

3. Fischer-Tropsch Diesel

3.1 Introduction

Fischer-Tropsch (FT) diesel is a synthetic fuel produced from the conversion of natural gas into a diesel fuel. The fuel thus formed is superior to crude oil based diesel in certain ways, principally the high cetane number and the zero sulfur content. It is also known as GTL diesel, where the acronym refers to “gas to liquid” conversion. Gas to liquid fuels conversion is of relevance to Australia, because of the large natural gas deposits in the North West Shelf.

The Fischer-Tropsch process has mainly been used during disruptions to crude oil supply. In Germany, during World War II, petrol and fuels were made from coal by the Fischer-Tropsch process. The only existing industrial scale Fischer-Tropsch refineries are in South Africa, built during the period of economic sanctions against the regime. Figure 3.1 shows Sasol’s synthetic petroleum facility process.

Exxon, Syntroleum (www.syntroleum.com) and Rentech (<http://www.rentechinc.com/>) are major US companies involved in Fischer-Tropsch, Gas-to-Liquids (GTL) conversion. Sasol Chevron (www.sasolchevron.com), which is headquartered in the UK, is considering Australia as the site of a US\$1billion first stage synthetic fuels plant aimed at the diesel market. Shell is also involved with GTL. They and others have patented proprietary processes, for the conversion of synthesis gas made from natural gas, coal, refinery bottoms, industrial off-gas and other hydrocarbon feedstock into clean sulfur-free and aromatics-free alternative fuels, naphtha and waxes. Beside their clean emissions qualities for conventional vehicles, GTL fuels can be sources of energy for fuel cell feedstock. Sulfur-free GTL fuels will not contaminate fuels cells and contain approximately twice the hydrogen than does methanol, another candidate feedstock for fuel cells.

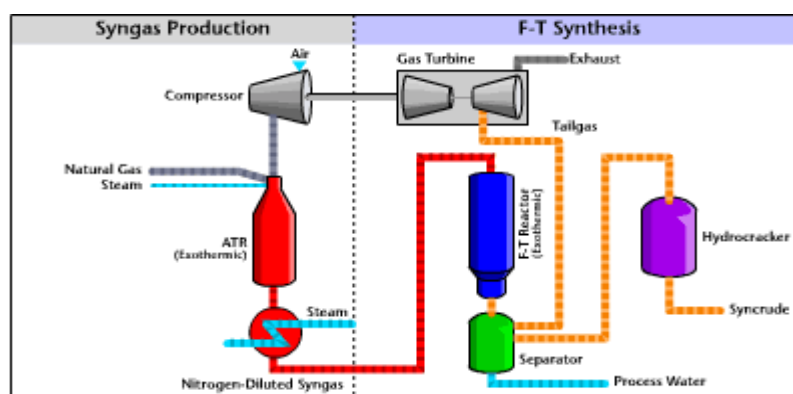


Figure 3.1
Schema for Syntroleum gas to liquid conversion facility
Source: http://www.syntroleum.com/sp1_gs.htm

There are a number of different options available for the implementing the Fischer-Tropsch process. Provided that a Fischer-Tropsch plant uses an oxygen feed then it produces a pure carbon dioxide stream. Such an implementation provides an option to collect and sequester the carbon dioxide.

This study is required to use Australian data where available. At the time of writing SASOL-Chevron was not in a position to submit emissions data that would be applicable to its

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production of FTD and the use of FTD in Australia. It is recommended that a separate study be undertaken when that data becomes available.

There have been some overseas studies that examined the full fuel-cycle (or well to wheel) emissions associated with Fischer-Tropsch diesel. Louis (2001) found that for passenger cars, embodied greenhouse gas emissions associated with FTD were less than those of petrol, but greater than those of conventional diesel. Even though FTD produces slightly lower tailpipe emissions, the upstream emissions of greenhouse gases during the production of FTD are much greater than those emitted during production of diesel. General Motors Corporation (2001) obtained similar, though less dramatic, results. The General Motors study found significantly greater well to wheel energy usage, but only marginally greater embodied greenhouse gas emissions.

3.2 Full Fuel Cycle Analysis

3.2.1 Upstream emissions

Production of Fischer-Tropsch diesel

The Fischer-Tropsch process produces a broad range of hydrocarbons using syngas (hydrogen and carbon monoxide mixture) as a feedstock. The products spectrum can be controlled by the choice of the catalyst, process configuration and operating conditions. Generally speaking, higher process temperatures ($>320^{\circ}\text{C}$) and iron based catalysts favour the production of lighter hydrocarbons suitable for petrol production, while cobalt based catalysts and lower process temperatures ($<250^{\circ}\text{C}$) tend to produce paraffins in the diesel and wax range.

Production of FTdiesel consists of three steps:

- Syngas production
- Hydrocarbons synthesis
- Product upgrading.

The overall process and delivery is outlined in Figure 3.2.

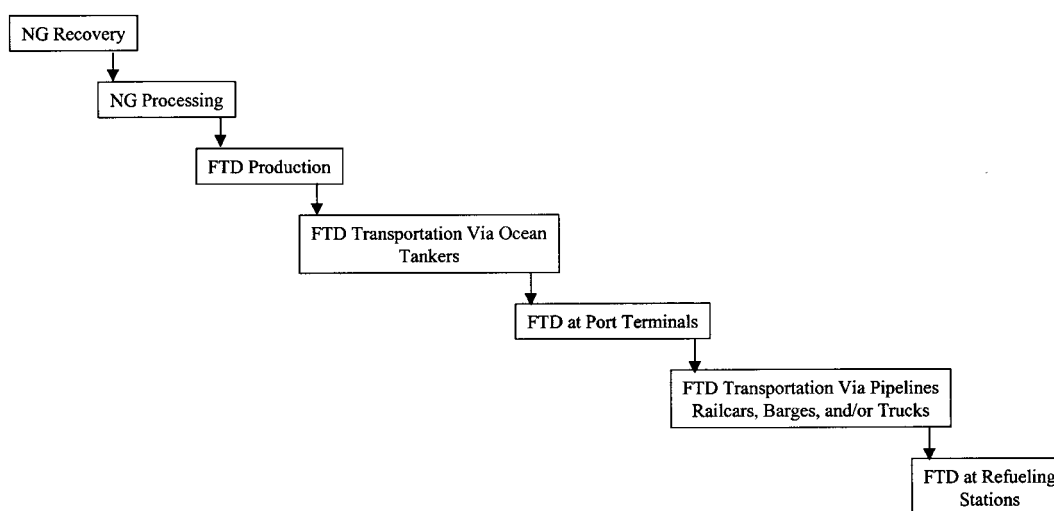


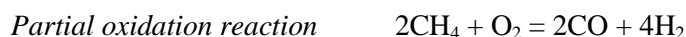
Figure 3.2
Flow diagram of Fischer-Tropsch diesel production and delivery.

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Conversion of natural gas to syngas via steam reforming is described in the chapter on hydrogen production. However, syngas generated by the steam reformer tends to have H₂/CO ratio of about 3 as per reaction



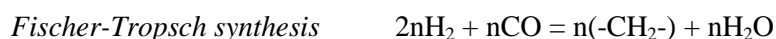
As an ideal H₂/CO ratio for Fischer-Tropsch process is about 2, an alternative syngas production process called partial oxidation is more often employed. It involves passing a mixture of desulfurised natural gas and pure oxygen (or air in the Syntroleum process) over a catalyst containing nickel or platinum group metal at temperatures above 900°C. The reaction proceeds as per equation



And the resulting syngas has H₂/CO ratio of 2. In some cases non-catalytic partial oxidation and/or auto-thermal reforming may be employed. Sasol Chevron uses auto-thermal technology at very low steam/carbon ratios.

Because natural gas feed for partial oxidation and syngas for the Fischer-Tropsch process should be free of sulfur to avoid catalysts poisoning, feed desulfurisation is required ahead of the partial oxidation reactor. 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% H₂ to convert organic sulfur compounds to H₂S. This is then followed by adsorption of H₂S over ZnO guard bed to reduce the sulfur level to less than 0.1 ppm wt which is the level that the oxidation and Fischer-Tropsch catalysts can tolerate.

The Fischer Tropsch synthesis reaction can be symbolically described by this equation:



In the above equation, the expression -CH₂- represents basic building block of the paraffin molecule. Straight chain paraffins are main products of the Fischer-Tropsch process configured for the production of the distillate, with minor quantities of isoparaffins and olefins also present in the products spectrum. Because of the paraffinic character, Fischer-Tropsch diesel has high cetane number and good combustion characteristics.

The reaction is carried out by passing syngas over cobalt based catalyst at temperatures between 180°C and 250°C at pressures between 2Mpa and 4Mpa. The Sasol process uses a slurry reactor where the catalyst is suspended in a hydrocarbon liquid, while the Shell process uses fixed bed reactor packed with catalyst pellets.

The product stream contains a broad range of hydrocarbons that require fractionation and processing. Light fractions, together with unreacted syngas are usually recycled. The naphtha fraction has to be reformed before being blended into petrol. Middle distillate does not require processing and constitutes high quality diesel fuel. Heavier fractions are usually cracked to maximise overall fuel yields.

In Australia the most likely location of the Fischer-Tropsch plant would be in north-western Western Australia. In such case the upstream emissions would arise from natural gas recovery and processing, syngas and Fischer-Tropsch processes, upgrading plant, transportation to the major cities and the distribution to retail outlets.

A whole range of fuels can be produced from natural gas by partial oxidation to synthesis gas (a mixture of H₂ and CO) and the subsequent conversion of this gas.

Shell's SMDS (Shell Middle Distillate synthesis) plant in Bintulu is an example. In this plant naphtha, kerosene and Fischer Tropsch Diesel (FTD) are produced as well as a number of specialized products. With a syngas yield of 95%, syngas conversion of 96%, liquid selectivity of over 90% and a refining and separation loss of 2%, the carbon efficiency of Fischer Tropsch Diesel production is higher than 80% (Seden and Punt, 1999). The energy efficiency of this part of the plant is 63%. Energy use and CO₂ emissions are presented in

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Table 3.1. The quoted carbon and thermal efficiencies in this paragraph refer to the next generation SMDS plants.

The syngas used to produce methanol is mainly produced by steam reforming of natural gas. Methanex gives an efficiency of 67% for auto-thermal reforming based on lower heating value (Methanex, 1999)

Assuming that the liquid fuels are mainly transported by road tanker, the transport efficiency is a function of the lower heating value of the fuel. These transport efficiencies are given in Table 3.1.

As noted in Table 1.1 of Part 1 of this report, the upstream emissions are based on the work of Wang and Huang (1999), with the assumption that the GTL facility will be located at the northwest shelf. The tailpipe emissions are those of Norton et al. (1998).

Table 3.1a
Energy use and GHG emissions output from the GREET model (Louis, 2001, Wang 1999).

	Energy efficiency	Energy use (MJ/MJ)	GHG (g/MJ)
FTD production	63	0.600	25.2
FTD transport	99.5	0.006	0.4

Table 3.1b
Energy use and GHG emissions output from the GREET model (Wang 1999) as applied in the upstream analysis.

	Unit	Value	Formulae/ Source
A Energy efficiency of process	% by energy	66.0%	Wang (1999)
B FTD Energy Content	MJ/kg	41.3	Fuel report
C Total Feedstock	MJ	62.6	B/A
D Energy use in process	MJ	21.29	C-B
E Energy content methane	MJ/kg	50	
F NG input	kg	1.25	C/E
G Carbon in NG	kg	0.939	F*12/16
H Carbon efficiency	% by weight	76%	Wang (1999)
I Carbon to FTD	kg	0.71	G*H
J Carbon Emitted	kg	0.225	G-I
K Emitted Carbon as CO2	kg	0.826	J*44/12
L CO2 emission factor per MJ NG used	kg CO2/MJ	0.0544	NGGI 2000
M NG consumed MJ	MJ	15.19	L/M
N Hydrogen Consumed by balance	MJ	6.10	D-M
O Hydrogen Energy content	MJ/kg	120	
P H Mass	kg	0.051	N/O
Q gas required for H content	kg	0.203	P*16/4
R gas required for energy	kg	0.30	M/E
S Gas used purely as feedstock	kg	0.75	F-(Q+R)

Energy consumption for the production of FTD was taken from Wang (1999), based on an energy efficiency figure for production, of 66%. This figure includes allowance for energy credits granted through co-generation of electricity from excess heat produced in the Fischer-Tropsch process. However the energy used in FTD production comes both from natural gas – (considered here as methane because all other products are assumed to be stripped off) and from hydrogen produced in the gas shift reaction used as part of the FTD process. It is

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important to estimate how much energy comes from each source as the hydrogen combustion does not produce CO₂. An estimate of the split between energy supplied by CH₄ and that supplied by H₂ is given below based on Wang's data claiming a 66% energy efficiency and a 77% carbon efficiency. The net result is 15.2 MJ being sourced from gas and 6.1MJ being from hydrogen produced.

3.2.2 Tailpipe emissions

Table 3.2 provides results for light vehicles, in particular Mercedes A-class vehicles. The diesel version of the A-Class (1.7L) uses 4.9 litre of diesel for 100 km on the same drive-cycle or 1.89 MJ/km. It is assumed that the other compression ignition vehicles (running on Fischer Tropsch Diesel or di-methylether) use the same amount of energy.

Greenhouse gas emissions are calculated from the calorific value of the fuel used and its carbon content. Only the natural gas vehicle emits a significant amount of methane, but even this is only equivalent to 0.6 grams of CO₂ per km. Energy use and greenhouse gas emissions from internal combustion engine vehicles are given in Table 3.2.

Table 3.2.
Energy use by and GHG emissions from internal combustion engine vehicles

ICE vehicle	Energy (MJ/km)	GHG (g/km)
Petrol	2.42	172
Natural gas	2.42	128
Diesel	1.89	131
Fischer Tropsch Diesel	1.89	128
Hydrogen	1.89	0

Source: Louis (2001)

Lom (pers. comm.) provided data on the relative performance of biodiesel and advanced GTL diesel. These data are reproduced in Table 3.3.

Table 3.3
Average results with biodiesel and GTL fuel on standard tests

Test	Euro R49 Biodiesel	Transient GTL
CO	-12%	-40%
HC	-40%	-40%
NOx	+20%	0
PM	+13%	-30%
Smoke	-70%	-50%
Fuel conservation	+15%	+10%
Power	-10%	-8%

Emissions from FTdiesel fuel have been examined by Schaberg et al. (1997), by Norton et al. (1998) and more recently by Durbin et al. (2000) who looked only at light commercial vehicles (pickup trucks). The results from Norton et al. (1998) are given in Table 3.4 for the engine tests and in Table 3.5 for the chassis dynamometer tests. As is evident in Tables 3.2 and 3.5 there are large differences between emissions from light vehicles and heavy trucks when expressed on a per distance basis. Most emissions increase roughly linearly with fuel consumption, though NOx appears to increase exponentially with load.

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Table 3.4
Exhaust emissions from hot-start FTP engine tests in g/bhp-h

	HC	CO	NO _x	PM	CO ₂
Conventional US #2 Diesel	0.346	1.584	5.373	0.120	643.75
California #2 Diesel	0.274	1.091	4.893	0.109	615.85
FT Diesel	0.198	0.968	4.607	0.104	611.49

Table 3.5
Exhaust emissions from the WVU 5-mile cycle in g/mile (Truck 2016)

	HC	CO	NO _x	PM	CO ₂	mpg*	BTU/mile
California #2 Diesel	0.89	4.26	12.8	0.59	1755	5.67	22541
FT Diesel for heavy vehicle (Norton, 1998)	0.50	3.21	11.2	0.48	1634	5.63	21947
FT Diesel for light vehicle (Wang, 1999)	0.05	2.76	0.06	0.03	268	36	3118

* miles per liquid gallon (not corrected for energy content)

The values of Table 3.5 were used in the quantitative calculations.

3.3 Results

The results given in this section compare the use of Fischer-Tropsch diesel and low sulfur diesel in heavy vehicles.

3.3.1 Emissions per unit energy

Table 3.6
Embodied emissions per MJ of FT diesel

Full Lifecycle	Units	LS diesel	FT diesel
Greenhouse	kg CO ₂	0.0858	0.0975
NMHC total	g HC	0.140	0.093
NMHC urban	g HC	0.111	0.050
NO _x total	g NO _x	1.044	0.996
NO _x urban	g NO _x	0.987	0.848
CO total	g CO	0.253	0.225
CO urban	g CO	0.242	0.192
PM10 total	mg PM10	40.7	25.5
PM10 urban	mg PM10	39.3	23.5
Energy Embodied	MJ LHV	1.18	1.78

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Table 3.7
Urban and total upstream emissions per MJ for FT diesel

Units	Units	LS diesel	FT diesel
Greenhouse	kg CO ₂	0.0191	0.0336
NMHC total	g HC	0.0565	0.0443
NMHC urban	g HC	0.027	0.001
NOx total	g NOx	0.100	0.153
NOx urban	g NOx	0.043	0.005
CO total	g CO	0.023	0.035
CO urban	g CO	0.012	0.001
PM10 total	mg PM10	5.42	2.11
PM10 urban	mg PM10	4	0.0763
Energy Embodied	MJ LHV	1.18	1.78

Table 3.8
Urban and total tailpipe emissions per MJ from FT diesel

Combustion	Units	LS diesel	FTdiesel
Greenhouse	kg CO ₂	0.067	0.064
NMHC total	g HC	0.084	0.049
NMHC urban	g HC	0.084	0.049
NOx total	g NOx	0.944	0.843
NOx urban	g NOx	0.944	0.843
CO total	g CO	0.230	0.191
CO urban	g CO	0.230	0.191
PM10 total	mg PM10	35.26	23.43
PM10 urban	mg PM10	35.26	23.43
Energy Embodied	MJ LHV	0	0

Table 3.9
Summary of life cycle emissions per MJ from FT diesel

		LS diesel	FTdiesel
Greenhouse kg	Precombustion	0.0191	0.0336
Greenhouse kg	Combustion	0.0667	0.0639
NMHC total g	Precombustion	0.0565	0.0443
NMHC total g	Combustion	0.0835	0.0491
NMHC urban g	Precombustion	0.0271	0.0009
NMHC urban g	Combustion	0.0835	0.0491
NOx total g	Precombustion	0.1000	0.1530
NOx total g	Combustion	0.944	0.843
NOx urban g	Precombustion	0.043	0.005
NOx urban g	Combustion	0.944	0.843
CO total g	Precombustion	0.0225	0.0346
CO total g	Combustion	0.2301	0.1907
CO urban g	Precombustion	0.0123	0.0010
CO urban g	Combustion	0.2301	0.1907
PM10 total mg	Precombustion	5.42	2.11
PM10 total mg	Combustion	35.26	23.43
PM10 urban mg	Precombustion	4.00	0.08
PM10 urban mg	Combustion	35.26	23.43
Energy Embodied MJ	Precombustion	1.18	1.78

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3.4 Emissions per unit distance travelled

Table 3.10
Embodied emissions per km from FT diesel

Full Lifecycle	Units	LS diesel	FTdiesel
Greenhouse	kg CO ₂	0.9250	0.9926
NMHC total	g HC	1.509	0.940
NMHC urban	g HC	1.192	0.524
NOx total	g NOx	11.250	10.305
NOx urban	g NOx	10.638	8.896
CO total	g CO	2.723	2.333
CO urban	g CO	2.612	2.010
PM10 total	mg PM10	438.4	266.1
PM10 urban	mg PM10	423.1	246.6
Energy Embodied	MJ LHV	12.7	17.10

Table 3.11
Urban and total upstream emissions per km for FT diesel

Precombustion	Units	LS diesel	FT diesel
Greenhouse	kg CO ₂	0.2060	0.3220
NMHC total	g HC	0.609	0.425
NMHC urban	g HC	0.292	0.009
NOx total	g NOx	1.080	1.460
NOx urban	g NOx	0.468	0.051
CO total	g CO	0.243	0.332
CO urban	g CO	0.132	0.009
PM10 total	mg PM10	58.4	20.3
PM10 urban	mg PM10	43.1	0.732
Energy Embodied	MJ LHV	12.7	17.1

Table 3.12
Urban and total tailpipe emissions per km from FT diesel

Combustion	Units	LS diesel	FT diesel
Greenhouse	kg CO ₂	0.719	0.671
NMHC total	g HC	0.900	0.515
NMHC urban	g HC	0.900	0.515
NOx total	g NOx	10.170	8.845
NOx urban	g NOx	10.170	8.845
CO total	g CO	2.480	2.001
CO urban	g CO	2.480	2.001
PM10 total	mg PM10	380.00	245.86
PM10 urban	mg PM10	380.00	245.86
Energy Embodied	MJ LHV	0	0

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Table 3.13
Summary of life cycle emissions per km from FT diesel

		LS diesel	FT diesel
Greenhouse kg	Precombustion	0.2060	0.3220
Greenhouse kg	Combustion	0.7190	0.6706
NMHC total g	Precombustion	0.6090	0.4250
NMHC total g	Combustion	0.9000	0.5153
NMHC urban g	Precombustion	0.2920	0.0089
NMHC urban g	Combustion	0.9000	0.5153
NOx total g	Precombustion	1.0800	1.4600
NOx total g	Combustion	10.170	8.845
NOx urban g	Precombustion	0.468	0.051
NOx urban g	Combustion	10.170	8.845
CO total g	Precombustion	0.2430	0.3320
CO total g	Combustion	2.4800	2.0006
CO urban g	Precombustion	0.1320	0.0094
CO urban g	Combustion	2.4800	2.0006
PM10 total mg	Precombustion	58.40	20.30
PM10 total mg	Combustion	380.00	245.85
PM10 urban mg	Precombustion	43.10	0.73
PM10 urban mg	Combustion	380.00	245.85
Energy Embodied MJ	Precombustion	12.70	17.10

3.4.1 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 3.14.

Table 3.14
Estimated one standard deviation uncertainties (in percent) for Fischer-Tropf diesel emissions

	g/MJ	g/t-km	g/p-km
CO ₂	10	9	11
NMHC	34	50	17
NOx	29	30	27
CO	111	144	78
PM10	45	39	50

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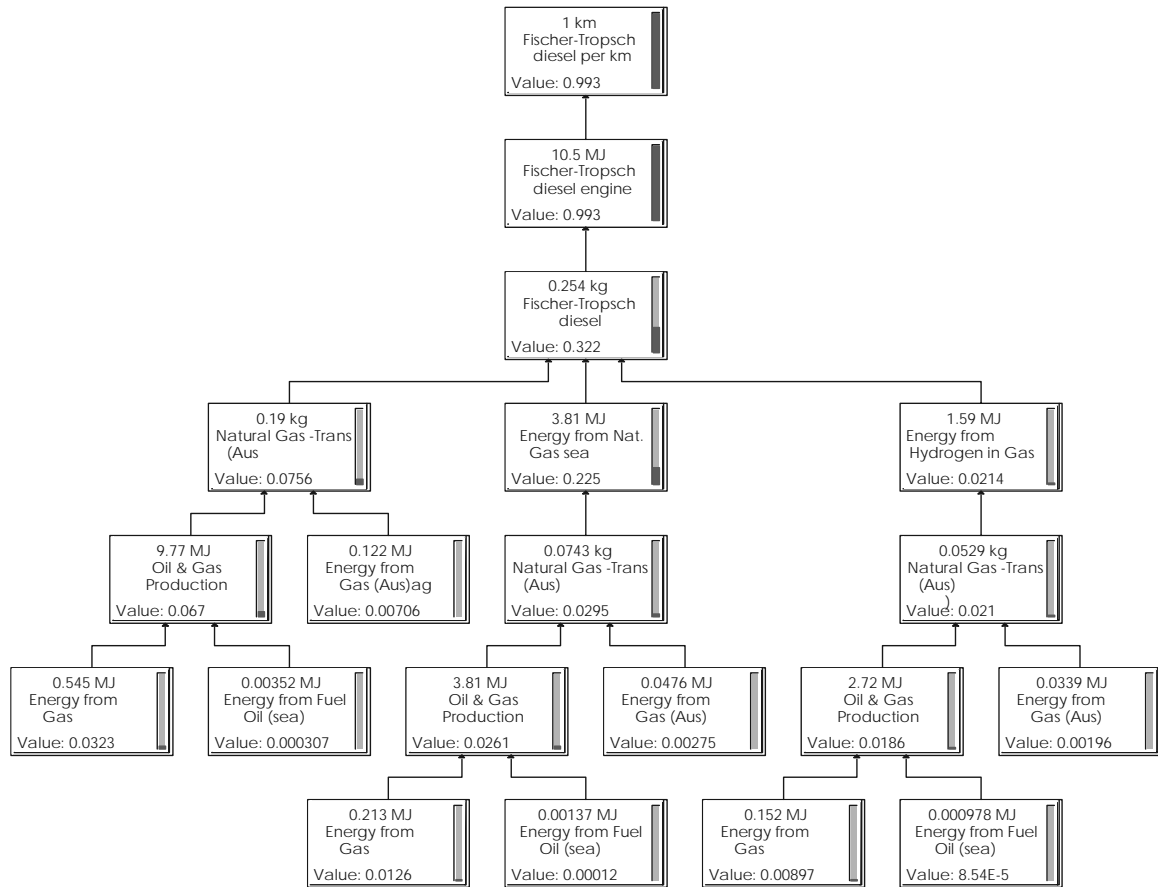


Figure 3.3
Embodied greenhouse gases emissions (kg CO₂e) from FTP diesel production and processing and use in vehicle

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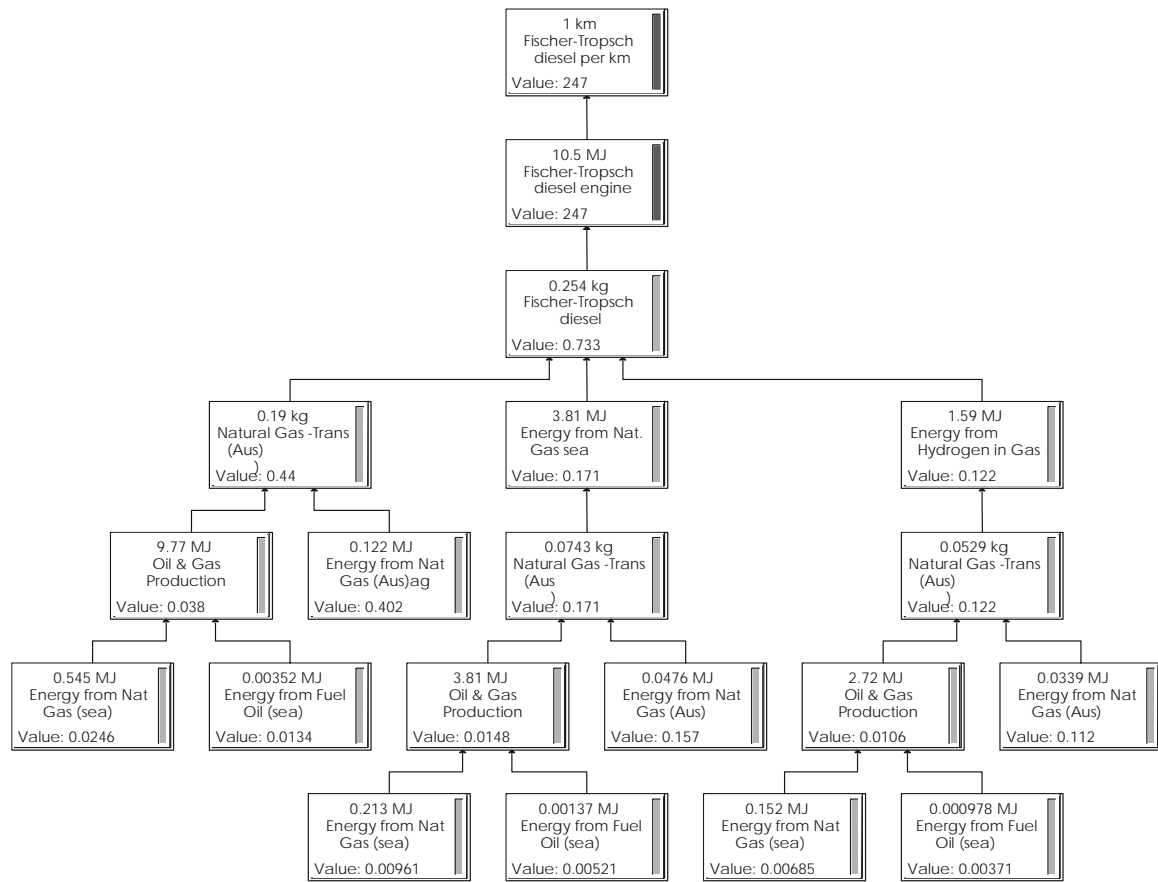


Figure 3.4

Exbodied particulate matter (mg - urban) from FTP diesel production and processing and use in vehicle

3.5 Viability and functionality

FT diesel has the same viability and functionality as diesel fuel. The fuel properties of the California diesel and the FT diesel (when converted from BTU/gal) used in the testing by Norton et al. (1998), as shown in Table 4 are given in Table 3.15.

Table 3.15
FT diesel fuel properties (MJ/L)

	California #2 Diesel	FT Diesel
Gross Heat of Combustion (HHV)	37.92	36.86
Nett Heat of Combustion (LHV)	35.56	34.36

SasolChevron (Goede, pers. comm.) point out that FT fuels:

- are already in use and production in South Africa where approximately 190,000 barrels per day are produced from either natural gas or coal gas;
- comply with South African Bureau of Standards (SABS 342-1998) specification for automotive diesel fuels to which the major automotive companies are co-signatories;
- are used by Ford South Africa as the first fuel with which to fill the tanks of new trucks;
- have similar refuelling and operational ranges to diesel;
- are compatible with existing diesel distribution and storage infrastructure as well as old, existing and future engine technologies (Schaberg et al., 1997);

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- enhance engine durability and prolong service intervals as a result of their low sulfur content (Weiss et al., 1987).

Some of these properties are shared with all ultra low sulfur diesel fuels. For example, very low sulfur is needed for future generations of catalyst systems.

3.6 Health Issues

FT diesel is an extremely low sulfur diesel, with sulfur content less than 10ppm. The health benefits, when compared to the low sulfur diesel reference fuel will be at least those of ultra low sulfur diesel (ULS).

A web search using “citydiesel” and “health” as search terms indicated that Finnish studies claim that there are 20% reductions in aromatics from the tailpipe of the vehicles using such extremely low sulfur diesel fuels.

In addition, material provided by SasolChevron notes that the total aromatic content of Sasol GTL fuel is approximately 0.4% by mass with PAH being less than 0.05%. The comparable low sulfur diesel values are 32.2% aromatics and 2.5% to 10% PAH. These order-of-magnitude reductions result in significant lowering of potential adverse health effects from emissions associated with FT diesel (Schaberg et al., 1997).

3.6.1 Production and transport

Particulate Matter

The LCA estimate for FT Diesel urban precombustion (truck) PM10 emissions of 1 mg/km is substantially less than the LSD estimate of 43 mg/km.

Air Toxics

The LCA estimate for FT diesel urban precombustion (truck) NMHC emissions of 0.011 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 toxics emissions from upstream activities.

3.7 Use

3.7.1 Particulate matter

The LCA estimate for FT Diesel combustion (truck) PM10 emissions of 246 mg/km is less than the LSD estimate of 380 mg/km.

3.7.2 Air toxics

The LCA estimate for FT Diesel combustion (truck) NMHC emissions of 0.515 g/km is less than LSD estimate of 0.900 g/km.

3.7.3 Summary

FT Diesel upstream emissions of both particles and NMHC are substantially less than LSD. FT Diesel tailpipe emissions of both particles and NMHC are less than LSD.

No comparative emissions data for FT Diesel and LSD has been identified for air toxics.

3.8 OHS Issues

The OHS issues in the lifecycle of FT Diesel are covered by a range of State and Commonwealth occupational health and safety provisions. While there will be different OHS

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issues involved in the production process associated with FT Diesel compared with LSD, no OHS issues unique to the production and distribution of FT Diesel have been identified.

3.9 Vapour Pressure Issues

No information was identified on vapour pressure issues associated with FT Diesel.

3.10 Summary

The advantages of FT Diesel are:

- FT Diesel contains virtually no sulfur or aromatics. In a properly tuned engine this is expected to lead to lower particle exhaust emissions.
- The absence of sulfur means that oxidation catalysts and particulate traps will operate at maximum efficiency.
- The existing diesel infrastructure can be used, unchanged, for Fischer-Tropsch Diesel.
- FT Diesel can be used in existing diesel engines.
- Diesel is one of the safest of the automotive fuels.
- An FT plant does not produce any of the less desirable co-products from a refinery, such as heavy fuel oil or coke.
- Provided an FT plant uses an oxygen feed, it produces a pure CO₂ stream that provides an option for the collection and sequestration of CO₂.

The disadvantages of Fischer-Tropsch diesel are:

- Diesel exhaust (including FT Diesel exhaust) is treated by the US EPA as an air toxic.
- Because of the extra processing energy, FT Diesel produces more embodied greenhouse gases than any of the conventional or alternative fuels studied in this report.

3.11 Environmental Impact and Benefits

Greene (1999) comprehensively reviews the environmental issues involved with GTL fuels. The environmental impacts are the same as those for diesel fuel, with the benefit of lower air pollutant emissions and increased resource security through a lowered dependence on imported oil.

An FTD plant does not produce undesirable co-products, unlike a refinery, which produces heavy fuel oil and coke.

3.12 ADR Compliance

Ultra low sulfur fuel is being introduced specifically to enable Euro4 fuel specifications to be met. The ADR have been based on this fuel. There should thus be no potential for an even lower sulfur fuel such as FT Diesel to compromise vehicles' compliance with gazetted ADR standards.

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