics will be mainly associated with combustion emissions in large urban centres. An accompanying disk to this report provides details of air toxic emissions from upstream activities.

<sup>\*</sup> There is limited evidence for these effects

12.5.2 Use

Particulate matter

The LCA estimate for PULP combustion (car) PM10 emissions is 80 mg/km.

Air toxics

The LCA estimate for PULP combustion (car) HC emissions is 0.280 g/km.

## 12.6 OHS Issues

The OHS issues in the lifecycle of PULP are well known and covered by a range of State and Commonwealth occupational health and safety provisions.

## 12.7 Vapour Pressure Issues

Evaporative emissions are a considerably more important issue for petrol or gasoline fuelled vehicles, than for diesel vehicles. There is evidence (see for example NRC, 1991) that evaporative emissions have been consistently under-estimated, and recent studies have continued to demonstrate the importance of evaporative emissions.

At a 1999 US workshop sponsored by the Coordinating Research Council (CRC) on On-Road Vehicle Emissions, (a summary is available at:

http://www.crcao.com/crcwebpage/reports/recent%20studies/9onroad%20workshop%20summary.pdf

Bob Gorse of the Ford Motor Company summarised results from several CRC and the Auto/Oil Air Quality Improvement Research Program vehicle evaporative emissions studies. Hot-soak, diurnal, and running loss emissions were evaluated using in-use passenger cars and light trucks captured at I/M lanes in Phoenix, using tank fuels during summer periods. The hot-soak study tested 300 1983-1993 model year vehicles; the diurnal study tested 150 1971-1991 model year vehicles, and the running loss study tested 151 1971-1991 model year vehicles. A new vehicle evaporative emissions program tested 50 1992- 1997 model year vehicles for hot-soak, diurnal and running loss emissions. The combined results from these studies of in-use vehicles by model year groups suggest that evaporative emissions may be equal in mass emission rates to those from exhaust emissions, and concludes that further emphasis should be placed on evaporative emissions studies in the future.

The CRC/Auto-oil study considers three sources of evaporative losses from vehicles: diurnal, hot-soak and running loss emissions. Running loss emissions have not been extensively characterised, but there is evidence (see, for example, Duffy *et al*, 1999) that diurnal emissions are enriched in the more volatile components of the fuel, and that hot-soak emissions have a composition close to that of the parent gasoline. This suggests that hot soak losses are a consequence of essentially complete evaporation of the fuel, whereas diurnal losses arise from vaporisation of the lighter, more volatile components.

## 12.8 Environmental Impact and Benefits

Ecologically sustainable development (ESD) is based on the principles of equity, efficiency and ecological integrity. The modern western economy is based on petroleum products, of which petrol, unleaded petrol, and premium unleaded petrol are examples. Though substantial arguments can be advanced that such an economy is not sustainable, in the sense that fossil fuels constitute a non-renewable resource, over the past three decades exploration activity has continually discovered new hydrocarbon reserves. In addition, the current concern over climate change has highlighted the burning of fossil fuels as one of the main causes. Thus even if one argues that the fossil fuel economy is economically efficient, it is more difficult to argue that it encourages equity or ecological integrity.

Petrol is refined from crude oil. Spills of crude oil, especially during transport in oil tankers at sea, pose an environmental hazard that contaminates marine life and bird life. Environmental damage from petrol itself can also occur, especially from leaks, at service stations and refuelling depots, which have been known to contaminate groundwater supplies.

This page left blank intentionally

## 13. Anhydrous Ethanol

### 13.1 Background

Development and use of alcohol fuels in transport have for the most part been driven by the desire in many countries to find renewable substitutes for imported petroleum-based fuels. Alcohol fuels have also been used as additives to conventional fuels to improve fuel characteristics. For petrol blends, ethanol is a known octane enhancer (a component added to petrol to increase octane rating and reduce engine knock) and oxygenate (a fuel or fuel additive containing hydrogen, carbon and oxygen in its molecular structure). Ethanol will easily blend with gasoline but blending with diesel requires an emulsifier or additive to form a stable fuel. Alcohols can be used in diesel engines by either modifying the fuel or by extensive engine adaptations.

More recently alcohol fuels have been the focus of attention as a possible means of reducing greenhouse gas emissions, and noxious urban emissions from transport. Results from several studies that have been conducted thoughout the world on exhaust emissions from ethanol blended fuels are often contradictory, making it difficult to generalise on emission outcomes and performance of ethanol blends. Furthermore, the tailpipe emissions from ethanol blended fuels varies markedly between different ethanol blends and different vehicle technologies.

Ethanol can be produced in two forms – hydrated and anhydrous. Hydrated ethanol has a purity of 95% suitable for blending with an ignition improver, or as a 15% emulsion in diesel that is known as diesohol. A second stage refining process is required to produce anhydrous ethanol (100% purity) for use in ethanol blends in petrol. Most industrial ethanol is denatured (to prevent oral consumption) by the addition of small amounts of an unpleasant or poisonous substance.

Anhydrous ethanol can be used as an additive in petrol, or as a fuel in its own right. Despite this, as an automotive fuel it is usually composed of 85% ethanol with 15% petrol (E85P) and this is the fuel that will be examined in this chapter. The reason for this is that the addition of 15% petrol improves the ignitability of alcohol, especially at low temperature. Other additives have also been trialled as ignition improvers. Ethanol is probably the most widely used alternative automotive fuel in the world, mainly due to Brazil's decision to produce fuel alcohol from sugar cane. Previous chapters have discussed diesohol, petrohol, and hydrated ethanol (for heavy vehicles). Because the only differences between hydrated and anhydrous ethanol are (i) the extra energy required for distillation, and (ii) the absence of an emulsifier when the anhydrous ethanol is blended with petrol, this chapter will deal with the use of anhydrous ethanol as a fuel for cars.

## 13.2 Full Fuel-Cycle Emissions

The upstream emissions associated with anhydrous ethanol are essentially the same as those associated with hydrated ethanol, with a requirement for extra energy input arising from the extra process step to transform the hydrated ethanol to anhydrous ethanol. According to Table 10 of the chapter on hydrated ethanol, 30% more energy is needed to convert hydrated ethanol to anhydrous ethanol. Our calculations also include the emissions associated with the production of the 15% of petrol added to the anhydrous ethanol.

### 13.2.1 Tailpipe emissions

Table 13.1 gives the tailpipe emissions (in kg) over the life of a typical vehicle using petrol and using oxygenated petrol (Maclean, 1998; 2000)

Table 13.1
ifetime exhaust emissions (kg) of air pollutants and carbon dioxide from petrol and oxygenated petrol.

	NMHC	СО	NOx	PM	ТНС	CO <sub>2</sub>
Petrol	36	494	58	12	60	53,676
E85P	35 <u>+</u> 35	536 <u>+</u> 484	38 <u>+</u> 38		66 <u>+</u> 66	48,564*

\*Renewable carbon, 85% of which is not considered to be a greenhouse gas.

These results agree with those of Arcoumanis (2000) who examined ethanol fuel for passenger cars and noted that tailpipe emissions of CO and hydrocarbons were 10% above Euro2 standards, NOx was 20% below Euro2,  $CO_2$  emissions were comparable, but particulate matter emissions were about half those of petrol vehicles.

### 13.3 Results

Wang et al. (1999) conducted a detailed study of the use of corn ethanol in the United States in terms of full fuel cycle energy and greenhouse gas emissions. Representative values for the results for the life cycle emissions associated with the use of anhydrous ethanol may be found in the chapter on hydrated ethanol. These may be taken as representative values when considered on a g/MJ, or g/km basis. When anhydrous ethanol is used in automobiles, the results will differ when expressed on a g/t-km basis. The variability and uncertainties associated with both forms of ethanol are expected to be the same.

#### 13.3.1 Emissions on a mass per unit energy basis

Full Lifecycle	Units	PULP	Ethanol azeotropic (molasses- expanded sys.bound.)	Ethanol azeotropic (molasses- economic allocation)	Ethanol azeotropic (wheat starch waste)	Ethanol azeotropic (wheat)	Ethanol azeotropic (wheat) fired with wheat straw	Ethanol azeotropic (woodwaste)	Ethanol azeotropic (ethylene)
Greenhouse	kg								
	$CO_2$	0.0888	0.0440	0.0679	0.0401	0.0651	0.0364	0.0173	0.1464
HC total	g HC	0.170	0.136	0.134	0.128	0.180	0.903	0.556	0.572
HC urban	g HC	0.141	0.126	0.126	0.120	0.126	0.849	0.548	0.507
NOx total	g NOx	0.185	0.186	0.185	0.162	0.325	0.276	0.128	0.343
NOx urban	g NOx	0.129	0.148	0.168	0.147	0.182	0.133	0.113	0.297
CO total	g CO	0.930	1.438	1.562	1.000	1.606	3.916	2.476	1.044
CO urban	g CO	0.920	1.431	1.558	0.997	1.002	3.306	2.476	1.028
PM10 total	mg PM10	38.2	35.0	34.5	51.2	53.5	72.9	55.0	38.3
PM10 urban	mg PM10	36.9	34.2	34.1	50.8	51.0	70.3	54.6	37.5
Energy embodied	MJ LHV	1.14	0.61	0.66	0.62	0.85	0.94	2.40	3.00

 Table 13.2

 Exbodied emissions per MJ for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Table 13.3
Precombustion emissions per MJ for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Precombustion	Units	PULP					Ethanol		
			Ethanol azeotropic (molasses- expanded sys.bound.)	Ethanol azeotropic (molasses- economic allocation)	Ethanol azeotropic (wheat starch waste)	Ethanol azeotropic (wheat)	azeotropic (wheat) fired with wheat straw	Ethanol azeotropic (woodwaste)	Ethanol azeotropic (ethylene)
Greenhouse	kg	0.01==		0.0444	0.0000	0.0 <b>7</b> 00	0.0001	0.0110	0.0001
	$CO_2$	0.0177	0.0377	0.0616	0.0338	0.0588	0.0301	0.0110	0.0821
HC total	g HC	0.0543	0.0231	0.0219	0.0158	0.0673	0.791	0.444	0.46
HC urban	g HC	0.026	0.013	0.014	0.008	0.014	0.737	0.436	0.395
NOx total	g NOx	0.094	0.126	0.125	0.102	0.265	0.216	0.068	0.283
NOx urban	g NOx	0.038	0.088	0.108	0.087	0.122	0.073	0.053	0.237
CO total	g CO	0.021	0.452	0.576	0.014	0.620	2.930	1.490	0.058
CO urban	g CO	0.011	0.445	0.572	0.011	0.015	2.320	1.490	0.041
PM10 total	mg PM10	5.19	1.96	1.48	18.1	20.4	39.8	21.9	5.25
PM10 urban	mg PM10	3.8	1.16	1.06	17.7	17.9	37.2	21.5	4.48
Energy embodied	MJ LHV	1.14	0.61	0.66	0.62	0.85	0.94	2.40	3.00

 Table 13.4

 Combustion emissions per MJ for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Combustion	Units	PULP	Anhydrous Ethanol with 15% PULP
Greenhouse	kg CO <sub>2</sub>	0.071	0.006
HC total	g HC	0.116	0.112
HC urban	g HC	0.116	0.112
NOx total	g NOx	0.091	0.060
NOx urban	g NOx	0.091	0.060
CO total	g CO	0.909	0.986
CO urban	g CO	0.909	0.986
PM10 total	mg PM10	33.06	33.06
PM10 urban	mg PM10	33.06	33.06
Energy embodied	MJ LHV	0	0

#### 13.3.2 Vehicle emissions - cars (g/km)

This section gives the calculated values for the emissions from cars, on a per-kilometre basis.

Table 13.5
Exbodied emissions per km for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Enll	Unite	DIIID	Ethanol	Fthanol			Fthanol		
r un L ifogyala	Units	TULI	azeotropic	azeotropic	Fthanol		azeotropic		
			(molasses- expanded sys.bound.)	(molasses- economic allocation)	azeotropic (wheat starch waste)	Ethanol azeotropic (wheat)	(wheat) fired with wheat straw	Ethanol azeotropic (woodwaste)	Ethanol azeotropic (ethylene)
Greenhouse	kg								
	$CO_2$	0.2148	0.1062	0.1641	0.0969	0.1571	0.0879	0.0417	0.3546
HC total	g HC	0.412	0.328	0.325	0.311	0.435	2.182	1.352	1.382
HC urban	g HC	0.342	0.304	0.306	0.291	0.306	2.052	1.332	1.227
NOx total	g NOx	0.447	0.448	0.446	0.392	0.785	0.668	0.309	0.830
NOx urban	g NOx	0.313	0.358	0.405	0.355	0.439	0.321	0.273	0.718
CO total	g CO	2.251	3.477	3.777	2.421	3.887	9.477	5.997	2.526
CO urban	g CO	2.227	3.467	3.767	2.414	2.424	8.007	5.987	2.487
PM10 total	mg PM10	92.5	84.8	83.6	123.7	129.4	176.2	132.9	92.7
PM10 urban	mg PM10	89.2	82.8	82.6	122.8	123.3	170.1	132.0	90.8
Energy embodied	MJ LHV	2.75	1.48	1.59	1.50	2.05	2.27	5.80	7.26

 Table 13.6

 Precombustion emissions per km for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Precombustion	Units	PULP					Ethanol		
			Ethanol azeotropic (molasses- expanded	Ethanol azeotropic (molasses- economic	Ethanol azeotropic (wheat starch	Ethanol azeotropic	azeotropic (wheat) fired with wheat	Ethanol azeotropic	Ethanol azeotropic
			sys.bound.)	allocation)	waste)	(wheat)	straw	(woodwaste)	(ethylene)
Greenhouse	kg CO <sub>2</sub>	0.0428	0.0911	0.1490	0.0818	0.1420	0.0728	0.0266	0.1990
HC total	g HC	0.132	0.0559	0.053	0.0383	0.163	1.91	1.08	1.11
HC urban	g HC	0.062	0.032	0.033	0.019	0.033	1.780	1.060	0.955
NOx total	g NOx	0.227	0.304	0.302	0.248	0.641	0.524	0.165	0.686
NOx urban	g NOx	0.093	0.214	0.261	0.211	0.295	0.177	0.129	0.574
CO total	g CO	0.051	1.090	1.390	0.034	1.500	7.090	3.610	0.139
CO urban	g CO	0.027	1.080	1.380	0.027	0.037	5.620	3.600	0.100
PM10 total	mg PM10	12.5	4.75	3.58	43.7	49.4	96.2	52.9	12.7
PM10 urban	mg PM10	9.19	2.81	2.58	42.8	43.3	90.1	52	10.8
Energy embodied	MJ LHV	2.75	1.48	1.59	1.5	2.05	2.27	5.8	7.26

# Table 13.7 Tailpipe emissions per km for premium unleaded petrol (PULP) and ethanol (mixed with 15% PULP)

Combustion	Units	PULP	Ethanol
Greenhouse	kg CO <sub>2</sub>	0.172	0.015
HC total	g HC	0.280	0.272
HC urban	g HC	0.280	0.272
NOx total	g NOx	0.220	0.144
NOx urban	g NOx	0.220	0.144
CO total	g CO	2.200	2.387
CO urban	g CO	2.200	2.387
PM10 total	mg PM10	80.00	80.00
PM10 urban	mg PM10	80.00	80.00
Energy embodied	MJ LHV	0	0

#### 13.3.3 Uncertainties

We use the uncertainty estimates given by Beer et al. (2000) on the basis of the tailpipe emissions to estimate the uncertainties associated with the above results to be as given in Table 6.19.

Estimated one	Ta standard deviation uncerta	able 13.8 inties (in percent) for hydrated	ethanol emissions
	g/MJ	g/t-km	g/p-km
CO,	15	15	13
HC	45	17	73
NOx	21	8	35
CO	40	36	46
PM10	46	45	46





Exbodied greenhouse gases emissions (kg CO<sub>2</sub>eq) from E85 in PULP production and processing and use in vehicle (Ethanol component is from molasses based on Sarina plant and using expanded system boundary allocation)



Figure 13.2 Exbodied particulate matter (mg - urban) from E85 in PULP production and processing and use in vehicle (Ethanol component is from molasses based on Sarina plant and using expanded system boundary allocation)

## 13.4 Viability and Functionality

There is considerable international experience on the use of ethanol in Brazil where sugar-derived ethanol is used as an automotive fuel. The ethanol used in Brazil is called Alcool and consists of 93% ethanol by volume. IEA Alternative Fuels Information Service (1996) note that "the techniques for the production and use of methanol and ethanol as a vehicle fuel are known. Obstacles that hinder the use of alcohols as a vehicular fuel are the relatively high costs of alcohol and the investments necessary to introduce an extra fuel."

The viability and functionality issues related to ethanol and its use in heavy vehicles (as diesohol) or in light vehicles (as petrohol) have been examined in previous chapters, and the same considerations will apply.

## 13.5 Health and OHS

Table 13.9 gives the exhaust emissions of air toxics given by MacLean (1988) that may also be found in the supporting documentation of MacLean and Lave (2000). The air toxic emissions are given in terms of mass emitted per vehicle lifetime, but are also given in terms of weighted emissions in terms of sulfuric acid equivalents. In both cases, ethanol produces a marked decline in the emissions of air toxics, except for the aldehydes but when their weighting factors are applied, the weighted air toxics emissions from ethanol are below those of petrol. For comparison, the weighted emissions for diesel exhaust are estimated to range from 37,000 to 80,000 grams sulfuric acid equivalent per lifetime.

	Benzene	1,3-butadiene	Formaldehyde	Acetaldehyde	Aggregate toxics
Petrol	1820	210	350	126	2506
CMU-ET weighted	1138	48	389	0.4	1575
E85	252	28	574	3472	4326
CMU-ET weighted	158	6.4	638	9.6	812

 Table 13.9

 Lifetime exhaust emissions (g) of air toxics from petrol and ethanol, along with weighted toxic emissions (grams sulfuric acid equivalent)

Ethanol fuels perform better than conventional fuels in terms of lower emissions of air toxics, except for aldehydes.

## 13.6 Environmental Issues

Environmental and ESD issues related to ethanol have been dealt with in Chapter 6. Ethanol is not persistent in the environment. Virtually any environment supporting bacterial populations is believed to be capable of biodegrading ethanol. Atmospheric degradation is also expected to be rapid.

When ethanol is derived from a renewable source than the greenhouse gas emissions from ethanol are lower than those of petrol because of the use of a renewable fuel in the blend. The particulate emissions are lowered as are the emissions of ozone precursors. The concentrations of emitted air toxics are lower from ethanol than from petrol.

## 13.7 Expected Future Emissions

Arcoumanis (2000) developed a model that examines a given alternative fuel relative to the reference diesel engine (Euro2) in terms of a specific regulated pollutant. A value of 1 implies identical

performance to the low sulfur diesel/Euro2 combination. A value greater than 1 implies inferior performance, whereas a value less than 1 indicates superior performance.

Table 13.10 lists the estimated emissions factors for ethanol. The columns in bold represent the standards relative to the Euro2 standard. The adjacent column gives the expected performance of ethanol. The estimates of Arcoumanis (2000) indicate that ethanol can be expected to meet all future Australian Design Rules for all pollutants, except for hydrocarbon emissions.

Technology	со	со	ТНС	ТНС	NOx	NOx	PM	PM	CO <sub>2</sub>	LCA CO <sub>2</sub>
Euro2	1.0	1.1	1.0	1.1	1.0	0.8		0.5	1.0	0.3
Euro3	1.05	0.9	0.59	0.8	0.6	0.5		0.5	1.0	0.25
Euro4	0.45	0.3	0.29	0.4	0.32	0.3		0.4	1.0	0.2

Table 13.10
Estimated emission factors for ethanol (E85P) under future technologies (PM is unregulated)

## 13.8 Summary

#### 13.8.1 Advantages

- As a renewable fuel, anhydrous ethanol made from bio-products, produces less fossil CO<sub>2</sub> than conventional fuels.
- Tailpipe emissions of NOx and PM appear to be lower on average.
- Air toxic levels (except for aldehydes) are lower than those of conventional fuels.

#### 13.8.2 Disadvantages

• Cold starting in cool climates is difficult unless ethanol is blended with petrol as a starting aid, or unless some other starting aid is used.

## 14. Petrohol

### 14.1 Background

Anhydrous ethanol can be used as an additive in petrol. We use the term petrohol for a blend of 10% anhydrous ethanol in premium unleaded petrol. The symbols E10P or E10PULP are also used for this fuel, depending on whether it is necessary to specify the type of petrol (P) with which the ethanol is blended. The upstream emissions associated with anhydrous ethanol and with premium unleaded petrol have been dealt with in separate chapters. This chapter will therefore not repeat the upstream production and processing information.

## 14.2 Full Fuel-Cycle Emissions

There has been substantial US interest in the use of ethanol in cars. The reason for this is that the Californian Government, through their Air Resources Board, requires vehicles to use "reformulated gasoline". Originally such reformulated gasoline could be made by blending MTBE (methyl tertiarybutyl ether) into petrol. Because of the contamination of Californian groundwater with MTBE the Californian Governor ordered the removal of MTBE from petrol and studies on the environmental and health effects of ethanol in petrol. The use of ethanol produces an oxygenated fuel that satisfies the requirements of Californian reformulated gasoline.

Oygenates are added to petrol to improve the anti-knock performance and to reduce emissions. Reuter et al (1992) studied European petrol oxygenated with MTBE, ETBE and ethanol and found that the emissions of oxygenated petrol are independent of the oxygenate that is used.

### 14.2.1 Tailpipe emissions

Anhydrous ethanol is rarely used as a fuel in its own right, though it is frequently used in a blend of 85% anhydrous ethanol with 15% petrol. Petrohol (petrol and ethanol blends that range from 5% to 26% ethanol) consists of a blend of anhydrous ethanol and petrol. In this chapter we will use the term petrohol (or E10PULP) to refer to 95 RON PULP with a 10% ethanol blend. Such fuel has an oxygen level of 3.5%. Table 1 gives the tailpipe emissions (in kg) over the 300,000 km life of a typical vehicle using petrol and using oxygenated petrol (Maclean, 1998; 2000). These values have been used for the tailpipe emissions in the subsequent full-fuel cycle analysis (with appropriate allowance for the fact that carbon dioxide emitted from any ethanol made from renewable fuels is not considered to be a greenhouse gas).

 Table 14.1

 Lifetime exhaust emissions (kg) of air pollutants and carbon dioxide from petrol and oxygenated petrol

	NMHC	СО	NOx	РМ	тнс	CO <sub>2</sub>
Petrol	36	494	58	12	60	53676
Oxygenated petrol	27 <u>+</u> 11	416 <u>+</u> 248	50 <u>+</u> 20		46 <u>+</u> 15	56425 <u>+</u> 289

## 14.3 Results

14.3.1 Emissions per unit energy

Full	Units	PULP	PULP		PULP				
Lifecycle			E10P		E10P		PULP	PULP	
			(molasses-	PULP E10P	(wheat	PULP	E10P	E10P	PULP
			exp.sys.	(molasses-	starch	E10P	(wheat	(wood	E10P
			bound.)	eco.allocat.)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	kg								
	$CO_2$	0.0888	0.0895	0.0913	0.0891	0.0911	0.0889	0.0874	0.0974
HC total	g HC	0.170	0.139	0.139	0.138	0.142	0.199	0.172	0.173
HC urban	g HC	0.141	0.111	0.112	0.111	0.112	0.168	0.145	0.141
NOx total	g NOx	0.185	0.175	0.174	0.173	0.185	0.181	0.170	0.186
NOx urban	g NOx	0.129	0.121	0.122	0.121	0.123	0.119	0.118	0.132
CO total	g CO	0.930	0.820	0.830	0.786	0.834	1.014	0.902	0.790
CO urban	g CO	0.920	0.811	0.821	0.777	0.777	0.958	0.893	0.779
PM10 total	mg								
	PM10	38.2	38.0	38.0	39.2	39.4	40.9	39.5	38.2
PM10 urban	mg								
	PM10	36.9	36.6	36.6	37.9	38.0	39.5	38.2	36.9
Energy	MJ								
embodied	LHV	1.14	1.10	1.10	1.10	1.11	1.12	1.23	1.28

 Table 14.2

 Exbodied emissions per MJ of petrohol based on ethanol from various feedstocks

 Table 14.3

 Precombustion emissions per MJ of petrohol based on ethanol from various feedstocks

Precombustion	Units	PULP	PULP		PULP				
			E10P		E10P		PULP		
			(molasses-	PULP E10P	(wheat	PULP	E10P	PULP E10P	PULP
			exp.sys.bo	(molasses-	starch	E10P	(wheat	(wood	E10P
			und.)	eco.allocat.)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	kg								
	$CO_2$	0.0177	0.0193	0.0211	0.0189	0.0209	0.0187	0.0172	0.0227
HC total	g HC	0.0543	0.0519	0.0518	0.0513	0.0554	0.112	0.0848	0.086
HC urban	g HC	0.026	0.025	0.025	0.024	0.025	0.081	0.058	0.055
NOx total	g NOx	0.094	0.096	0.096	0.094	0.107	0.103	0.092	0.108
NOx urban	g NOx	0.038	0.042	0.044	0.042	0.045	0.041	0.040	0.054
CO total	g CO	0.021	0.055	0.065	0.021	0.068	0.248	0.136	0.024
CO urban	g CO	0.011	0.045	0.055	0.011	0.012	0.192	0.127	0.014
PM10 total	mg								
	PM10	5.19	4.93	4.9	6.19	6.38	7.89	6.49	5.19
PM10 urban	mg								
	PM10	3.8	3.59	3.58	4.88	4.9	6.41	5.18	3.85
Energy	MJ								
embodied	LHV	1.14	1.10	1.10	1.10	1.11	1.12	1.23	1.28

Combustion Units PLILD PLILD PLILD	
E10P E10P PULP PULP	
(molasses- PULP E10P (wheat PULP E10P E10P PUI	Р
exp.sys.bo (molasses- starch E10P (wheat (wood E10	Р
und.) eco.allocat.) waste) (wheat) WS) waste) (ethyl	ene)
Greenhouse kg	
CO, 0.071 0.070 0.070 0.070 0.070 0.070 0.070 0.070 0.070	'5
HC total g HC 0.116 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087	37
HC urban g HC 0.116 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087	37
NOx total g NOx 0.091 0.078 0.078 0.078 0.078 0.078 0.078 0.078 0.078	8
NOx urban g NOx 0.091 0.078 0.078 0.078 0.078 0.078 0.078 0.078 0.078	8
CO total g CO 0.909 0.766 0.766 0.766 0.766 0.766 0.766 0.766 0.766	66
CO urban g CO 0.909 0.766 0.766 0.766 0.766 0.766 0.766 0.766 0.766	66
PM10 total mg	
PM10 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06	)6
PM10 urban mg	
PM10 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06 33.06	)6
Energy MJ	
embodied LHV 0 0 0 0 0 0 0 0 0 0	

 Table 14.4

 Tailpipe emissions per MJ of petrohol based on ethanol from various feedstocks

 Table 14.5

 Summary of exbodied emissions per MJ of petrohol based on ethanol from various feedstocks

		PULP	PULP		PULP				
			E10P		E10P		PULP	PULP	
			(molasses-	PULP E10P	(wheat	PULP	E10P	E10P	PULP
			exp.sys.bo	(molasses-	starch	E10P	(wheat	(wood	E10P
			und.)	eco.allocat.)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	Precombustion	0.0177	0.0193	0.0211	0.0189	0.0209	0.0187	0.0172	0.0227
Greenhouse	Combustion	0.0711	0.0702	0.0702	0.0702	0.0702	0.0702	0.0702	0.0747
HC total	Precombustion	0.0543	0.0519	0.0518	0.0513	0.0554	0.1120	0.0848	0.0860
HC total	Combustion	0.1157	0.0868	0.0868	0.0868	0.0868	0.0868	0.0868	0.0868
HC urban	Precombustion	0.0257	0.0247	0.0248	0.0243	0.0248	0.0813	0.0578	0.0545
HC urban	Combustion	0.1157	0.0868	0.0868	0.0868	0.0868	0.0868	0.0868	0.0868
NOx total	Precombustion	0.0937	0.0962	0.0961	0.0944	0.1070	0.1030	0.0917	0.1080
NOx total	Combustion	0.091	0.078	0.078	0.078	0.078	0.078	0.078	0.078
NOx urban	Precombustion	0.038	0.042	0.044	0.042	0.045	0.041	0.040	0.054
NOx urban	Combustion	0.091	0.078	0.078	0.078	0.078	0.078	0.078	0.078
CO total	Precombustion	0.0212	0.0548	0.0645	0.0206	0.0680	0.2480	0.1360	0.0240
CO total	Combustion	0.9091	0.7656	0.7656	0.7656	0.7656	0.7656	0.7656	0.7656
CO urban	Precombustion	0.0113	0.0451	0.0551	0.0112	0.0116	0.1920	0.1270	0.0136
CO urban	Combustion	0.9091	0.7656	0.7656	0.7656	0.7656	0.7656	0.7656	0.7656
PM10 total	Precombustion	5.19	4.93	4.90	6.19	6.38	7.89	6.49	5.19
PM10 total	Combustion	33.06	33.06	33.06	33.06	33.06	33.06	33.06	33.06
PM10	Precombustion								
urban		3.80	3.59	3.58	4.88	4.90	6.41	5.18	3.85
PM10	Combustion								
urban		33.06	33.06	33.06	33.06	33.06	33.06	33.06	33.06
Energy	Precombustion								
embodied		1.14	1.10	1.10	1.10	1.11	1.12	1.23	1.28

#### 14.3.2 Emissions per unit distance

Full	Units	PULP	PULP		PULP				
Lifecycle			E10P		E10P		PULP	PULP	
			(molasses-	PULP E10P	(wheat	PULP	E10P	E10P	PULP
			exp.sys.	(molasses-	starch	E10P	(wheat	(wood	E10P
			bound.)	eco.allocat.)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	kg								
	$CO_2$	0.2148	0.2164	0.2209	0.2157	0.2204	0.2150	0.2114	0.2358
HC total	g HC	0.412	0.336	0.335	0.334	0.344	0.481	0.415	0.418
HC urban	g HC	0.342	0.270	0.270	0.269	0.270	0.407	0.350	0.342
NOx total	g NOx	0.447	0.423	0.423	0.418	0.449	0.440	0.412	0.453
NOx urban	g NOx	0.313	0.292	0.296	0.292	0.299	0.289	0.285	0.320
CO total	g CO	2.251	1.986	2.009	1.903	2.018	2.454	2.182	1.911
CO urban	g CO	2.227	1.962	1.986	1.880	1.881	2.317	2.159	1.886
PM10 total	mg								
	PM10	92.5	91.9	91.8	95.0	95.4	99.1	95.7	92.6
PM10 urban	mg								
	PM10	89.2	88.7	88.7	91.8	91.9	95.5	92.5	89.3
Energy	MJ								
embodied	LHV	2.75	2.65	2.66	2.65	2.70	2.71	2.99	3.10

 Table 14.6

 Exbodied emissions per km of petrohol based on ethanol from various feedstocks

 Table 14.7

 Precombustion emissions per km of petrohol based on ethanol from various feedstocks

Precombustion	Units	PULP	PULP E10P (molasses- exp.sys. bound.)	PULP E10P (molasses- eco.allocat.)	PULP E10P (wheat starch waste)	PULP E10P (wheat)	PULP E10P (wheat WS)	PULP E10P (wood waste)	PULP E10P (ethylene)
Greenhouse	kg								
	$CO_2$	0.0428	0.0466	0.0511	0.0459	0.0506	0.0452	0.0416	0.0550
HC total	g HC	0.132	0.126	0.125	0.124	0.134	0.271	0.205	0.208
HC urban	g HC	0.062	0.060	0.060	0.059	0.060	0.197	0.140	0.132
NOx total	g NOx	0.227	0.233	0.233	0.228	0.259	0.250	0.222	0.263
NOx urban	g NOx	0.093	0.102	0.106	0.102	0.109	0.099	0.096	0.130
CO total	g CO	0.051	0.133	0.156	0.050	0.165	0.601	0.329	0.058
CO urban	g CO	0.027	0.109	0.133	0.027	0.028	0.464	0.306	0.033
PM10 total	mg								
	PM10	12.5	11.9	11.8	15	15.4	19.1	15.7	12.6
PM10 urban	mg								
	PM10	9.19	8.69	8.68	11.8	11.9	15.5	12.5	9.32
Energy	MJ								
embodied	LHV	2.75	2.65	2.66	2.65	2.7	2.71	2.99	3.1

Combustion	Units	PULP			PULP				
			PULP E10P		E10P		PULP	PULP	
			(molasses-	PULP E10P	(wheat	PULP	E10P	E10P	
			exp.sys.	(molasses-	starch	E10P	(wheat	(wood	PULP E10P
			bound.)	eco.allocat.)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	kg								
	$CO_2$	0.172	0.170	0.170	0.170	0.170	0.170	0.170	0.181
HC total	g HC	0.280	0.210	0.210	0.210	0.210	0.210	0.210	0.210
HC urban	g HC	0.280	0.210	0.210	0.210	0.210	0.210	0.210	0.210
NOx total	g NOx	0.220	0.190	0.190	0.190	0.190	0.190	0.190	0.190
NOx urban	g NOx	0.220	0.190	0.190	0.190	0.190	0.190	0.190	0.190
CO total	g CO	2.200	1.853	1.853	1.853	1.853	1.853	1.853	1.853
CO urban	g CO	2.200	1.853	1.853	1.853	1.853	1.853	1.853	1.853
PM10 total	mg								
	PM10	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
PM10 urban	mg								
	PM10	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
Energy	MJ								
embodied	LHV	0	0	0	0	0	0	0	0

 Table 14.8

 Tailpipe emissions per km of petrohol based on ethanol from various feedstocks

Table 14.9								
Summary of exbodied emissions	per km of	petrohol						

		PULP	PULP		PULP				
			E10P		E10P		PULP	PULP	
			(molasses-	PULP E10P	(wheat	PULP	E10P	E10P	PULP
			exp.sys.	(molasses-	starch	E10P	(wheat	(wood	E10P
			bound.)	eco.allocat)	waste)	(wheat)	WS)	waste)	(ethylene)
Greenhouse	Precombustion	0.0428	0.0466	0.0511	0.0459	0.0506	0.0452	0.0416	0.0550
Greenhouse	Combustion	0.1720	0.1698	0.1698	0.1698	0.1698	0.1698	0.1698	0.1808
HC total	Precombustion	0.1320	0.1260	0.1250	0.1240	0.1340	0.2710	0.2050	0.2080
HC total	Combustion	0.2800	0.2100	0.2100	0.2100	0.2100	0.2100	0.2100	0.2100
HC urban	Precombustion	0.0622	0.0599	0.0600	0.0589	0.0600	0.1970	0.1400	0.1320
HC urban	Combustion	0.2800	0.2100	0.2100	0.2100	0.2100	0.2100	0.2100	0.2100
NOx total	Precombustion	0.2270	0.2330	0.2330	0.2280	0.2590	0.2500	0.2220	0.2630
NOx total	Combustion	0.220	0.190	0.190	0.190	0.190	0.190	0.190	0.190
NOx urban	Precombustion	0.093	0.102	0.106	0.102	0.109	0.099	0.096	0.130
NOx urban	Combustion	0.220	0.190	0.190	0.190	0.190	0.190	0.190	0.190
CO total	Precombustion	0.0513	0.1330	0.1560	0.0499	0.1650	0.6010	0.3290	0.0582
CO total	Combustion	2.2000	1.8526	1.8526	1.8526	1.8526	1.8526	1.8526	1.8526
CO urban	Precombustion	0.0272	0.1090	0.1330	0.0272	0.0280	0.4640	0.3060	0.0329
CO urban	Combustion	2.2000	1.8526	1.8526	1.8526	1.8526	1.8526	1.8526	1.8526
PM10 total	Precombustion	12.50	11.90	11.80	15.00	15.40	19.10	15.70	12.60
PM10 total	Combustion	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
PM10 urban	Precombustion	9.19	8.69	8.68	11.80	11.90	15.50	12.50	9.32
PM10 urban	Combustion	80.00	80.00	80.00	80.00	80.00	80.00	80.00	80.00
Energy	Precombustion								
embodied		2.75	2.65	2.66	2.65	2.70	2.71	2.99	3.10

### 14.3.3 Uncertainties

In the absence of information on the variability and uncertainties associated with E10P emissions, we assume that the uncertainties are the same as those associated with diesohol (E15D).



Exbodied greenhouse gases emissions (kg CO<sub>2</sub>eq) from E10 in PULP production and processing and use in vehicle (Ethanol component is from molasses based on Sarina plant and using expanded system boundary allocation)





Exbodied particulate matter (mg - urban) from E10 in PULP production and processing and use in vehicle (Ethanol component is from molasses based on Sarina plant and using expanded system boundary allocation)

The exbodied greenhouse gas emissions depicted in Figure 14.1 reflect a combination of the fuel economy obtained by using petrohol, and the fact that 10% of the petrohol consists of a renewable fuel whose carbon dioxide emissions are not treated as a greenhouse gas. On the basis of the data in MacLean (1998) the emissions of  $CO_2$  for premium unleaded petrol is 172 g/km whereas for petrohol it is 188 g/km.



Figure 14.3

Allowing for the renewable components of petrohol means that 216 gram of exbodied greenhouse gases are emitted per kilometre.

Examining Figure 14.3 it may be noted that the tailpipe emissions of greenhouse gases from petrohol come to 170 g/km  $CO_2$ -equ. This is from 0.216 - 0.046 kg, as shown in the bottom part of the second and third boxes. The actual tailpipe emissions of  $CO_2$  consist of 170 g/km from the petrol (being 0.9 x 188 g/km), and 11 g from combustion of 5.7 g of ethanol. This comprises 181 g/km.

The expected greenhouse gas saving of 11 g/km by using ethanol does not eventuate because of the altered fuel economy. An equivalent petrol fuelled vehicle emits 172 g/km  $CO_2$ -equ. Furthermore, the greenhouse gas benefit of 2 g/km is negated by the greater upstream processing energy in the production of ethanol so that the exbodied greenhouse gas emissions of petrol are 215 g/km whereas those of petrohol are very slightly higher at 216 g/km.

## 14.4 Viability and Functionality

There is considerable international experience on the use of ethanol as a blend in petrol in the United States, where it is needed under the legislation requiring the use of reformulated gasoline, and in Brazil where sugar derived ethanol is used as an automotive fuel and also as a blend (gasohol). No special engine modification or handling precautions are needed when using a 10% ethanol blend. Such widespread international experience indicates that the viability and functionality of petrohol will be much the same as of the corresponding petrol with which the ethanol is blended.

The web site (<u>http://www.greenfuels.org/ethaques.html</u>) of the Canadian Renewable Fuels Association answers many questions related to the viability and functionality of ethanol in the form of questions and answers. These are reproduced here.

### 14.4.1 Safety and handling

#### Is it safe to handle fuel ethanol blends?

The WHMIS Material Safety Data Sheet (MSDS) reveals that the properties of ethanol blends are substantially the same as conventional gasoline blends. Occupational health and safety risks presented

by the use of ethanol gasoline do not appear to be any different than those posed by conventional gasoline blends.

Do ethanol blends need special handling or storage?

Only in special circumstances. The gasoline marketer should pump any accumulated water from the storage tank, and add a final filter to the dispensing hose. It is wise also to check seasonally used small engines such as chainsaws and outboard motors (which are more susceptible to water contamination) for the presence of water, and drain the tank if necessary.

#### 14.4.2 Warranty

What is the effect of using ethanol-blended fuels on the manufacturer's warranty of my vehicle? When the use of ethanol began in 1979, most automobile manufacturers did not even address alcohol fuels. As soon as each manufacturer tested their vehicles, they approved the use of a 10% ethanol blend. Today, all manufacturers approve the use of 10% ethanol blends, and some even recommend it for environmental reasons.

#### 14.4.3 Functionality

Is it necessary to make changes to my vehicle in order to use ethanol-blended fuels? All cars built since the 1970s are fully compatible with up to 10% ethanol in the mixture.

#### Will ethanol-blended fuels work in fuel-injected engines?

Yes. It may be necessary to change the filter more frequently. Ethanol helps to clean out the fuelinjection system, and may aid in the maintenance of a cleaner engine. Since 1985, all ethanol blends and nearly all non-ethanol gasolines have contained detergent additives that are designed to prevent injector deposits. These detergents have been very effective in addressing this issue.

#### Does ethanol in the fuel work as an effective gas line anti-freeze?

Gas line anti-freeze contains alcohol-usually methanol, ethanol, or isopropyl, which can be used up to a 0.3% level in a car's fuel tank. All alcohols have the ability to absorb water, and therefore condensation in the fuel system is absorbed and does not have the opportunity to collect and freeze. If an ethanol blend contains 10% ethanol, it is able to absorb more water than a small bottle of isopropyl, and eliminates the need and expense of adding a gas line anti-freeze.

#### Will ethanol burn valves?

Ethanol will not burn engine valves. In fact, ethanol burns cooler than gasoline. Ethanol high-powered racing engines use pure alcohol for that reason.

#### Will using ethanol-blended fuels plug the fuel filters in my vehicle?

Ethanol can loosen contaminants and residues that have been deposited by previous gasoline fills. These can collect in the fuel filter. This problem has happened occasionally in older cars, and can easily be corrected by changing fuel filters. Symptoms of a plugged fuel filter will be hesitation, missing, and a loss of power. Once your car's fuel system is clean, you will notice improved performance.

#### Can I mix fuels?

Yes. All gasolines in Canada (including low-level ethanol blends) must meet the specifications of the Canadian General Standards Board (CGSB). They are all interchangeable.

#### Operational range

What is the effect of using ethanol-blended fuels on fuel economy?

Changes in fuel economy are minimal. While a 10% ethanol blend contains about 97% of the energy of 'pure' gasoline, this is compensated by the fact that the combustion efficiency of the ethanolblended fuel is increased. The net result is that most consumers do not detect a difference in their fuel economy, although many people using ethanol-blended fuels have said that their fuel economy has improved.

The US National Science and Technology Council (1997) conducted a comprehensive examination of oxygenated fuels and determined that "with regard to fuel economy, the theoretical change in fuel economy as a result of the addition of oxygenates to gasoline is in the range of a 2% to 3% reduction in fuel economy."

## 14.5 Health

### 14.5.1 Production and transport

Anhydrous ethanol can be used as an additive in petrol. The upstream emissions associated with anhydrous ethanol and with premium unleaded petrol have been dealt with in separate chapters. This chapter will therefore not repeat the upstream production and processing information.

#### Particulate matter

See anhydrous ethanol and PULP sections.

The LCA estimates for E10PULP urban precombustion (car) PM10 emissions are:

- Wheat: 12 mg/km
- Wheat WS: 16 mg/km
- Wheat starch waste: 12 mg/km
- Molasses (alternative allocation): 9 mg/km
- Molasses: 9 mg/km
- Woodwaste: 13 mg/km
- Ethylene: 9 mg/km

#### Air toxics

See anhydrous ethanol and PULP sections.

The LCA estimates for E10PULP urban precombustion (car) HC emissions are:

- Wheat: 0.060 g/km
- Wheat WS: 0.197 g/km
- Wheat starch waste: 0.059 g/km
- Molasses (alternative allocation): 0.06 g/km
- Molasses: 0.060 g/km
- Woodwaste: 0.140 g/km
- Ethylene: 0.132 g/km

#### 14.5.2 Use

Table 14.1 gives the tailpipe emissions (in kg) over the life of a typical vehicle using petrol and using oxygenated petrol (Maclean, 1998; 2000)

#### Particulate matter

The estimate for PULP and E10PULP combustion (car) PM10 emissions is 80 mg/km.

#### Air toxics

Table 14.10 gives the exhaust emissions of air toxics given by MacLean (1988) that may also be found in the supporting documentation of MacLean and Lave (2000). The air toxics emissions are given in terms of mass emitted per vehicle lifetime, but are also given in terms of weighted emissions in terms of sulfuric acid equivalents. In both cases, petrohol produces a marked decline in the emissions of air toxics. For comparison, the weighted emissions for diesel exhaust are estimated to range from 37,000 to 80,000 grams sulfuric acid equivalent per lifetime.

<b>Table 14.10</b>
Lifetime exhaust emissions (g) of air toxics from petrol and oxygenated petrol, along with CMU-ET <sup>1</sup> weighted
toxic emissions (grams sulfuric acid equivalent)

	Benzene	1,3-butadiene	Form- aldehyde	Acet- aldehyde	Aggregate toxics
Petrol	1820	210	350	126	2506
CMU-ET weighted	1138	48	389	0.4	1575
Oxygenated petrol	840	126	336	84	1386
CMU-ET weighted	525	29	373	0.2	927

Motor vehicle emissions data indicates that the use of ethanol results in substantial reductions in air toxics emissions. According to the USEPA (1993) substantial reduction in benzene, 1,3 butadiene, refuelling vapours and particulate matter occur, while formaldehyde would be emitted at levels similar to gasoline vehicles. They claim that acetaldehyde emissions may increase substantially, though Table 14.10 does not support this contention.

Oxygenated fuels perform better than conventional fuels in terms of lower emissions of air toxics. Armstrong (2000) reviews the health effects of ethanol vapours coming from ethanol blended petrol and finds no evidence of any health effects. The Californian Office of Environmental Health Hazard Assessment (1999) found similar results. The main thrust of this latter report was to compare ethanol in relation to MTBE as a fuel oxygenate. They concluded that "the direct effects of ethanol (if any public exposure were to occur) would be substantially less severe than the effects of MTBE."

### 14.5.3 Summary

E10PULP tailpipe particulate and HC emissions are lower than PULP emissions irrespective of the feedstock. E10PULP tailpipe emissions of benzene, 1,3 butadiene, are substantially less than petrol vehicles, while formaldehyde emissions are similar. There is contradictory information about the emissions of acetaldehyde tailpipe emissions with some studies showing and increase while other show a decrease compared with petrol. More research is required to clarify this issue.

## 14.6 OHS Issues

Ethanol in solution is hazardous according to Worksafe Australia, with high flammability, moderate toxicity, and is a moderate irritant. The flash point of the fuel emulsion becomes that of alcohol when the alcohol content exceeds 5% of the volume.

Ethanol fuels increase permeation of elastomers that have been used in automotive applications (eg: rubber hoses, plastic fuels tanks). Research is required to quantify the permeation impacts of ethanol. (Harold Haskew & Associates, 2001).

The OHS issues in the lifecycle of ethanol are covered by a range of State and Commonwealth occupational health and safety provisions. While there will be different OHS issues involved in the production process associated with ethanol based fuels compared with LSD, no OHS issues unique to the production and distribution of ethanol have been identified.

## 14.7 Vapour Pressure Issues

There is contradictory information about evaporative emissions from ethanol added fuels. Some studies indicate that the use of ethanol results in substantial reductions in refuelling vapours. Others state that to contain evaporative emissions from vehicles using alcohol fuel, measures may need to be implemented to control fuel vapour pressure, and control evaporative emissions from diesel fuel vehicles.

<sup>&</sup>lt;sup>1</sup> Carnegie Mellon University Equivalent Toxicity

The higher vapour pressure of ethanol/gasoline blends compared to neat gasoline is a concern in their use. The effects of ethanol addition to PULP do not appear to have been specifically studied, but other studies with ethanol/gasoline blends provide useful guides to the magnitude of the effects.

Effects of ethanol addition on Reid vapour pressure have been summarised in a National Research Council report (NRC, 1999) produced for the USEPA, as follows:

Studies indicate that fuel RVP increases as ethanol is initially added. The greatest RVP increase occurs with an ethanol content of about 5 vol % and is about 1 psi (~ 6.9 kPa). For ethanol concentrations greater than 5 vol %, the RVP slowly decreases

There are comprehensive studies of ethanol blends (CARB, 1998), which show that adding 10% ethanol to gasoline, resulting in an increase of RVP from 48 kPa to 55 kPa, increases the evaporative hydrocarbon emissions by an estimated 40%. The impacts of these increases on ozone-forming potential are discussed below.

Evaporative emission system technologies designed to reduce evaporative emissions from vehicles using gasoline and gasoline blended with 10 percent ethanol have also been examined (Louis Browning of ARCADIS Geraghty & Miller, reported in CRC (1999)). When using ethanol in gasoline, evaporative emissions are almost twice as high as when using gasoline without ethanol due to much higher permeation rates. This study also showed that by using low permeation materials, evaporative emissions could be substantially reduced from both fuels.

### Effects of ethanol blends on ozone forming potential

CARB (1998) report overall increases of 40% in evaporative emissions in a 10% ethanol/gasoline blend using multi-day test procedures. As a consequence of this increase in evaporative emissions CARB estimate that use of a 10% ethanol blend would result in an overall increase of about 17% in ozone forming potential for the ethanol blend compared to a fully complying (RVP less than 7 psi or 48 kPa) gasoline. On this basis they have recommended against the use of 10% ethanol blends.

Similarly the NRC (1999) concludes that the use of an ethanol-containing fuel with a 1 psi higher RVP is likely to produce a negative air quality impact.

By contrast, the USEPA have recently (USEPA, 2000) proposed an adjustment to the reformulated gasoline VOC standard to encourage the use of ethanol blends given the beneficial impacts of ethanol on CO emissions in particular. It should be noted, however, that this increased use is associated with strict controls on the volatility of the gasoline with which the ethanol is blended, and hence requires changes to refinery practice and co-operation between refiners and ethanol manufacturers.

In any case evaporative emissions are a critical issue in the use of ethanol blends, and need to be evaluated with direct reference to Australian conditions, including emissions performance of the Australian fleet and current refinery practice.

## 14.8 Environmental Issues

Environmental and ESD issues associated with ethanol are discussed in Chapter 6.

Ethanol is not persistent in the environment. Virtually any environment supporting bacterial populations is believed to be capable of biodegrading ethanol. Atmospheric degradation is also expected to be rapid.

The tailpipe greenhouse gas emissions from petrohol (from renewable sources) are lower than those of petrol because of the use of a renewable fuel in the blend, but this advantage is offset by reduced fuel economy. On a life-cycle basis the source of the ethanol is crucial in determining whether it is, or is not, climate friendly. Only petrohol made from wood waste has lower exbodied greenhouse gas emissions than premium unleaded petrol. Provided that ethylene is not used as the feedstock, then the exbodied emissions of air toxics are lower from petrohol than from petrol. The increased evaporative emissions from petrohol indicate the possibility of increased emissions of ozone pre-cursors.

## 14.9 Expected Future Emissions

Arcoumanis (2000) developed a model that examines a given alternative fuel relative to the reference diesel engine (Euro2) in terms of a specific regulated pollutant. A value of 1 implies identical performance to the low sulfur diesel/Euro2 combination. A value greater than 1 implies inferior performance, whereas a value less than 1 indicates superior performance.

Table 14.11 lists the estimated emissions factors for oxygenated petrol. The columns in bold represent the standards relative to the Euro2 standard. The adjacent column gives the expected performance of petrohol. The estimates of Arcoumanis (2000) indicate that petrohol can be expected to meet all future Australian Design Rules for all pollutants.

Technology	СО	СО	THC	THC	NOx	NOx	CO <sub>2</sub>	LCA CO <sub>2</sub>
Euro2	1.0	0.9	1.0	0.9	1.0	1.0	1.0	0.9
Euro3	1.05	0.6	0.59	0.5	0.6	0.6	1.0	0.85
Euro4	0.45	0.3	0.29	0.3	0.32	0.3	1.0	0.8

 Table 14.11

 Estimated emission factors for petrohol under future technologies (PM is unregulated)

## 14.10 Summary

#### 14.10.1 Advantages

- As a renewable fuel it should produce less fossil CO<sub>2</sub> than conventional fuels, but the decrease in energy content of the ethanol means that more fuel has to be burnt. This increased fuel consumption, combined with the greater processing energy of the ethanol, means that exbodied greenhouse gases generally increase (albeit very slightly), the only exception being the case of ethanol made from wood waste.
- Tailpipe emissions of CO and HC appear to be lower on average.
- Air toxic levels decrease as the ethanol concentration increases.

### 14.10.2 Disadvantages

- There are high hydrocarbon evaporative emissions that require adjustment of the vapour pressure of the base petrol to which ethanol is added.
- There are problems of phase stability in the petrol mixture if water is present.

## 15. Hydrogen

## 15.1 Introduction

Cars, trucks and buses can burn pure hydrogen in an internal combustion engine, or use it in a fuel cell to drive an electric motor. The fuel cell option is generally considered preferable for the long term, because although it requires more changes to existing vehicle design, it allows for higher efficiency and hence a longer range on the same amount of fuel. This section will thus consider the upstream emissions associated with producing hydrogen of the purity required for fuel cells.

Hydrogen is the chemical element with the smallest molecular mass. Hydrogen is not found as a free element on earth. Because of its high reactivity, it is always bonded to other molecules. As a result hydrogen for automotive use has to be man made.

The hydrogen energy content per unit mass is high. Compared to petrol for example, it is three times as high. On a volume basis, the energy content of hydrogen is relatively small. Both properties can be found in Table 15.1

Physical properties of hydrogen				
	Lower calorific value	Lower calorific value		
	Mass basis (MJ/kg)	Volume basis (MJ/L)		
Hydrogen	119.9	8.9*		
Petrol	41.2	31.0		
Diesel oil	42.9	36.1		

	Table 15	.1
Physical	properties	of hydrogen

\* Liquid hydrogen at -253°C

Gaseous hydrogen is very light (90 grams per cubic metre [g/Nm<sup>-3</sup>]) at ambient conditions and rises in air. Burning hydrogen rises in air as well. This is in contrast to burning petrol, for example, which stays at ground level.

All mixtures of hydrogen and air with a volumetric hydrogen content between 4% and 75% are inflammable. Compared to mixtures of petrol and air, this is a wide range. Hydrogen can burn in mixtures with air from very lean (excessive air) to rich (excessive fuel). The ignition energy is very low, so the combustion process can be initiated easily. The flame propagation speed of burning hydrogen is high. In an experimental spark ignited engine with direct gaseous hydrogen injection, flame speeds up to 40 m/s have been measured, at various engine speeds. The flame speeds obtained with internal mixture formation were significantly higher than those with external mixture formation (Meier et al., 1994). These high flame speeds necessitate engine adaptation.

The important safety aspects for handling hydrogen are discussed in the next section.

## 15.2 Full Fuel-Cycle Analysis

### 15.2.1 Tailpipe

We consider only fuel-cell powered vehicles. Such hydrogen vehicles have virtually no emissions, even of NOx, because fuel cells operate at temperatures that are so much lower than internal combustion engines that NOx is not formed from the nitrogen and oxygen in the air. Theoretically, a hydrogen-fuelled fuel cell vehicle emits only water vapour.

DaimlerChrysler in Europe established a subsidiary, EvoBus GmbH to fit a limited number of vehicles with the latest generation of fuel cells and use them in buses being used for public transport.



#### Energy consumption in urban drive cycle (All figures\* in MJ per 100 bus-km)

Figure 15.1 Energy consumption in urban drive cycle for buses (Graham, 2000)

During March 2000, a hydrogen fuel cell bus (NeBus) was exhibited in Perth and Melbourne. Figure 15.1 reproduces the energy consumption for the NeBus along with some comparative energy consumption (Graham, 2000). During operation, though energy is being used, this study will assume that the tailpipe emissions are purely water vapour.

Following on from these demonstrations, Perth will operate three fuel cell buses by late 2002. BP will invest more than \$1 million in Western Australia to establish a hydrogen manufacture and supply chain. A small purification unit at the BP Kwinana refinery will produce the requisite high quality hydrogen for the buses.

### 15.2.2 Upstream

#### Production of Hydrogen

Hydrogen can be produced through steam reforming of natural gas, cleanup of industrial byproduct gases, or electrolysis of water. This section will consider only steam reforming of natural gas.

The main commercial processes specific for the manufacture of hydrogen are steam reforming of natural gas or other hydrocarbons, coal gasification, and water electrolysis. Relatively small quantities of hydrogen are produced by steam reforming of naphtha and partial oxidation of natural gas. Oil refineries also recover hydrogen from some of their process units, most commonly from reformers.

Overall, the main chemical reactions used in these processes are as follows :

Steam reforming	$CH_4 + 2H_2O = CO_2 + 4H_2$
Naphtha reforming	$C_nH_{2n} + 2n H_2O = nCO_2 + 3nH_2$
Partial oxidation	$CH_4 + O_2 = CO_2 + 2H_2$
Coal gasification	$C+2H_2O=CO_2+2H_2$
Water electrolysis	$2H_2O = 2H_2 + O_2$

Worldwide, hydrogen as a raw material for the chemical industry is produced predominantly from natural gas (about 70%), with other petroleum feedstocks, coal, and water electrolysis accounting for the remainder. Process steps involved in natural gas reforming are illustrated in Figure 15.2.



Figure 15.2 Diagram of the process for hydrogen production from natural gas incorporating PSA purification (from Spath and Mann, 2001).

In steam reforming, hydrocarbons contained in natural gas (mostly methane) are converted to synthesis gas (mixture of  $H_2$ , CO, CO<sub>2</sub>) by reaction with steam over a catalyst in a primary reformer furnace. This process is usually operated at 800–870°C and 2.2–2.9 MPa, using a Ni-based catalyst.

Because hydrocarbon feeds for steam reforming should be free of sulfur, feed desulfurisation is required ahead of the steam reformer. The desulfurisation step usually consists of passing the sulfur-containing natural gas feed at about 300–400°C over a CoMo catalyst in the presence of 2–5% H<sub>2</sub> to convert organic sulfur compounds to H<sub>2</sub>S.

This is then followed by adsorption of  $H_2S$  over a ZnO guard bed to reduce the sulfur level to less than 0.1 ppmwt which is the level that the reforming catalyst can tolerate.

The gas and process steam mixture is then introduced into the primary reformer. This reformer is a direct natural gas fired chamber containing rows of nickel-alloy tubes filled with the catalyst pellets. The gas leaving the primary reformer is about 76.7% H<sub>2</sub>, 12% CO, 10% CO<sub>2</sub>, and 1.3% CH<sub>4</sub>. Up to 95% conversion of CH<sub>4</sub> can be achieved in the primary reformer.

In the next step, the CO is converted to  $CO_2$  and hydrogen by the water gas shift (WGS) reaction step:

*Water gas shift reaction*  $CO + H_2O = H_2 + CO_2$ 

The combination of this reaction with those occurring in the reformer gives the overall reaction stoichiometry presented earlier.

This reaction is first conducted on a chromium-promoted iron oxide catalyst in the high temperature shift (HTS) reactor at about 370°C at the inlet. Converted gases are cooled outside of the HTS and are sent to the low temperature shift (LTS) converter at about 200–215°C to complete the water gas shift reaction. The LTS catalyst is a copper–zinc oxide catalyst supported on alumina. The product gas after WGS contains about 77% H<sub>2</sub>, 18% CO<sub>2</sub>, 0.30% CO, and 4.7% CH<sub>4</sub>.

The gas is then cooled and  $CO_2$  scrubbed out by hot potassium carbonate or other processes such as MEA, methyldiethanolamine (MDEA) or other similar technology. The scrubbed gas contains about 98.2% H<sub>2</sub>, 0.3% CO, 0.01% CO<sub>2</sub>, and 1.5% CH<sub>4</sub>.

Remaining carbon oxides are converted to methane by passing the gases reheated to about  $315^{\circ}$ C over a methanation catalyst, usually containing about 35% Ni supported on refractory material. Over this catalyst, CO and CO<sub>2</sub> are hydrogenated to CH<sub>4</sub>. A typical hydrogen product is 98% H<sub>2</sub> and 2% CH<sub>4</sub>.

As an alternative to scrubbing out the CO<sub>2</sub> followed by methanation, the shifted gas can be purified by pressure-swing adsorption (PSA) when high purity hydrogen is desirable. PSA is used in nearly all cases where high purity (>99%) hydrogen is needed. Pressure-swing adsorption utilizes the fact that larger molecules such as CO, CO<sub>2</sub> and CH<sub>4</sub> can be separated from the smaller hydrogen gas molecule by selective adsorption on high surface area materials such as molecular sieves. Hydrogen has a very weak affinity for adsorption. The process of pressure-swing adsorption is capable of producing very pure (>99.9%) hydrogen at recoveries of 70–90%, depending on the number of adsorption stages.

In applications where an ultra-pure hydrogen is required, for example in proton exchange membrane (PEM) fuel cells used in vehicles, final purification may be achieved by using palladium membranes. This process utilises the fact that hydrogen diffuses through palladium metal at high temperatures (about  $600^{\circ}$ C).

Upstream emissions in hydrogen production arise from natural gas recovery and purification, heat requirements of the steam reformer and energy demand of all process units. Further emissions arise from the chemistry of the process as illustrated by chemical equations. In a

sense, hydrogen production can be seen as "decarbonisation" of natural gas, with all carbon converted into carbon dioxide.

Spath and Mann (2001) recently revised their earlier calculations in relation to the life cycle assessment of hydrogen production from natural gas steam reforming. Their updated estimates have been used in the quantitative parts of the life-cycle calculations.

Use



The fuel cell works by bringing about a controlled reaction between hydrogen and oxygen. The hydrogen passes through the fuel cells electrolyte in the form of positively charged ions (protons). It then combines with oxygen in the air to form water leaving behind negatively charged electrons. As a negative charge accumulates on one side of the electrolyte and a positive charge on the other, an electric voltage is generated, which is then converted and drives the vehicle via the electric wheelinub motors.



Figure 15.3 depicts the details of a PEM fuel cell. Because fuel cell vehicles are in a very early state of development, it is difficult to predict what the energy consumption of this type of vehicles will be in a mature situation. However, some indications can be given. From previous research it was found that the energy efficiency of a fuel cell vehicle without regenerative breaking is 42 - 48%, from vehicle tank to wheels. For fuel cell vehicles with regenerative braking, this figure is 46-55% (van Walwijk et al., 1996). These figures are supported by a recent publication of Mercedes Benz. For a concept fuel cell van (rolling laboratory type), a part load efficiency of 40% is reported (van Walwijk et al., 1996).

## 15.3 Results

#### 15.3.1 Emissions per unit energy

Table 15.2           Exbodied emissions (per MJ) for hydrogen (from natural gas)					
Full Lifecycle	Units	LS diesel	Hydrogen (from natural gas)		
Greenhouse	kg CO <sub>2</sub>	0.0834	0.0832		
HC total	g HC	0.138	0.033		
HC urban	g HC	0.110	0.001		
NOx total	g NOx	1.016	0.053		
NOx urban	g NOx	0.986	0.035		
CO total	g CO	0.249	0.012		
CO urban	g CO	0.240	0.005		
PM10 total	mg PM10	39.7	0.7		
PM10 urban	mg PM10	39.3	0.4		
Energy embodied	MJ LHV	1.16	1.41		

 Table15.3

 Precombustion emissions (per MJ) for hydrogen (from natural gas)

			Hydrogen
Precombustion	Units	LS diesel	(from natural gas)
Greenhouse	kg CO <sub>2</sub>	0.0167	0.0832
HC total	g HC	0.0548	0.0332
HC urban	g HC	0.126	0.001
NOx total	g NOx	0.073	0.053
NOx urban	g NOx	0.043	0.035
CO total	g CO	0.019	0.012
CO urban	g CO	0.010	0.005
PM10 total	mg PM10	4.4	0.676
PM10 urban	mg PM10	4	0.435
Energy embodied	MJ LHV	1.16	1.41

			Hydrogen
		LS diesel	(from natural gas)
Greenhouse kg	Precombustion	0.0167	0.0832
Greenhouse kg	Combustion	0.0667	0.0000
HC total g	Precombustion	0.0548	0.0332
HC total g	Combustion	0.0835	0.0000
HC urban g	Precombustion	0.1262	0.0011
HC urban g	Combustion	0.0835	0.0000
NOx total g	Precombustion	0.0726	0.0527
NOx total g	Combustion	0.944	0.000
NOx urban g	Precombustion	0.043	0.035
NOx urban g	Combustion	0.944	0.000
CO total g	Precombustion	0.0191	0.0121
CO total g	Combustion	0.2301	0.0000
CO urban g	Precombustion	0.0096	0.0046
CO urban g	Combustion	0.2301	0.0000
PM10 total mg	Precombustion	4.40	0.68
PM10 total mg	Combustion	35.26	0.00
PM10 urban mg	Precombustion	4.00	0.44
PM10 urban mg	Combustion	35.26	0.00
Energy embodied MJ	Precombustion	1.16	1.41
Energy embodied MJ	Combustion	0	0

 Table 15.4

 Summary of exbodied emissions from hydrogen

#### 15.3.2 Emissions per unit distance

Full Lifecycle	Units	LS diesel	Hydrogen (from natural gas)
Greenhouse	kg CO <sub>2</sub>	0.9250	0.8970
HC total	g HC	1.509	0.358
HC urban	g HC	1.192	0.012
NOx total	g NOx	11.250	0.568
NOx urban	g NOx	10.638	0.372
CO total	g CO	2.723	0.131
CO urban	g CO	2.612	0.049
PM10 total	mg PM10	438.4	7.3
PM10 urban	mg PM10	423.1	4.7
Energy embodied	MJ LHV	12.7	15.2

 Table 15.5

 Exbodied emissions (per km) for hydrogen (from natural gas)

			Undrogen
Precombustion	Units	LS diesel	(from natural gas)
Greenhouse	kg CO <sub>2</sub>	0.2060	0.8970
HC total	g HC	0.609	0.358
HC urban	g HC	0.292	0.012
NOx total	g NOx	1.080	0.568
NOx urban	g NOx	0.468	0.372
CO total	g CO	0.243	0.131
CO urban	g CO	0.132	0.049
PM10 total	mg PM10	58.4	7.28
PM10 urban	mg PM10	43.1	4.68
Energy embodied	MJ LHV	12.7	15.2

 Table 15.6

 Precombustion emissions (per km) for hydrogen (from natural gas)

 Table 15.7

 Exbodied emissions summary (per km) for hydrogen (from natural gas)

		LS diesel	Hydrogen (from natural gas)
Greenhouse kg	Precombustion	0.2060	0.8970
Greenhouse kg	Combustion	0.7190	0.0000
HC total g	Precombustion	0.6090	0.3580
HC total g	Combustion	0.9000	0.0000
HC urban g	Precombustion	0.2920	0.0120
HC urban g	Combustion	0.9000	0.0000
NOx total g	Precombustion	1.0800	0.5680
NOx total g	Combustion	10.170	0.000
NOx urban g	Precombustion	0.468	0.372
NOx urban g	Combustion	10.170	0.000
CO total g	Precombustion	0.2430	0.1310
CO total g	Combustion	2.4800	0.0000
CO urban g	Precombustion	0.1320	0.0492
CO urban g	Combustion	2.4800	0.0000
PM10 total mg	Precombustion	58.40	7.28
PM10 total mg	Combustion	380.00	0.00
PM10 urban mg	Precombustion	43.10	4.68
PM10 urban mg	Combustion	380.00	0.00
Energy embodied MJ	Precombustion	12.70	15.20
Energy embodied MJ	Combustion	0	0

There is insufficient information with which to estimate quantitatively the uncertainties associated with the use of hydrogen as a fuel.

## 15.4 Viability and Functionality

Important advantages of fuel cells are: high energy efficiency, because the efficiency is not limited to the maximum efficiency of thermal energy processes; low emissions during operation, though manufacturing of fuel cells may cause emissions; and low noise production.

However, fuel cells have some disadvantages as well. Compared to internal combustion engines, the disadvantages are: fuel cells are very expensive; and fuel cells are large and heavy per kW output. Most research concentrates on reducing these disadvantages.

Three different methods for on-board hydrogen storage have been considered (van Walwijk et al., 1996):

- high pressure hydrogen gas
- hydride, where hydrogen is chemically bound to a metallic material
- cryogenic storage of liquid hydrogen, at low temperature.

The storage method used for the NeBus is shown in Figure 15.4.



Figure 15.4 Storage method for the NeBus hydrogen bus

#### 15.4.1 Safety

Safety is an important issue regarding hydrogen production, transport and use in a vehicle (refuelling, on-board storage and in case of collisions). In this section, safety aspects of hydrogen when used as fuel for road vehicles are discussed. First, the circumstances in which hydrogen can be dangerous and the reasons for this, are discussed.

Hydrogen rises when it is released into the open air. Its safety is then similar to that of conventional fuels. However, in closed rooms, hydrogen is more dangerous than conventional fuels. Hydrogen can burn in mixtures with air from very lean - with excess air - to very rich.

The flame propagation speed is very high, which gives the combustion an explosive character. A spark from a light switch can start the combustion process for example. A (local) pressure peak can also ignite hydrogen-air mixtures. These pressure peaks are not found in the open air but may occur in closed rooms at locations where different pressure waves interfere.

Two notorious accidents contributed to the general concern regarding the safety of hydrogen. In 1937, the 'Hindenburg' airship burnt down in a few seconds, and in 1990 a Space Shuttle exploded just after take-off. Both had hydrogen on-board. At the accident with the 'Hindenburg' relatively few spectators were hurt because the burning hydrogen rose in the air. Because of the high flame propagation speed, an accidental hydrogen fire never lasts long.

Refuelling of hydrogen vehicles is discussed later. To avoid explosions, evaporating hydrogen is extracted during the refuelling process. For example, BMW has developed a fully automatic refuelling system which may be safely used by anyone. For on-board storage of hydrogen, some hydrogen has to be vented when a hydrogen vehicle is not used over a longer period of time, because the fuel tank cannot be 100% isolated. A safety valve in the vehicle tank prevents excessive tank pressures. Sensors inside the vehicle can detect hydrogen and the vehicle windows can be opened automatically if so required. Evaporative hydrogen losses will also occur when the vehicle is parked in a garage. To avoid ignitable mixtures of hydrogen in air, four different measures can be taken:

- Hydrogen can be exhausted by a spark free venting system
- A small fuel cell can be mounted in the vehicle. Evaporating hydrogen can then be used in this fuel cell to generate electricity, which can be stored in the vehicle batteries to be used later. This type of fuel cell has not been developed yet.
- Evaporated hydrogen can be stored in a metallic hydride, in which it is chemically bound to a metallic material. More information on hydride storage can be found in section 12.5. It has to be kept in mind that heat is generated when hydrogen is being stored in a metallic hydride.
- When the hydrogen vehicle is equipped with a fuel cell instead of a combustion engine, the fuel cell can be used to convert the evaporated hydrogen automatically into electrical energy which may be stored in the batteries.

The safety of hydrogen fuel systems is important during vehicle collisions. There is substantial testing designed to ensure leakproof hydride tanks, and to place the vehicle tank inside the safety cage of vehicles so as to reduce the risk of damage to the tank during a collision.

Van Walwijk et al. (1996) report that accidents with hydrogen vehicles are no worse than those with LPG or natural gas. However, they also point out that no results from collision tests with hydrogen vehicles could be found in the literature.

### 15.4.2 Warranty

Hydrogen powered vehicles are supplied by the engine manufacturer.

### 15.4.3 Functionality of the fuel under the full range of Australian conditions

There is no reason to expect any lack of functionality of hydrogen under Australian conditions.

#### 15.4.4 Fuel energy density and vehicle operational range

The driving ranges of comparable diesel and hydrogen vehicles are different, when the mass of fuel tank and fuel are the same. It is smaller for hydrogen vehicles. The diesel vehicle can

drive twice the distance. The specifications for the DaimlerChrysler NeBus specify 7 roofmounted pressure resistant cylinders (weighing 1,900 kg) to give a range of 250 km, with a passenger capacity of 34 seated and 24 standing (58 passengers). These figures are similar in range to earlier generation CNG buses and compare to a typical range of 400 km for an equivalent diesel bus (Cannon and Sun, 2000).

BMW has been working on liquid storage systems. Mass and storage volume are acceptable. A disadvantage is the storage temperature of -253°C for liquid hydrogen, which requires an insulated vehicle tank. In a vehicle, the storage tank is not refrigerated. This results in evaporative losses when the engine is not running. Due to the unavoidable leaking of heat to the storage tank, some hydrogen will evaporate. This gas must be able to escape (or must be used) to avoid excessive pressures and to maintain a low temperature in the vehicle tank. The fact that the energy of the heat is used as evaporation energy helps to maintain a low temperature in the vehicle as well. With appropriate insulation and a tank pressure of 5 bar, it is possible to avoid venting for three or four days. After that period, the evaporative losses continue.

#### 15.4.5 Refuelling requirements

To refill a hydrogen vehicle, an onward (for liquid hydrogen) and a return (for gaseous hydrogen from the vehicle tank) hose are connected to avoid losses of hydrogen during refuelling. BMW has developed a refuelling system in which, after connecting the hoses to the vehicle, the complete system - including the vehicle part - is flushed with helium before the refuelling commences. This is to avoid ignitable mixtures of hydrogen and air. After the system has been flushed, the refuelling of the vehicle may commence.

Most hydrogen vehicles are being refuelled with liquid hydrogen. When refuelling a cold hydrogen tank with liquid hydrogen, approximately 10% of the hydrogen will become gaseous upon entering the tank. For warm vehicles, the percentage can increase up to 25%. These evaporative losses are being exhausted back to the storage tank of the refuelling station. In this way losses of hydrogen can be avoided, including the loss of energy, which is directly related to a loss of hydrogen.

Refuelling time of vehicles with a tank for liquid hydrogen at (-253°C) is between three and ten minutes, when the vehicle tank is cold. However, an empty vehicle tank will slowly warm up to ambient temperature. Refuelling of a tank that is at ambient temperature has to be done relatively slowly. The refuelling time of a hydrogen vehicle can thus rise to ten times the refuelling time of a petrol vehicle.

Refuelling time of hydrogen vehicles with metallic hydride storage tanks is lengthy compared to conventionally fuelled vehicles. Heat is generated when the hydrogen is bound to the metallic hydride. This heat has to be removed during the refuelling process.

## **15.5 Health Issues**

There are no air pollutant or greenhouse gas emissions during operation. The only emissions that may be of concern arise during precombustion.

### 15.5.1 Production and transport

Upstream emissions in hydrogen production arise from natural gas recovery and purification, heat requirements of the steam reformer and energy demand of all process units. Further emissions arise from the chemistry of the process.

### Particulate matter

The LCA estimate for hydrogen urban precombustion (truck) PM10 emissions of 5 mg/km is substantially less than the LSD estimate of 43 mg/km.

#### Air toxics

The LCA estimate for hydrogen urban precombustion (truck) HC emissions of 0.012 g/km is substantially less than the LSD estimate of 0.292 g/km.

The public health effects of air toxics will be mainly associated with combustion emissions in large urban centres. An accompanying disk to this report provides details of air toxic emissions from upstream activities.

#### 15.5.2 Use

We consider only fuel-cell powered vehicles. Such hydrogen vehicles have virtually no emissions, even of NOx, because fuel cells operate at temperatures that are so much lower than internal combustion engines that NOx is not formed from the nitrogen and oxygen in the air. Theoretically, a hydrogen fuelled fuel cell vehicle emits only water vapour.

#### Particulate matter

The LCA estimate for hydrogen combustion (truck) PM10 emissions of 0 mg/km is substantially less than the LSD estimate of 380 mg/km.

#### Air toxics

The LCA estimate for hydrogen combustion (truck) HC emissions of 0 g/km is substantially less than the LSD estimate of 0.900 g/km.

#### 15.5.3 Summary

Hydrogen upstream emissions of both particles and HC are substantially less than LSD. Hydrogen has no tailpipe emissions of particles or air toxics.

## 15.6 OHS Issues

There are a range of OHS issues that must be considered when handling hydrogen.

Safety is an important issue regarding hydrogen production, transport and use in a vehicle (refuelling, on-board storage and in case of collisions). Hydrogen rises when it is released into the open air. Its safety is then similar to that of conventional fuels. However, in closed rooms, hydrogen is more dangerous than conventional fuels. Hydrogen can burn in mixtures with air from very lean - with excess air - to very rich. The flame propagation speed is very high, which gives the combustion an explosive character. A spark from a light switch can start the combustion process for example. A (local) pressure peak can also ignite hydrogen-air mixtures. These pressure peaks are not found in the open air but may occur in closed rooms at locations where different pressure waves interfere.

Safety is also an important issue for on-board storage of hydrogen. It has already been discussed in the section on viability and functionality.

## **15.7 Vapour Pressure Issues**

Most hydrogen vehicles are being refuelled with liquid hydrogen. Evaporative losses during refuelling can be exhausted back to the storage tank of the refuelling station. In this way losses of hydrogen can be avoided, including the loss of energy, which is directly related to a loss of hydrogen.

## 15.8 Environmental Impact and Benefits

Hydrogen is a gaseous fuel with no air pollutant or greenhouse gas emissions. It thus cannot contaminate soil or water. Provided that an environmentally sustainable system can be produced then the use of hydrogen would be highly beneficial. Manins (1992) proposed an innovative scheme based on using tidal power to dissociate hydrogen and thus run a hydrogen economy. The theoretical potential is great for environmental benefits provided the technology can be implemented.

This page left blank intentionally