Atrax Energi

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Annex XXXI

**Synthetic gasoline and diesel oil
produced by Fischer-Tropsch Technology**

A possibility for the future?

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Annex XXXI

Assessment of production and use of synthetic vehicle fuels

Gasification

Feedstock

Fischer-Tropsch Technology

LCA

Scenarios

LD-vehicle emission tests on synthetic gasoline

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Abstract

This report is the result of an annex (annex XXXI, Fischer-Tropsch Fuels) initiated by the International Energy Agency's Implementing Agreement on Advanced Motor Fuels.

The annex has been managed by Atrax Energi AB, Björn Rehnlund, acting as the operating agent of the annex. The work in the annex has been carried out in co-operation with the Swedish Transportation Research Institute – TFK, Magnus Blinge and the Technical University of Denmark - DTU, Jesper Schramm and Ulrik Larsen.

In this report the possibilities to produce synthetic gasoline and synthetic diesel oil from biomass, and also from natural gas, by Fischer-Tropsch (FT) Technology are analysed and discussed.

After an introduction of the technology as such, environmental aspects and the life cycle perspective of synthetic gasoline and diesel oil are discussed, and some possible national/regional scenarios are analysed and presented.

Vehicle emission tests with synthetic gasoline carried out at DTU are described and discussed in this report as well.

Based on the result of the analysis and the vehicle emission tests presented in the report, a first SWOT analysis of Fischer-Tropsch technology is then presented, and finally some main conclusions are drawn.

During the execution of the annex Sasol in South Africa, Nykomb Synergetics in Sweden, Chemrec in Sweden, the Technical University of Denmark, VTT in Finland, the Värnamo gasification research project in Sweden, and the Black liquor gasification project in Piteå, Sweden have been visited.

Some of the most important conclusions are that:

- FT-Fuels such as FT- Diesel (FTD) and FT-Gasoline (FTG) produced through Coal-To-Liquid, (CTL), Gas-To-Liquid (GTL) and Biomass-To-Liquid (BTL) technologies can contribute to reducing the dependency on crude oil.

- FTD and FTG are attractive for use in neat form and also as components in blends with low quality diesel and gasoline, to upgrade fuels to meet the ever more stringent regulations.

- Production and use of GTL has the potential of contributing about the same or slightly less greenhouse gas to the atmosphere than production and use of conventional diesel. Production and use of CTL emits more than twice as much greenhouse gases than traditional fuels. Production and use of BTL reduces the emissions of greenhouse gases by 60 – 90 % compared to fossil diesel and gasoline.

- The technology to gasify biomass is not yet ready for market introduction. Further research and development are needed in this area.

- The FT process is still a relatively expensive technology and requires large-scale production plants or further development, in order to be economically viable. The option of making FTD and/or FTG from remotely located and/or low quality (flare gas) resources of natural gas is today less capital intensive than other production methods.

- According to information from Sasol it is possible to produce FT-fuels with coal as feedstock to a market competitive price as soon as the crude oil price is higher than 30 to 40 USD per barrel.

- The production and use of FT-fuels reduces smog-inducing matter with about 90 % and the emissions affecting acidification and eutrofication are about 5 – 40 % reduced.

- Compared to conventional diesel, various kinds of pollutant emissions are reduced with the vehicle use of FT-fuels: HC, CO, NOx, PM, SOF, VOF and PAHs.

- A biomass based FT production scenario will have a large impact on the feedstock transport and logistic systems and many obstacles must be considered. It will not only be investment costs for the plants, but also for infrastructure around the plant and a significant amount of heavy traffic towards the fuel production plants will be the result of this system.

- To substitute 15 % of the EU 15 countries transport fuel consumption would for example require an area of the size of Poland and it would furthermore require 122 FT-plants of 1.6 GW each.

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1. Background

Alternative fuels and related issues, like supply of raw material, production technology, distribution technology and engine technology have been analysed and discussed for more than three decades. During this time several production and engine technology tests have been performed, with a broad range of alternative fuels that were produced from fossil feedstock as well as from biomass. Different alternative fuels have also been used in fleet tests, ranging from a couple up to several hundreds of vehicles. In some countries the use of primarily methane (natural gas and biogas), LPG/Motor gas, ethanol (sometimes methanol) and bio-diesel have been introduced on the commercial market. Good examples of a growing commercial market can be found in Brazil, the USA, and Sweden.

The reasons behind these discussions and the introduction of alternative fuels on the market were initially supply and security of supply, starting with the first oil crises in the beginning of the 1970:ies. In a second phase during the 1980:ies, the emissions from the transport sector and their impact on environment and health became an important issue when discussing alternative fuels and their possibility to reduce the emissions and their impact when replacing gasoline and diesel oil. However, with "new" reformulated versions of gasoline and also diesel oil, in combination with new engine technologies as well as exhaust gas after treatment, the pollutant emissions from the transportation sector have been reduced drastically.

Since the mid 1990s, as an effect of the awareness of the risk of a climate change and its likely connection to the emission of greenhouse gases, the interest in alternative fuels has focused on fuels from biomass, or rather carbon dioxide neutral fuels.

One example of the increasing awareness and the interest in alternative fuels was when the European commission in May 2003 took a decision on a directive for the promotion of bio fuels and other renewable fuels. The aim of the directive is to increase the use of alternative fuels in Europe to certain levels. For example in the directive concerning the promotion of alternative fuels, 5.75 percent of the total vehicle fuel consumption based on energy content is set up as a voluntary minimum level for the use of alternative fuels -mainly ethanol, bio-diesel and methane- by the year 2010.

The possibility to produce bio diesel (Fatty Acid Methyl Esters, FAME) from for example soybeans and rapeseed, at least on a national base, is often rather restricted. The situation for grain based ethanol production is the same. If it is possible to produce ethanol from cellulose in the future, the number of feedstock options will grow substantially. Still, there will probably not be enough raw material for the production of sufficient fuel ethanol, with maybe exceptions for countries like the USA, Sweden, Finland, Canada and some Eastern European countries. If we in the medium term really want to replace gasoline and diesel oil with an alternative liquid vehicle fuel, a much broader range of alternative raw materials for the production of the fuels must be used. Examples of such raw materials are different types of garbage and rest products from farming and forest harvesting.

But these "new" types of raw material will be much more difficult to ferment (aerobic or anaerobic) than the well-defined raw materials such as grain or woodchips that are used today. To be able to use this kind of heterogeneous raw material, we probably have to apply a

technology in which we first have to gasify the raw material/feedstock, followed -when necessary- by a shift and reformation of the raw gas to a synthesis gas, that is finally followed by a chemical process reaction of the gas to different kinds of synthetic fuels such as methanol, dimethyl-ether (DME), synthetic gasoline (alkylate) and synthetic diesel oil (paraffin).

In this report the possibility to produce synthetic gasoline and synthetic diesel oil from biomass but also from natural gas based on so-called Fischer-Tropsch Technology is analysed and discussed.

2. Introduction

Fischer-Tropsch Technology (FT) can be described as a technology to convert synthesis gas that is containing carbon monoxide and hydrogen into hydrocarbon products. These hydrocarbon products are predominantly liquid at ambient conditions but also gaseous and solid reaction products may occur. The liquid hydrocarbon produced can be used -after different treatments such as distillation, hydro cracking, cleaning and upgrading/refining- as raw material for chemical industries, as fuels for stationary applications, or as vehicle fuel.

When used as fuel, the FT-products are normally described as synthetic diesel oil and synthetic gasoline. Compared to crude oil products, the FT-hydrocarbons/FT-Fuels have a very low content or rather absence of compounds such as sulphur, nitrogen and heavy metals. Furthermore the content of aromatics is very low.

The FT-technology was first applied in Germany during the 1930:ies with gasified coal as raw material for the production of the synthesis gas that is used in the FT-synthesis process. However, at that stage the technology was rather expensive and not very efficient, which made it difficult to compete with at that time cheaper crude oil when looking for supply of hydrocarbons/fuels. The FT-Technology was used by Germany during the Second World War to complement the limited availability of petroleum products caused by the war situation.

Although not being a fully commercial technology at that time, the development of the technology continued over the years, probably mostly because the technology as such was fascinating from a scientific point of view, but maybe also because some foreseeing decision makers could imagine the technology as relevant from a future strategic supply point of view.

FT-Technology developed over time to both higher efficiency as well as lowered production costs and higher diversification or rather a better possibility to design the synthesis products, even though upgrading/ distillation /hydro cracking is still needed. This development together with the fact that natural gas after reforming and shifting could be used as a raw material for the FT-synthesis has furthermore lead to an increased use of the technology and the awareness that FT-technology could be used to obtain value from stranded natural gas. Using FT-Technology makes it possible to convert remotely located natural gas to liquid hydrocarbon products. These products are easier to transport and they have a value on the world market. The Shell plant in Malaysia is an example.

It is also possible that in locations where feedstock for synthesis gas production is available, in combination with a shortage of energy supply, the production of FT-Fuels can be recommended. One obvious example of this is Sasol's plants in South Africa, in which a rather huge part of South Africa's consumed gasoline -during the time of the oil embargo caused by the apartheid system- was produced with abundant coal as feedstock. Certainly the situation might be the same for other raw materials such as different kinds of biomass.

Furthermore, in a world with decreasing possibilities to supply the transportation sector with oil based fuels, at least to a reasonable price, the market has to find new fuels that can be used in the existing vehicle fleet and infrastructure or it has to find new methods to produce fuels similar to the fossil fuels such as diesel oil and gasoline from "new" raw materials.

FT-products similar to diesel oil and gasoline can be produced from synthesis gas produced from gasified coal as well as natural gas. It is also possible to use synthesis gas from gasified biomass. In other words, the FT process is a flexible technology concerning raw material as well as the final product, and almost all carbon containing material that can be gasified can be used as a raw material for production of synthesis gas.

Another issue of importance that is increasing the interest for the FT-Technology and its possibilities is the situation in the Middle East. A situation that time after time has shown the world that supply of fuel is not just a question of knowing the existence of oil resources/new possible oil resources and the possibility to buy them to a reasonable price, but that it is also very much a question of access to these resources/products. This also makes the possibility to produce fuels similar to diesel oil and gasoline from other raw materials than crude oil (national available feedstock's) an important security issue.

Today, with a situation where the oil price -as well as the price of more or less all oil products- increases fast and seems to reach and remain on an all time high level, it is also quite clear that synthetic fuels produced from natural gas and coal can compete on the market very well without any substantial subsidies. It might also be possible that such fuels produced from biomass can be produced to a cost that will make them competitive on the fuel market. However, for these biomass-based fuels there are still some research and development activities concerning the gasification step that have to be carried out first.

Finally, it is important to note that when biomass is used as raw material for the production, there is also the possible advantage of largely reduced net emissions of carbon dioxide. However, this is much dependent on how you manage your process from cradle to grave. To what extent are you using energy generated from fossil sources, are you making the best use of residual energy from the process, or are you using biomass also for the production of the energy needed for the process, from cradle to grave?

The process using natural gas as raw material for a FT-synthesis is commonly referred to as the gas to liquid process (GTL), while the process using coal as a raw material for the gasification to synthesis gas -used in the FT-process- is referred to as the coal to liquid process (CTL). The process using gasified biomass for production of synthesis gas used for FT-synthesis is referred to as the biomass to liquid process (BTL). BTL is sometimes also used for the process using biogas from anaerobic digestion of biomass to biogas (methane with an biological origin) to be used as a raw material (after reforming, shifting and cleaning) for the FT-synthesis to a liquid fuel.

Just a couple of years ago the interest shown by oil companies for the FT Technology and its possibilities was at a very low level. At least that was what they showed to people outside the companies. However, in parallel to a steady as well as substantially increasing price of crude oil -together with more and more visible climates effects and political initiatives to increase the use of alternative fuels- the interest has not only increased, but it has rather exploded. Today, most oil companies have initiatives on the agenda to explore the FT-Technology and to prepare for a future production from natural gas at first. Of course not all products will be used for vehicle purposes. Also production of chemicals will be of great interest for the producers.

Table 1. Ongoing or planned projects (plant construction) spring 2006, [1]

Company/Producer	Location	Prod. Capacity, BpD	Feedstock	Start-up
Sasol				
	Sasolburg, South Africa	5600	Coal/NG	1955, 1993
	Secunda South Africa	150 000	Coal	1980, 1995
Sasol/Chevron				
	Escravos, Nigeria	34 000	Natural gas	2006
	North Field, Ras Laffan, Qatar	34 000	Natural gas	2006
Sasol/Shell				
	Gillberton, Pennsylvania, USA	5000	Waste coal	2007
Shell				
	Bintulu, Malaysia	15 000	Natural gas	1993
	North Field, Qatar	140 000	Natural gas	2009
Exxon Mobil				
	Baton Rouge, Louisiana, USA	200	Natural gas	1993
BP				
	Nikiski, Alaska, USA	300	Natural gas	2003
PetroSA				
	Mossel Bay, South Africa	22 500	Coal	1991
Statoil/PetroSA	Mossel Bay, South Africa	1000	Natural Gas	2004
Choren				
	Alfa plant Freiberg, Germany	7,5	Biomass	2003
	Beta plant, Freiberg, Germany	340	Biomass	2006
TU Freiberg/Lurgi				
	Freiberg, Germany	180	Biomass/Coal	2009

What 'future' really means in this case is hard to define. According to personal contacts at Sasol it is possible to produce synthetic fuels with coal as feedstock to a market competitive price as soon as the crude oil price is higher than 30-40 USD per barrel. With today's prices (60-70 USD per barrel, SEP 2006) the construction of new production plants as well as production of synthetic fuels in existing plants should already be economical realistic and on its way. To some extent this is indeed the situation (see the table above) but still many of the actors seem to be somewhat hesitant, probably waiting to see if the oil price will decrease again. One important question in this perspective is of course: Will this happen, and if so, what will be the 'normal' oil price in the near future and in the long-term perspective?

One other issue that might restrict the initiatives concerning production of synthetic fuels is that today bio based ethanol and bio diesel (FAME) are the alternative fuels that most experts believe will be the first to replace gasoline and diesel oil. This might be true. Ethanol and bio diesel have for many years already been used on a commercial scale, mainly in Brazil, the USA and Sweden. It is possible to blend ethanol with gasoline at least up to 20 %, or even to use it in almost neat form (E85) in Otto engines (E85 in Flexi Fuel Vehicles) while it is possible to use bio diesel in blends with diesel oil as well as in neat form in diesel engines. However, it is worthwhile not to forget that the quantities of raw material that can be produced for the production of ethanol -such as grain and sugar beets- are restricted. Furthermore, if in the future it will be possible to produce ethanol on a market scale from cellulose (straw, woodchips, etc.), the raw material potential will increase but it will still be restricted. Perhaps the restrictions will be limited in countries such as Sweden, the USA, Russia, Canada and some countries in East Asia, but in most other countries the raw material production capacity will be limited. Concerning the raw material for bio diesel -such as rapeseed, soybeans, etc.- the situation is very similar.

Concerning the synthetic fuels produced with FT-Technology the situation is quite different, even though the feedstock -fossil as well as biomass based- for FT-Fuels of course in the long term are also restricted.

- To begin with, these FT-fuels can be produced from natural gas and coal. This gives us maybe a couple of hundred years to act and develop new technical solutions in the field of engine technology, new engine concepts, new fuels and new forms of energy production and storage. However, to cope with the climate change, this probably has to be followed by technical solutions in the field of CO_2 sequestration.
- Secondly, FT Fuels can also be produced from almost all kinds of carbon containing material, including biomass. The only real issue to develop is how to gasify the different raw materials. This gives the FT-Fuels a rather good advantage compared to ethanol and bio diesel when it comes to compare the supply situation.
- Thirdly, synthetic diesel oil and synthetic gasoline can be designed to be more or less identical in their properties compared to crude oil based diesel oil and gasoline. This guaranties that these synthetic fuels can be used in neat form as well as in any level of blending, and in old vehicles as well as in new vehicles with new technical concepts.

In other words, FT-Fuels seem to have a much better perspective not only concerning supply of raw materials for the production, but also when it comes to use in the existing vehicle fleet as well as in new engine concepts.

Finally it is also of interest to notice that the FT-process gives rise to a number of by-products that often have a high value on the market, such as chemicals, rest gases and heat that can be used for electricity production in a combined cycle process.

Numerous process configurations for the conversion of biomass to FT-fuels are possible. Parameters that will have an effect on the efficiency, the economy and the product distribution are for example:

- Gasification methods
    - Atmospheric or pressurised
    - Air-blown or oxygen-blown
    - Indirect or indirect
- Gas cleaning methods. Since coal, natural gas and biomass and consequently the raw gas will contain contaminants -such as for example H_2S, NH_3, dust and alkali.
- Need for and type of reforming and shifting to reach the optimum output and H_2/CO ratio
- Reactor types
- Catalyst type and preparation
- The "use" of the gas
    - Recycling of gas to obtain a maximum quantity of liquid fuels (full conversion mode)
    - Combined cycle for electricity production (once through mode)
- The use of by products

In environmental calculations for vehicles using alternative fuels, the production method of the fuel itself is very important. Different production methods can give big differences in emissions, particularly of CO_2. The scope of this report is to present a feasible set of LCA data on production of Fischer-Tropsch fuels, from a global perspective and on a large-scale basis. 5 LCA reports have been found that suit this purpose and that are regarded to be of good quality. These studies are summarized and compared. The results can be regarded as fully sufficient and valid for the purpose of this study.

The enormous amounts of biomass needed to substitute all fossil fuels used in the world will probably have large impacts on other parts of the economy besides the energy sector. The demand for transport will increase dramatically. There is also a substantial need for investments in production plants and infrastructure for the new energy system. In a first attempt to make the consequences visible of the impact that a biomass based Fischer-Tropsch production process will have on the logistic- and transportation systems for a selected number of representative countries, four scenarios are analysed in terms of the need for available land and biomass resources and the effect on the demand for transportation. The scenarios are:

- Finland, with forest residues as feedstock for biomass based F-T Fuel
- Poland, with energy forest as feedstock for biomass based F-T Fuel
- Denmark, with energy forest as feedstock for biomass based F-T Fuel
- USA, with Natural Gas as feedstock for fossil F-T Fuel

In order to get an overview of the emission performance of FT fuels, an investigation has been carried out. During the study the goal was to find any available data on emissions from

vehicles or engines fuelled by FT gasoline or FT diesel. Unfortunately, it has not been possible to find any data on emissions from FT gasoline powered engines. At this point in time it seems that there have not been made studies in this area or at least that they haven't been made publicly available. For that reason the literature review in chapter 8 will only discuss emissions from diesel powered engines and vehicles.

Since no emission measurement data from cars fuelled by FT gasoline was found to be publicly available, a series of measurements were conducted at the Technical University of Denmark.

Emission performance tests were performed on a VW Golf 1.6L FSI 2003 with an odometer reading of ca. 48000 km. With otherwise similar conditions three different fuels were tested: a regular Danish octane 95 unleaded gasoline, Aspen 4T octane 95 alkylate gasoline and a South African gasoline product mainly made via the FT process from natural gas. The tests were done in order to evaluate eventual emissions advantages of the three fuels. The Swedish Aspen 4T fuel was brought into the project as a reference fuel representing FT gasoline as it could be made in its most ideal form. Aspen 4T is pure alkylate gasoline made synthetically from gas.

The goal of the investigation is to examine the emission performance of FT gasoline including pollutants such as hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx) and particulate matter (PM). An analysis of the soluble organic fraction (SOF) of the PM regarding the carcinogenic polycyclic aromatic hydrocarbons (PAH) is also included.

3. Gasification

As described earlier, the preparation of synthesis gas can be divided into three major technology steps:

- Gasification
- Cleaning
- Shifting and reforming
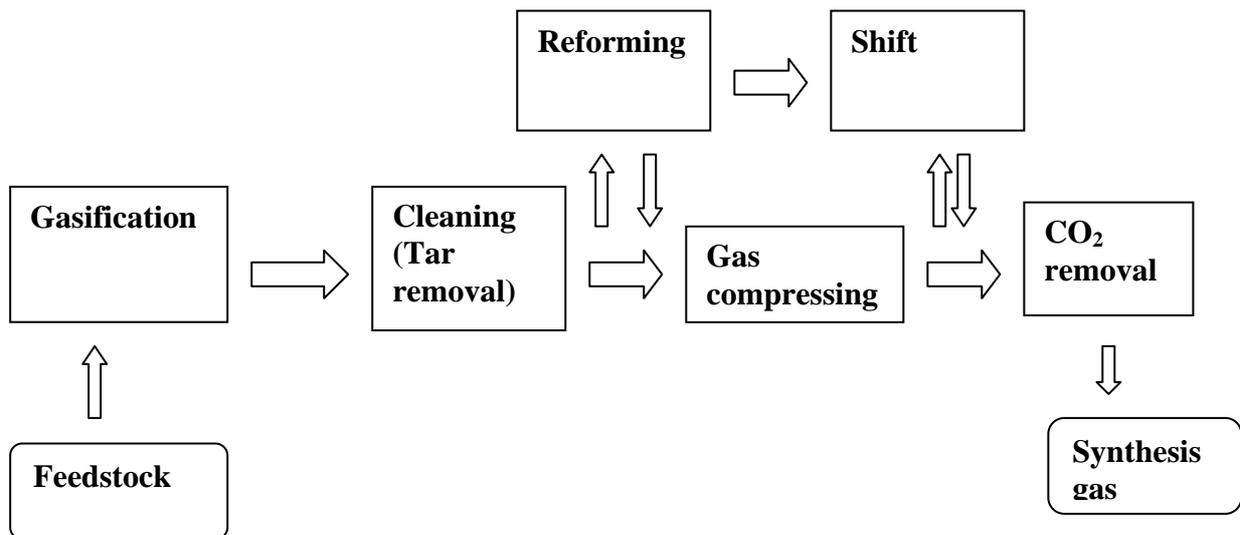
Gasification is the process where solid or sometimes even heavy liquid carbon containing fractions are turned into synthesis gas or sometimes even into a light liquid fraction. Cleaning is where impurities and ballast gases are removed from the synthesis gas, reforming is used where mainly the CH_4 fraction is converted into CO and H_2 with the help of steam, while shifting is the process where the H_2/CO ratio is adjusted also with the help of steam. When feedstock with a low content of hydrogen is used, hydrogen may have to be added to the process in the form of water and/or steam in the gasification step.

If natural gas is used as raw material, the preparation of the synthesis gas will include only cleaning and reforming and sometimes shifting.

There are also technologies that can be used for the whole range of feedstocks such as for example high temperature partial oxidation. This can be considered to be a kind of gasification including methane reforming.

The design of the synthesis gas preparation section will mainly depend on the required product mix and the available feedstock. However, it is important to remember that the synthesis gas preparation step is a very important part of the whole solid/gas to liquid concept. Two strong reasons for that are that the gas preparation compared to the FT synthesis and the product work up:

- Is the most expensive part regarding investments?
- Is the process step that consumes most of the total energy that is required?

Even though the required product mix as well as the feedstock will very much determine the design of the production step, it is from en economical point of view important to take these two facts into account.

Coal tended to be the main feedstock for many years in countries such as the USA, South Africa and Australia, as well as in developing countries such as India and China. However, today the use of natural gas and other sources -such as biomass or waste from industry and municipals- as feedstock for synthesis gas production might grow in countries without a domestic supply of coal.

Also the climate change problem will probably contribute to a growing use of renewable sources, more and more replacing the fossil ones.

The gasification process is a reaction between the raw material (coal) (with or without hydrogen association) and hydrogen (usually steam) and/or oxygen. The product, the synthesis gas, contains mainly hydrogen, carbon monoxide, carbon dioxide and methane.

Oxygen blown gasification is preferred to air blow since the nitrogen in the air will contribute to a build up of an inert in the system. Also pressurized gasification is preferred compared to gasification at atmospheric pressure.

In the table below some of the advantages and disadvantages of different types of gasification are shown/compared.

Table 2 Advantages and disadvantages of different types of gasification

Pressurized	Atmospheric
+ Less costs at larger scale	+ Less costs at small scale
+ Small upstream equipment	- Larger upstream equipment
- Higher costs at small scale	
Oxygen blown	**Air blown**
+ No build up of N_2	+ Less costs
- Expensive air separation plant needed at small scale plants	- Build up of N_2
	- Large upstream equipment

After the gasification step the gas, depending on what it will be used for, mostly has to be cleaned from impurities and undesirable components like for example sulphur and particulates. Also depending on the raw material for the gasification as well as the use of the synthesis gas use:

- The amount of methane (CH_4) might have to be converted to CO and H_2,
- The H_2/CO ratio might have to be adjusted to what is preferred (often 2:1),
- The amount of CO_2 might have to be removed since it might be an inert if the FT-Catalyst does not have any activity for CO_2 shifting.

Gasification is a rather perfect way to go from the more simple way of utilization of an energy source (solid or liquid) by combustion to a much more diversified utilization, changing the carbon containing material into a product that can be used for/as:

- Energy production (heat and electricity – Integrated Gasification Combined Cycle, IGCC),
- Liquid fuels (synthetic gasoline and diesel oil),
- Chemicals,
- Fuel for fuel cells (hydrogen).

3.1 Coal gasification

The first companies to convert coal to combustible gas through pyrolysis were chartered in 1912, while the first true gasifier, a Lurgi moving bed gasifier, was already operational in 1887. During the 1930`s the first commercial coal gasification plants were constructed, followed by town gas applications in the 1940`s. In the 1950`s chemical process industries started applying gasification for hydrogen production and later for fuel production.

Sasol is today probably the largest single user of the gasification technology (coal). The first Sasol gasification plant was put into operation in the middle of the 1950`s.

The total production capacity in operation around the world today -concerning gasification for the purposes of chemical industry and synthetic transport fuels- is about 11 GW [2] (mainly coal as raw material) while the total synthesis gas production capacity is about 40 GW [3] (including natural gas as raw material).

Coal is a polymeric substance without repeating monomers, with hydrocarbon chains, mineral matters and moisture as the main constituents. The composition and structure of coal affects what purposes the coal can be used for. According to the degree of metamorphism, coal tends to be classified in different categories ranging from lignite (brown coal) to anthracite. Over time coal gradually changes from lignite to sub-bituminous coal, to bituminous coal and to anthracite [4]. For gasification only lignite, sub-bituminous coal and bituminous coal are used [5].

The properties (chemical and physical) of coal are changing from one source to another. Since the design of the gasifier -and as a result of that the efficiency of the gasifying process- depends on the properties of the raw material (coal), it is of great importance to carry out different tests and analyses of the coal that is meant to be used, before designing the gasifier or changing from one coal source to another in an existing gasifier.

Examples of such properties are:

- Particle size distribution
- Caking properties
- Water content
- Ash melting point
- Ash composition

- Sulphur content
- Tar production
- Heating value

Although some international standards exist, most of the tests seem to be developed by engaged companies, and because of that they are mostly private property.

The gasification of coal (in the gasifier) can be divided into separate process steps such as:

- Drying
- Pyrolysis producing gas, tars an solid char residues
- Gasification or partial oxidation of the solid char and pyrolysis tars
- Combustion of coal in an air/stem or oxygen/stem environment

After that, the only solid forms are the remaining minerals etc., in the form of ash.

Using oxygen and steam for the gasification, the chemical reaction will at first be the following steam carbon reaction and the partial oxidation reaction:

$$C + H_2O \Rightarrow CO + H_2$$

$$C + {}^1/_2 O_2 \Rightarrow CO$$
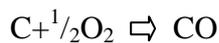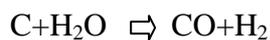
This will be followed by the water-gas shift reaction as well as methanisation reactions.

$$CO + H_2O \Rightarrow CO_2 + H_2$$

$$CO + 3H_2 \Rightarrow CH_4 + 2H_2O$$
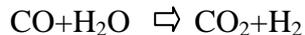
The water-gas shift reaction can be used to adjust the H_2/CO ratio in the synthesis gas.

Concerning the gasification technology and the design of the gasifiers, a number of different solutions exists today. More than 100 different solutions can be found in the literature [6]. However, some of these technologies are still in the R&D stage or at a laboratory scale.

The different types of gasifiers can mostly be divided into one of the following categories:

- Fixed bed or moving bed gasifiers
- Fluidised bed gasifiers
- Entrained flow gasifiers

As can be seen, the classification is mainly based on the type of rector bed, which also is a question about how the contact between the solid (coal) and the gas phase during the gasification is solved.

Furthermore, one sub-classification used is how the solid and the steam/oxygen are injected into the gasifier: counter current or co-current. Sometimes another classification is used; it is related to the operation temperature interval, which can be low or high. Low temperature gasifiers tend to be more thermally efficient, but with a low throughput. High temperature gasifiers have a higher throughput but to reach high thermal efficiency it will be necessary to

recover energy/heat downstream the gasifier. Furthermore, low-temperature gasifiers release the mineral content of the solid/coal as ash, while high-temperature gasifiers predominantly leave the minerals as a molten slag.

3.1.1 Fixed bed/moving bed (counter current) gasifier

In the fixed bed/moving bed (counter current) gasifier the coal moves downward in the gasifier while the locations of the different processing zones in the gasifier are fixed. Normally the feedstock enters the top of the gasifier during operation and through a coal lock hopper, being pressurized before entering the real pressurized gasification process. During its way down, the feedstock is consumed and at the bottom only ash remains. The produced raw gas leaves the gasifier at the top. After leaving the gasifier, the gas is cleaned from particulates, tars and oils through scrubbing in a wash cooler. This scrubbing procedure also decreases the raw gas temperature. The tars and oils are often utilized as feedstock for the production of valuable market products like coke and creosotes.

Until today the co-current fixed bed seems not to have been able to operate commercially, even though the concept has been studied and analysed several times.

Fixed bed gasifiers are most suitable for solid feedstocks such as coarse coal, while they have certain limitations handling fine coal. There is also a possibility of excessive coal segregation inside the fixed bed gasification unit, combined with a broad particle size distribution which may lead to problems maintaining uniform gas flow through the coal bed, which brings the risk of unstable gasifier operation. This risk often leads to a decision to duplicating instead of scaling up gasifier units. The purpose is to maintain high plant availability as far as possible, even if larger units would provide better economic performance and lower total maintenance costs.

Another shortcoming of the fixed bed gasifier is the high consumption of steam, which results in lower overall efficiency. However, this also results in a higher hydrocarbon production so that the synthesis gas will contain a H_2/CO ratio that is more or less directly suitable for FT-processes.

Today mainly three types of fixed bed gasifiers exist:

- The Sasol-Lurgi fixed bed dry bottom gasifier (pressurized).
- The British Gas Lurgi (BGL) slagging gasifier.
- The Bharat Heavy Electricals Ltd dry ash (BHEL) gasifier.

Sasol in South Africa operates approximately 100 Sasol-Lurgi gasifiers.

Below is a picture of a typical Sasol-Lurgi gasifier.
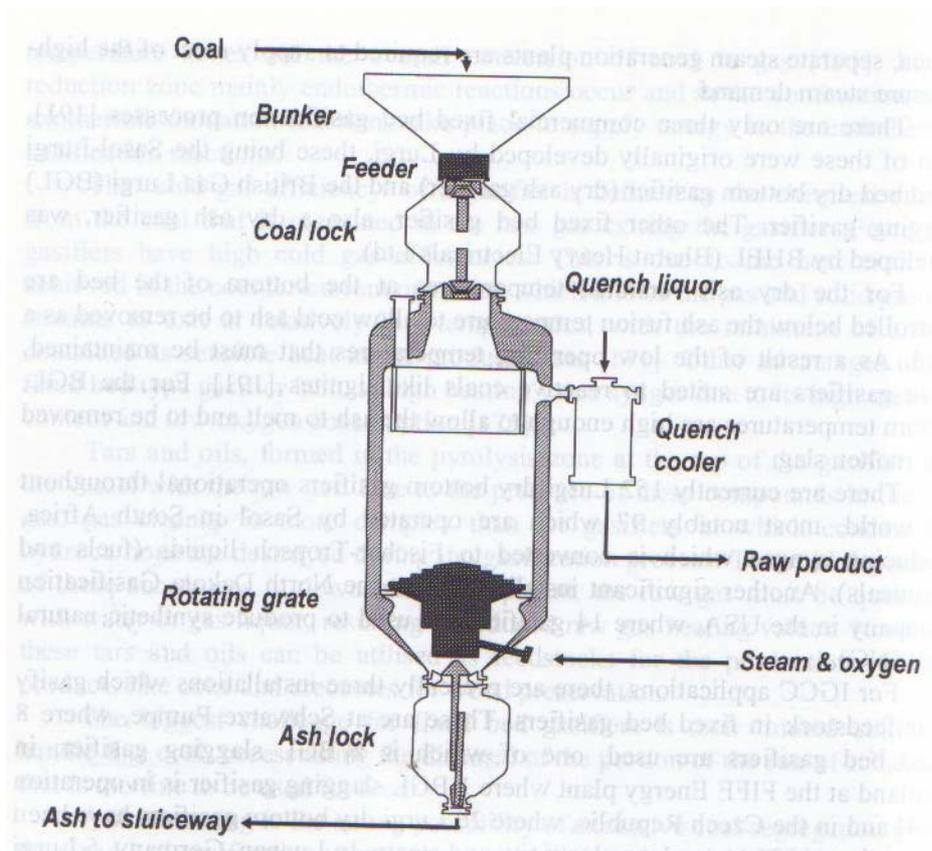
Figure 1 Sasol-Lurgi fixed bed dry bottom gasifier [7]

3.1.2 Fluidised bed gasifier

A fluidised bed gasifier consists of a vertical and cylindrical refractory lined vessel. Coal and air enter the gasifier through a burner at the bottom of the vessel, ensuring thorough mixing of coal and air (or another oxidant).

When the coal enters the vessel the volatile compounds are released, burn rapidly and supply heat to the gasification process. The resulting gas forms large bubbles that rise to the centre of the gasifier, which makes char in the bed move down the sides of the reactor back to the fluidised bed. The fluidised bed is maintained in fluidised form by injecting controlled amounts of steam, air and recycled gas through nozzles in the combustion zone.

Above the fluidised bed are cyclones that separate solids from the outlet gas and below the fluidised beds are units for ash cooling. If necessary there are also dry fly ash removal and wet gas scrubbing systems.

Fluidised bed gasifiers are usually operated at atmospheric pressure and at relatively low temperature, so it is possible to adapt to smaller capacities such as 20 tons per hour [8]. Normally no pyrolysis by-products are produced. They are instead combusted to provide energy for the gasification reactions and the raw outlet gas is more or less free of hydrocarbons, except methane.

The use of steam and oxygen during the gasification process in a fluidised bed gasifier is normally rather low.

Fluidised bed gasifiers are also suitable for other solid material than coal, for example different kinds of biomass.

Examples of different types of fluidised bed gasifiers are:

- The Kellog Rust Westinghouse (KRW) gasifier, (see picture below)
- The high temperature Winkler (HTW) gasifier
- The transport gasifier (Kellog, Brown and Root Inc)
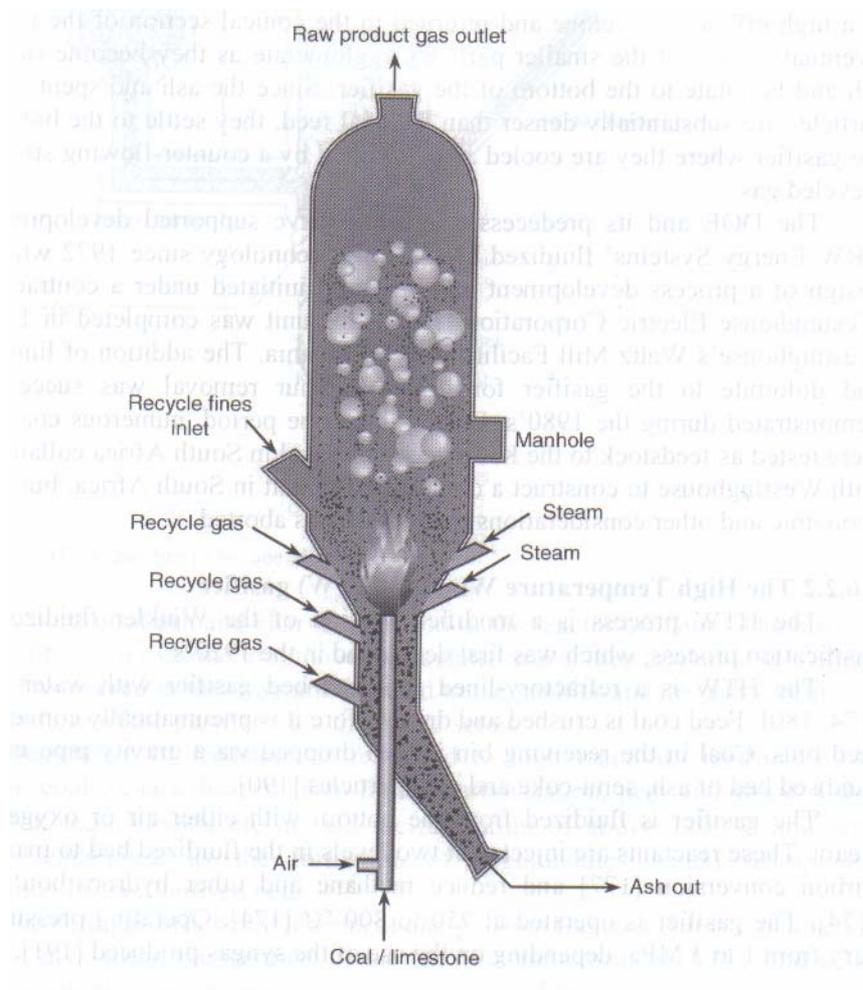
Figure 2 KRV Gasifier [7]

3.1.3 Entrained gasifiers

The entrained flow type of gasifier works co-current, as a plug flow reactor. The feed is introduced to the reactor together with the oxidant and steam or liquid water and flows co-currently at high speed resulting in a short gas residence time. Because of that pulverised coal is demanded to ensure carbon conversion.

All types of entrained flow gasifiers are today of the ash slagging type [6].

The entrained flow gasifier can use a wide range of feedstocks. This includes organic wastes, biomass as well as different solids and liquids including pulverised (fine) coal.

The operating temperature is high (above ash slagging temperature) to ensure synthesis gas free from tars etc. However, this may have an impact on the durability of the equipment, in combination with the need of expensive material choice.

To maintain high thermal efficiency the heat present in the raw gas leaving the gasifier has to be recovered.

The resulting product/gas from an entrained gasifier is often clean enough to avoid gas cleaning or processing of remaining hydrocarbons. Because of that the technology can be used as add-on to existing refineries/gasifiers that are producing undesired by-products.

The entrained gasifier offers advantages but there are also disadvantages; for example the high temperature causes material wear. One reason for operating at high temperatures is that otherwise it would not be possible to obtain high carbon conversion. Gasification of coal with high ash content can also cause problems with the thermal efficiency and oxidant requirements. Also operating at atmospheric pressure can be seen as a problem, since the synthesis gas has to be pressurized for most applications.

Some examples of the most used entrained flow gasifiers are:

- The Texaco gasifier
- The Shell gasifier
- The Lurgi Multi-purpose gasifier (MPG)
- The E-gas two stage gasifier
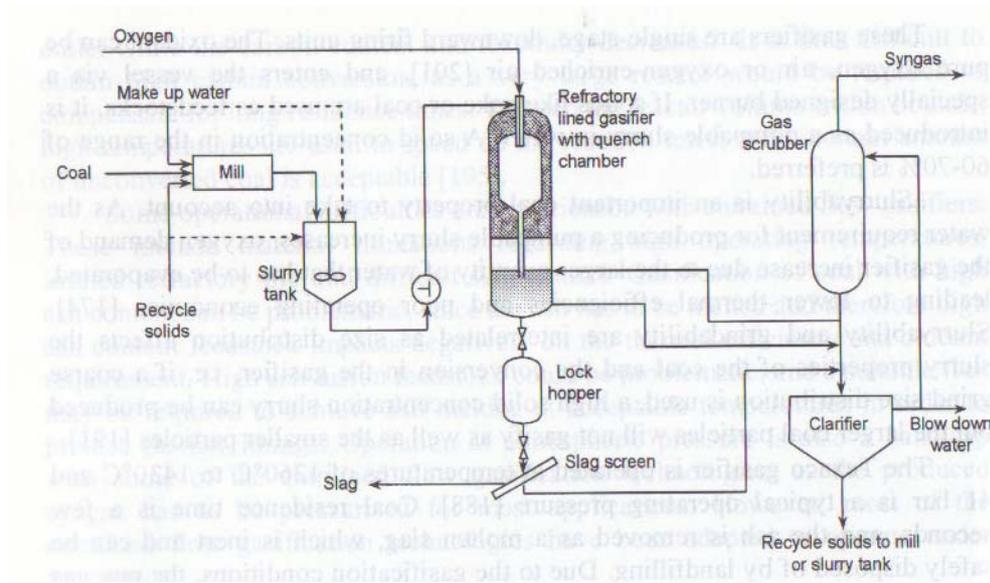
Figure 3 Texaco gasifier with quenching [9]

For each of the gasifier types mentioned above, there are different solutions that differ on details, often developed and designed by a commercial company and sometimes named after the company.

How to choose a gasifier when designing a plant is an issues that of course depends much on the solid to be gasified (type of coal), but it is also depending on the required composition of the final product and how the gasifying process can be combined with supporting systems, waste disposal, by product sales, etc.

Examples of such issues, beyond the feedstock characteristics, that have to be considered are:

- Quality requirements for the final upgraded gas
- By-product handling and by-product qualities requirements in case they are sold
- Operating characteristics
- Site specific conditions
- Environmental issues (legislation/demands)

Depending on the available feedstock and the choice of operating parameters, different types of gasifiers will be most suitable.

Before the synthesis gas from a gasifier can be used in for example turbines or can be fed into heat exchangers, it is necessary to remove entrained solids and other impurities. To do so, the gas has to be cooled directly after the gasifier. This may affect the energy efficiency and gives the gasification process a not so favourable position compared to gas reforming of natural gas, in which this cooling step is not necessary. In most existing plants the solids are washed out by water scrubbing in venture scrubbers or wash towers. However, the use of ceramic candle filters has improved the possibilities to remove solids at lower gas temperatures of approximately 500 degrees C. [10]. At 500 degrees C the alkali-compound could still be removed as a solid without forming corrosive alkali-sulphates [9].

3.2 Biomass gasification

Biomass can be a rather wide variety of different carbon containing materials. Some examples are:

- Wood/woodchips
- Rest products/by-products from forest harvesting
- Rest products from sawmills (sawdust etc.)
- Chipped energy wood
- Agricultural wastes such as straw
- Organic wastes
- Organic sludge

The more homogeneous and clean the feedstock is, the better the synthesis gas will be, without impurities etc.

The biomass feedstock might have to be pre-treated prior to gasification to obtain for example size reduction and cleaning from impurities (magnetic separation for metals). If the feedstock is too wet -above approximately 15 % moisture- also drying might be a necessary pre-treatment of the biomass, depending on the technology that will follow (see the chapter about the Technical University of Denmark). Without drying of wet feedstock, the cold gas efficiency in gasification would be too low [11]. If possible, drying would preferably be done with rest energy from the process, in the form of for example flue gas or low quality steam.

After drying, the first process step that the fuel is going trough during heating is pyrolysis. The pyrolysis reaction starts at approximately 230 ^{o}C. During the pyrolysis step/reactions, thermally unstable components such as lignin in biomass are broken down and evaporated as volatile components. The resulting pyrolysis gas consists mainly of tar, polycyclic aromatic hydrocarbons (PAH), methane (CH_4), steam and carbon dioxide (CO_2). The solid remains or residuals are carbon structures (coke) and ashes. Tars formed during pyrolysis can be sticky and are known to often be highly carcinogenic. The tar also represents a great challenge to the machinery/engines/turbines when remaining in the product gas.

The actual gasification happens at temperatures above 700 ^{o}C when the heated coke is allowed to react with a gasification agent such as oxygen, air or steam. During the gasification step the coke is gradually broken down into CO, CO_2, CH_4 and H_2. The gasification can happen in a pile of coke – a fixed bed – or in a fluid. Fixed bed gasification processes can be divided into two basic different process designs:

- Counter current (up draft) gasification
- Co current (down draft) gasification

In counter current gasification, the gasification agent is flowing in the opposite direction as the fuel/coke. It enters at the end of the gasification bed and leaves the process along with the pyrolysis gas at the beginning of the pyrolysis, or even at the drying zone. In counter current gasification the product gas is not very hot, but contains all of the tars from the pyrolysis reaction. The tar levels from counter current gasification plants tend to exceed 2 g/Nm^3 [12].

Fluid bed processes can exceed this level by at least one order of magnitude. This is because the pyrolysis happens much faster and therefore produces much more tar.

In co current gasification, the gasification agent is added before the gasification zone, sometimes even before the pyrolysis zone, and leaves at the end of the gasification zone. When the pyrolysis gas is forced through the glowing coke bed, a large fraction of tars will be broken down and gasified. Because of that the gas will contain magnitudes less tar than that of counter current gasification.

However, in recently developed co current gasification processes is being experimented with a small high-temperature zone where temperatures exceed 1100 to 1200 $^{\circ}$C. When pyrolysis gases pass this zone, large fractions of the tars are broken down/cracked in milliseconds. This technology combined with the tar reduction in the glowing coke bed reduces the tar levels to as low as 0.025 to 0.100 g/Nm^3. One example of this technology will be described below, the DTU two stage gasifier.

3.2.1 Biomass gasification at the Technical University of Denmark

3.2.1.1 Background

In 1989 the Biomass Gasification Group (BGC) was established at the Department of Mechanical Engineering of the Technical University of Denmark (DTU) in Copenhagen. Since then research on thermal gasification of biomass as well as on the end use of the product gas for heat and power purposes have been carried out.

Today, the BGC has three operational gasifiers for research and development studies:

- The Viking Gasifier that is an 80 kW, unmanned, automated and essentially tar free gasifier, with an integrated gas engine for heat and electricity production based on the two-stage gasification process and fuelled by wood chips.
  So far, electricity has been produced for more than 2 500 hours at the gasifier, based on in situ gasified woodchips as feedstock.
- The Low-Temperature Circulating Fluid Bed gasifier (LT-CFB gasifier) that is a 500 kW gasifier for "difficult" fuels with high alkali contents.
  The LT-CFB gasifier has been successfully operated on straw containing more than 12 % ash, pig manure and chicken litter.
  Also its smaller 50 kW predecessor is still operational.
- The Low-Tar gasifier (BIG) is a new fluid bed implementation of the low tar two-stage gasification process intended for large-scale two stage gasification plants.

The aim of the activities at BGC and the operational gasifiers is to contribute with knowledge and experiences to the development of the technology for thermal gasification of biomass as well as to the end-use of the gas. Examples of end-use applications for heat and power generation are:

- Stirling engines
- Steam turbines
- Gas turbines
- Fuel cells

One example of the end-use of the gas is the production of liquid alternative fuels such as:

- DME
- Methanol
- Synthetic gasoline and diesel oil

Since 1989 at BGC:

- Fundamental theoretical know-how has been developed.
- A significant base of practical experiences has been established.
- A number of instruments and dedicated test stands have been developed.
- A number of computer-based simulation tools have been developed.

3.2.1.2 Research at BGC

The research areas at BGC include:

- The two stage gasification of biomass
- The Low Temperature – Circulating Fluidised Bed gasification for difficult bio based fuels
- Internal Combustion engines fuelled completely or partly by gas from gasified wood
- Gas cleaning
- Modelling
- Fuel (biomass) properties

The two stages gasification process

The two stages gasification process is characterized by having pyrolysis and gasification in separate reactors with an intermediate high temperature tar-cracking zone. This arrangement allows for a very accurate control of the process temperature, which can be used to reduce the tar content in the product gas to an extremely low concentration – even without gas cleaning (approximately 25 mg/Nm^3).

The two-stage Viking gasifier was commissioned at DTU in the autumn of 2005 and is designed for continuous unattended operation. Later a cyclone was added to remove particulates from the hot gas stream.

Below is a picture from BGC`s web site that is schematically showing the Viking with a hot screw conveyer used as the pyrolysis reactor. Typical temperatures are shown in red.
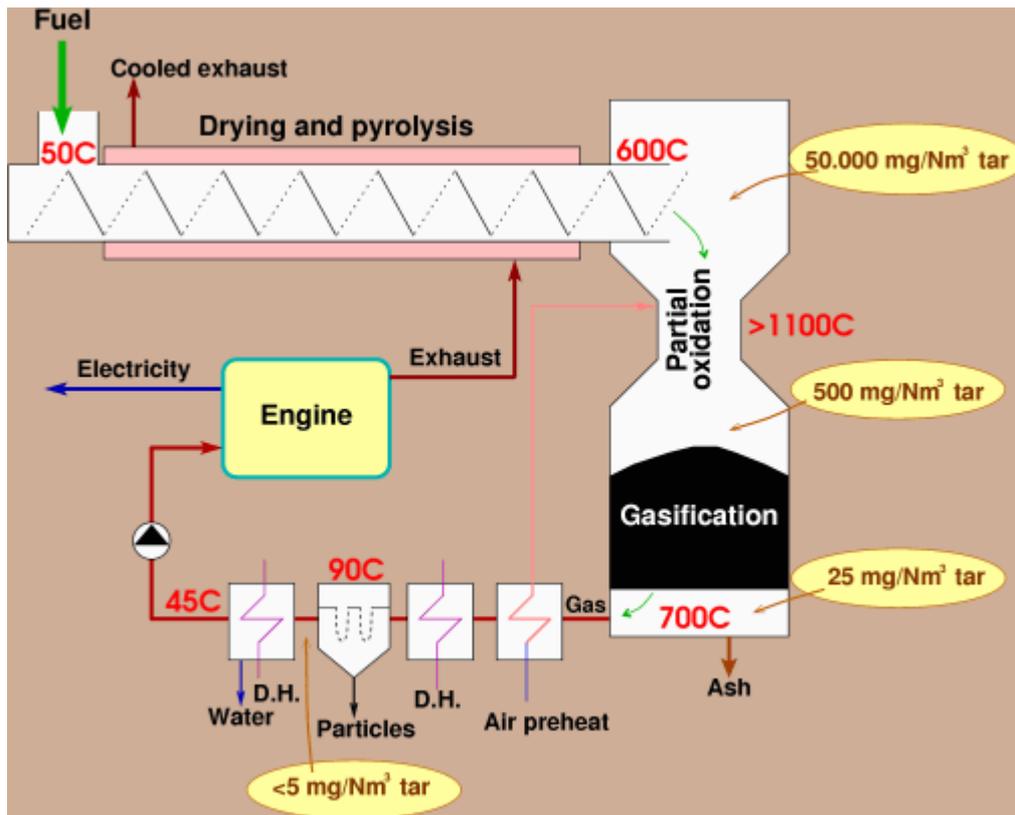
Figure 4 Two-stage gasifier

The fuel is fed directly into the screw/pyrolysis unit. The fuel can be dry or it may contain up to approximately 45 % water.

In the pyrolysis unit/screw the biomass under atmospheric pressure is heated to 600 °C with a retention time of about 30 to 60 minutes. The necessary heat for the pyrolysis comes from the exhaust gas from the engine. At this temperature the volatiles/pyrolysis gas escape as gaseous tar components, leaving dry coke. Both coke and pyrolysis gas leave the screw/pyrolysis unit and enter the partial oxidation zone.

In the partial oxidation zone, fractions of the pyrolysis gas together with air and steam reach a temperature of 1150-1400 °C. This leads to an immediate (milliseconds) and almost complete (99 %) oxidation of the pyrolysis tars that decompose into simple gases. However, soot particulates are formed in this zone.

The partial oxidation is then followed by the actual gasification, which takes place in the glowing coke bed in the lower part of the gasifier. In the coke bed the coke from the fed of biomass reacts with steam and oxygen, producing CO, CO_2, H_2 and CH_4. In the coke bed the tars are also further reduced to a level not exceeding 30 mg/Nm^3 in the product gas. In the coke bed the temperature of the product goes down from about 700 °C at the top to 600 °C at the bottom.

After the coke bed the gas is cooled down from 600 to 90 °C. Since this is a temperature well above the water dew point, condensing will be mainly avoided in the cooler and the water is instead adsorbed on and carried by the soot particulates in the gas.

After the cooler the particulates are separated from the product gas in a particles filter (bag filter) (mainly soot). The majority of the remaining heavy tars are removed from the gas, leaving less than 5 mg/Nm^3 of particulates in the gas.
After the bag filter the gas is further cooled down from 90 to 45 ^{o}C and lead to a modified diesel engine for electricity production. However, because of the high hydrogen content, the gas has also proven to be an excellent fuel for spark ignition engines.

With the use of a modern gas engine the electric efficiency probably will exceed 35 %, while the total energy efficiency will exceed 100 % [12].

3.2.1.3 The LT-CFB gasification process

In 1999 a 50 kW LT-CFB gasifier was erected at BGC. Autumn 2003 a new 500 kW LT-CFB gasifier was erected. However, the smaller and older one was still operational in 2005.

The sketch below, taken from the BGC web site, shows the concept of the LT-CFB gasifier including the intended mass flow.
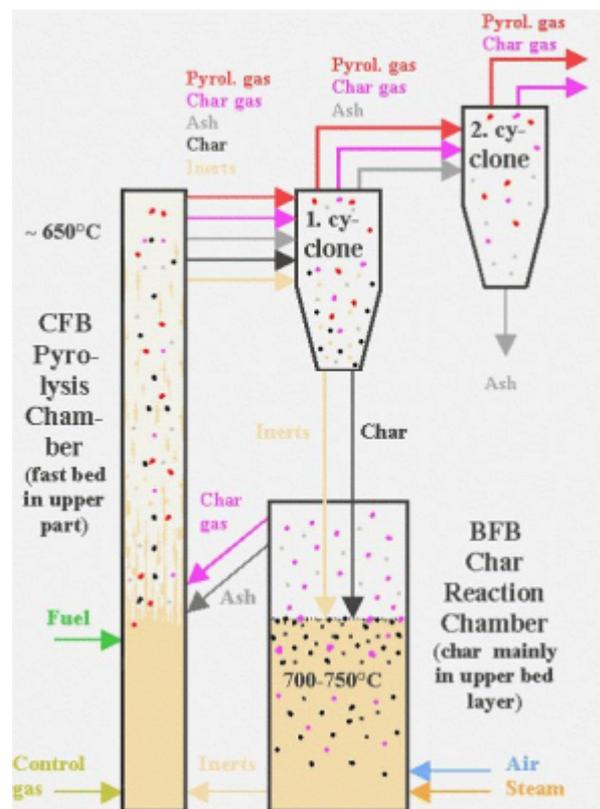
Picture 5 LT-CFB gasifier

The fuel enters the pyrolysis chamber and is pyrolysed at approximately 650 ^{o}C.

The pyrolysis is fast because of good thermal contact between the fuel and hot sand/bed material. This results inter alia in a small and highly reactive char residue.

The gas lifts the char and sand upwards in the pyrolysis chamber, and in a primary cyclone char and sand are separated from the gas and are led to the char reaction chamber.

The char is gasified in a slowly bubbling fluidised bed (BFB) in the char reaction chamber at ~730°C using air and steam.

The produced char gas is led to the pyrolysis chamber, where the gas contributes to the high velocity in the upper part. The produced small and light ash particles will not be retained by the primary cyclone, but will follow the gas stream and instead be retained by the secondary cyclone.

Silica sand is used as a heat carrier between the overall exothermic reactions during the gasification to the endothermic pyrolysis. The sand is led from the bottom of the char reaction chamber to the pyrolysis chamber and circulated back via the primary cyclone.

The intention of the LT-CFB concept is to be able to gasify so called "difficult" bio based feedstocks. So far the LT-CFB concept has only been tested on straw, pig manure and briefly on wood, but as the figure below (from the BGC web-site) indicates, the LT-CFB process might be suitable for a number of other problematic solid feedstocks.
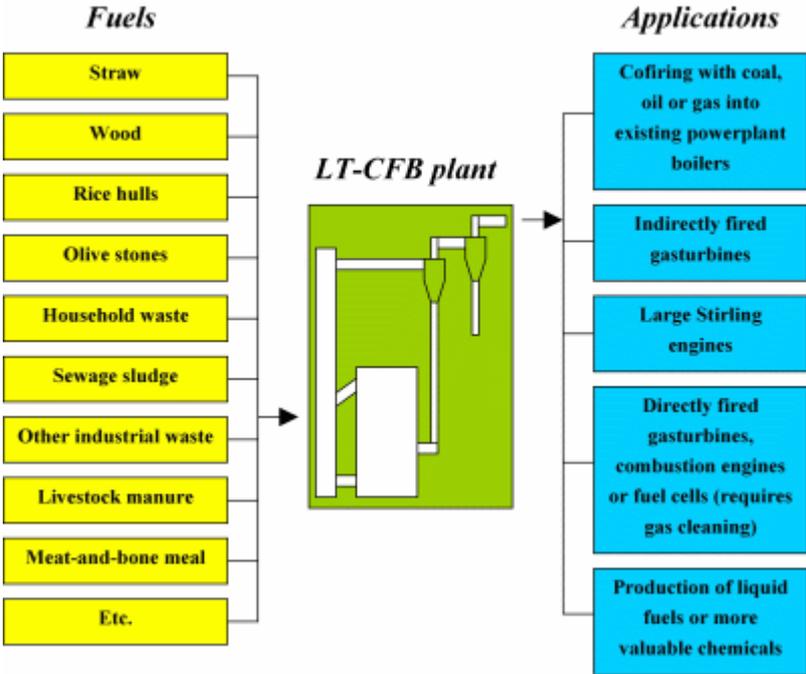
Picture 6 LT-CFB concept

3.2.1.4 The low tar BIG gasifier

The Low-Tar BIG gasifier is a new fluid bed implementation of the low tar two-stage gasification process intended for large-scale two stage gasification plants.

The two-stage gasification process will be somewhat modified compared to the Viking gasifier in order to scale up to the size of combined heat and power plants of 1 MW electricity and above.

The scaled up gasification concept combines the advantages of:

- Stage divided gasification
- Drying feedstock (biomass) with superheated steam
- Pyrolysis with superheated steam
- Partial oxidation
- Gasification with steam

Drying with superheated stem as well as pyrolysis with superheated steam are both well-known technologies.

The scaled up two-stage gasification concept can be designed as a scaled up moving bed reactor or a scaled up fluid bed reactor.

Common advantages for the scaled up gasification plant will be:

- Lower tar content
- High cold gas efficiency
- Simple gas cleaning equipment
- A stable process
- Clean flue gas that can be used for district heating in condensed mode without cleaning of condensate
- No fire hazards
- Low maximum temperatures in gasifier
- Low soot production
- Low emissions from combustion
- Well suited process for fuel with moisture content around 40 to 60 %

3.2.2 The Värnamo gasification plant, Sweden

3.2.2.1 The first R, D&D program at the Värnamo gasification plant

During the years 1991 to 1993 the Sydkraft owned pilot plant for pressurized air-blown gasification of biomass in Värnamo, Sweden, was erected. During 1993 to 1995 the plant was taken into operation and during 1995 to 1999 a demonstration program was carried out.

Besides Sydkraft, also Foster Wheeler, Electricity France (EdF) and Energi E2 were involved in the work. The project was financially supported by Elforsk AB (Birka Energi, Göteborgs Energi and Tekniska Verken, Linköping), the Swedish Energy Authority and the EU.

The gasification plant was integrated with a combined gas- and steam turbine cycle (IGCC) for electricity and heat production with a maximum electricity production of 6 MW as well as a maximum heat output of 9 MW. The total fuel effect was around 18 MW.

The goals of the demonstration program were to:

- Evaluate performance, environmental data, fuel flexibility, system solutions and separate components function and performance.
- Propose modifications of systems and components to fulfil performance and environmental requirements/demands with a satisfying accessibility and economy for future plants.
- Evaluate operation and maintenance costs of the plant, with the purpose to be able to draw conclusions concerning these items for future plants.
- Analyse, based on the results of the program, technical and economical options for the technology used.

The picture below [13] shows an overarching and somewhat simplified process scheme for the whole process from fuel loading to electricity and heat delivery. However, this picture does not include the back-to-back situated fuel production plant in which the fuel is pre-treated and dried before it is delivered to the storage silo of the production plant.
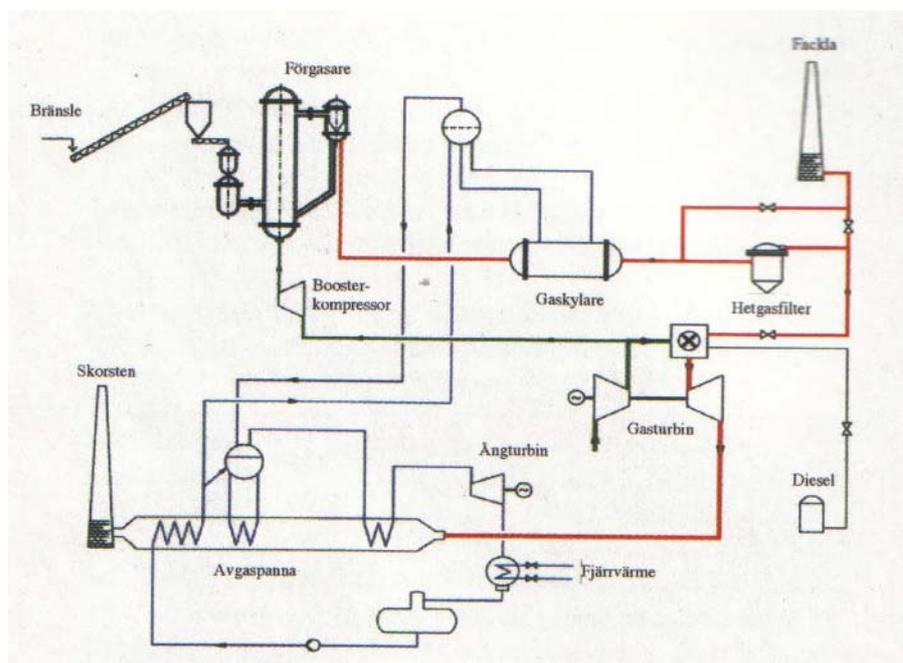
Figure 7 Process scheme, Värnamo Plant, Sweden

The wood is dried -using a flue gas dryer- to moisture content of 5 to 20 %, in a separate fuel preparation plant. The dried and crushed biomass is pressurised in a lock hopper system and is fed by screw feeders into the circulating fluidised bed (CFB) gasifier. The fluidisation medium of the gasifier is air, the operating temperature is 950 to 1000°C and

the pressure is approximately 18 bars. About 10 % of the air is extracted from the gas turbine compressor, compressed further in a booster compressor, and then injected into the bottom of the gasifier.

After the gasifier, the produced gas flows to a gas cooler and a hot gas filter. The gas cooler cools the gas down to a temperature of 350 to 400°C. After cooling, the gas enters the candle filter vessel where particulate clean up occurs. The gas generated is burning in the combustion chamber and expands through the gas turbine, generating electricity.

The figure below shows more details about the gasification plant.
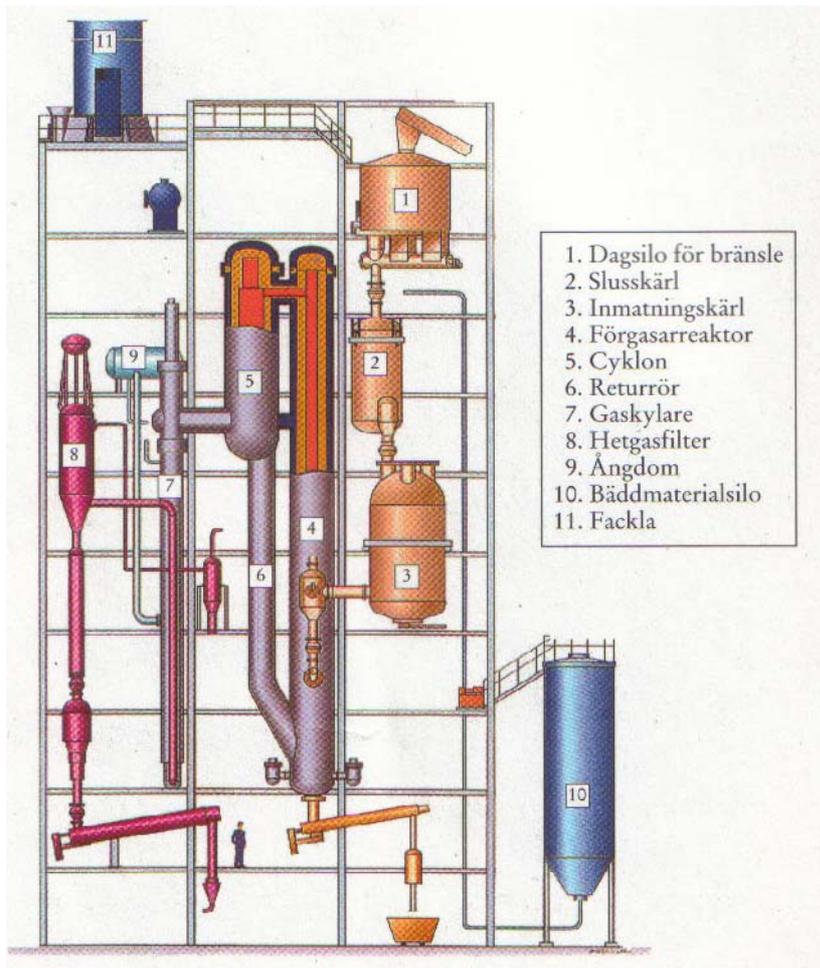
Picture 8 Gasification plant, Värnamo Plant, Sweden [13]

1. Storage silo, 2 and 3 fuel loading (lock hopper) system, 4 pre-gasifier, 5 Cyclone, 6 Gas feedback system, 7 gas cooler, 8 heat gas filter, 9 Steam production, 10, bed material silo, 11 Flare.

During the program period different fuels such as woodchips, bark, energy forest products (Salix), straw and Refused Derived Fuels (RDF) were tested.

Even though the project was operated as a R & D project, the production of heat and electricity were, during normal operational conditions, delivered to Värnamos local district heating system and electricity grid.

During the program period a number of technical and construction improvements were carried out and taken into operation. Especially interesting to mention here are modifications in the fuel loading system, the pre gasification system, the gas cooling system and the heat gas filtration system. These modifications have inter alia resulted in reduced problems with coating of the gas cooler surface and improved strength and tenacity of the material in the filters (choice of new filter material etc.).

Results and conclusions of the first R, D&D program

In general all the equipment has functioned well, although smaller adjustments have been necessary in some of the subsystems. Especially in the second half of the demonstration program the whole system has been running well and no significant problems occurred. Furthermore, the gasifier and the gas turbines have worked well with all types of fuels, even with RFD.

The accessibility was low in the beginning but during the program period became better and better, even though the types of fuels tested during the program period in general became more and more difficult to gasify.

Since the gasifier was constructed to gasify mainly forest residues, bark and wood chips, it has been necessary to make pellets of fuels with low bulk density such as straw. This pelletizing was necessary to make it possible to feed the minimum amount of fuel per time unit.

Also the ash system has been constructed based on forest residues, bark and woodchips as the main fuel, although the amount of ash when gasifying straw and RFD can be up to 5 times higher.

The table below shows the main components (vol-%) and the variation of them in the normal product gas.
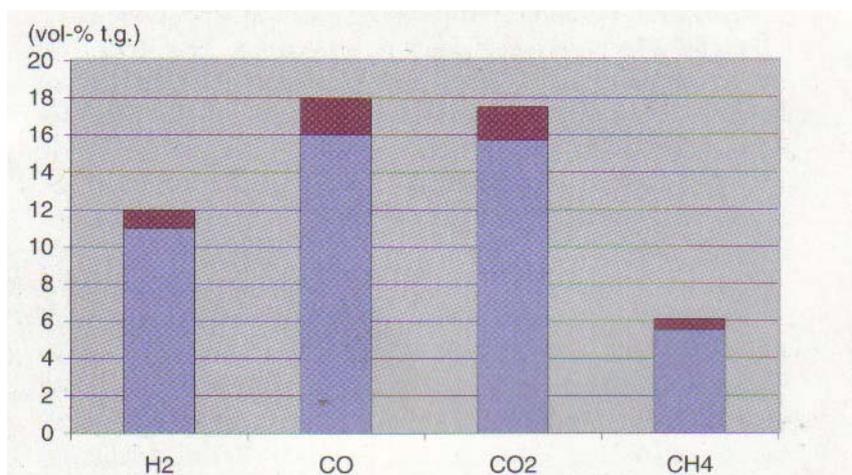
Table 3 Main components in the product gas including normal interval of variation, marked in red [13].

The particulate emissions from the gasification plant have never been higher than 5 mg/Nm^3, and during normal operational conditions they have never been lower than 1 mg/Nm^3. The emissions of carbon monoxide have during normal operational conditions (full load) been around 50 to 100 ppm, while the emissions of unburnt hydrocarbons were below 1 ppm most of the time. Concerning nitrous emissions, the level of these emissions is depending on the amount of nitrogen in the fuel, which has resulted in emissions levels between 50 and 150 ppm depending on the fuels tested.

Based on the results from the Värnamo project, it is concluded (in the report) that gasification of biomass for the production of heat and electricity is a good opportunity for the future, but of course it is very much dependent on the price of fossil fuels.

The results achieved can be summarised as follows:

- High pressure technology works
- Gas produced can be burnt in a gas turbine under stable conditions
- Hot gas filtration is efficient and reliable
- Technology is capable of gasifying "difficult" fuels
- No harmful effects identified on gas turbine or other components
- NOx emissions are slightly high at present for some fuels, but solutions are available
- Emissions of hydrocarbons (HC) are very low and emissions of dioxins are below detection level, even for chlorine rich fuels
- IGCC is competitive with conventional biomass technology for condensing applications, at today's fuel cost
- Biomass gasification technology is highly suitable for retrofit to existing IGCC

However, items that have to be further developed -according to the project and the report- are for example:

- Pressurizing of the fuel
- Gas cooling
- Inert gas feeding
- Choice of proper gas temperature in the heat gas filters
- Technical measures to reduce the tar and coal amount in the filter ash
- New ways/measures to reduce the emissions of primarily nitrogen oxides

The Värnamo plant was shut down in the year 2000 after the test program had been completed, because revenues from the sales of power and heat did not cover the operating costs.

3.2.2.2 The second R, D&D program at the Värnamo gasification plant - The CHRISGAS project

After the year 2000, the question what would be the best use of the unique Värnamo plant facility has been discussed. These discussions have inter alia included:

- Using the plant for further IGCC developments
- Rebuild the facility to produce synthesis gas

An analysis by the Swedish government identified the development of synthesis gas production from biomass as a key technology for large scale, cost efficient production of liquid bio fuels. In this context the Värnamo plant was discussed as a possible R&D centre for gasification studies. In order to decrease the economic risk for private stakeholders it was concluded that the availability of the plant in such a case must be guaranteed by public funding. In order to do this, the model proposed was to establish a non-profit organisation under the control of an educational institution. After discussions, the University of Växjö accepted to take the lead with the assignment to establish a European Biomass Gasification Centre at the Värnamo plant, The Växjö Värnamo Biomass Gasification Centre (VVBGC). In 2004, the EC 6th Framework program and The Swedish Energy agency jointly founded the CHRISGAS project.

The aim of the project is to demonstrate the production of clean hydrogen-rich synthesis gas from biomass.

The CHRISGAS project is scheduled to run for 5 years, beginning September 2004.

At the heart of the project is the Växjö Värnamo Biomass Gasification centre (VVBGC).

16 partners representing industry and research from 7 EU member states are involved in the project:

- University of Växjö, Sweden
- TPS Termiska processer, Sweden
- Royal Technical High School, Stockholm, Sweden
- Paul Schumacher, Germany
- Forschungszentrum Jüllich, Germany
- TK Energi, Denmark
- Centro de Investigaciones, Energéticas Medioambientales y Technológicas, Spain
- TU Delft, The Netherlands
- Valutec, Finland
- Växjö Värnamo Biomass Gasification Centre, Sweden
- Universitá di Bologna, Italy
- Catator, Sweden
- S.E.P. Scandinavian Energy Project, Sweden
- KS Ducente, Sweden
- Linde – Linde Engineering Division, Germany
- Växjö Energi, Sweden

In accordance with the EC 6th Framework Program, the objective of the CHRISGAS project is to bring together and organize the skills and expertise within Europe in the field of synthesis gas production for synthetic vehicle fuels on the basis of renewable energy sources.

The main Scientific and Technological objective of the project is to manufacture within a 5-year period, and at scale of 18 MW thermal, a clean hydrogen-rich gas from biomass.

This could be expressed somewhat more detailed, as:

- Conversion of solid bio fuel into a medium calorific value gas by gasification at elevated pressure using a steam and oxygen mixture.
- Purification of generated gas at high temperature e.g. in a high temperature filter, and by catalytic or thermal steam reforming of not only tars, but in particular of methane and other light hydrocarbons, to generate a raw synthesis gas consisting mainly of carbon monoxide and hydrogen as energy carriers suitable for conditioning of the hydrogen rich raw synthesis gas to the quality stipulated for synthesis gas.
- Development of the feed system based on a piston feeder.
- Operating the Värnamo plant on different types of solid bio fuel feedstocks.

The intermediate product is seen as the first step towards the production of commercial quality hydrogen, vehicle fuels and others; a new, renewable, affordable and clean energy carrier both for stationary and transport applications that will be widely exploited after 2010.

Furthermore, the following criteria have been proposed as quantitative targets in the CHRISGAS project to assess progress towards the scientific and technical objectives:

Table 4

	At the end of year 3	At the end of year 5
Demonstration of biomass feed capacity of plant (tonne/hr)	> 0.5	> 2
Demonstration of raw synthesis gas operation capacity (Nm^3/hr wet gas)	> 500	> 3 500
Gas quality, H_2 equivalent (H_2+CO), (% of dry N_2 free gas)	> 20	> 50
Hydrocarbons (CH_4 and above) in gas (% of dry N_2 free gas)	< 10	< 5
Minimum duration of single measurement period (hours)	8	36
Total accumulated operating hours	100	2000

In the CHRISGAS project other activities such as research-related networking, training and dissemination, as well as socio-economic research on the impact of a commercially sized vehicle fuel plant in a city and the non-technical market obstacles to exploitation are also included.

Examples of desktop studies to be included under the frame of the CHRISGAS project are:

- Studies, based mainly on experimental results obtained in the project, of the conditioning of the produced gas to a quality suitable for manufacture of a variety of other potential products.

The conditioning is to be accomplished by catalytic water gas shift to adjust the CO/H_2 ratio, catalytic hydrogenation of minor contaminants followed by removal of carbon dioxide and other acidic gases in a conventional wash system or in novel selective processes for the removal of sulphur.

- Studies of the production of automotive fuels from various bio fuels, at the scale and cost representative of typical biomass fuel chains in various regions in Europe, as determined by specific studies that will be performed within the project, thereby giving realistic data for the future production potential on an European scale.

- Studies to estimate the socio-economic impact of the technology in terms of emissions, both on local air quality as well as on the impact on national and globe scale, e.g. regulated emissions and greenhouse gases (considering also its´ potential with respect to the EU environmental goals as expressed in response to the Kyoto Agreement, the directive on Bio fuels and other renewable fuels for transport (2003/30/EC), etc).

3.2.3 Black liquor gasification, Sweden

3.2.3.1 Background

Black liquor from a craft pulp industry contains approximately 15 to 17 % solids, mostly consisting of dissolved organics from the wood and spent pulping chemicals. The organic material originates from dissolved lignin and carbohydrates. Today the black liquor from craft pulp industries is burnt (similar to heavy oils) in concentrated form (over 70 % solids) in the recovery boiler.

Table 5 Typical Black liquor composition [1]

Component	**% Mass**
C	35.7
H	3.7
S	4.4
O	4.4
Na	35.8
K	19.0
Cl	1.1
N	0.3
Total (%)	100.0

Table 6 Combustion Characteristics [1]

Bl, Dry Solids	% Mass	80 %
HHV	MJ/kg, DS	14.50
NHV	MJ/kg, DS	12.29

The main purpose of burning the black liquor is to recover chemicals for the cocking cycle in the pulp mill. However, energy will be produced as heat/steam, as a by-product from the

cooling of the recovery boiler. As much heat as possible is recovered in the pulp mill, while the surplus heat either is pumped out with the cooling water, or when possible it (steam) is used for electricity production, district heating or in neighbouring industries etc.

Figure 9, typical flow diagram of the chemical recovery cycle in a craft pulping process [14].
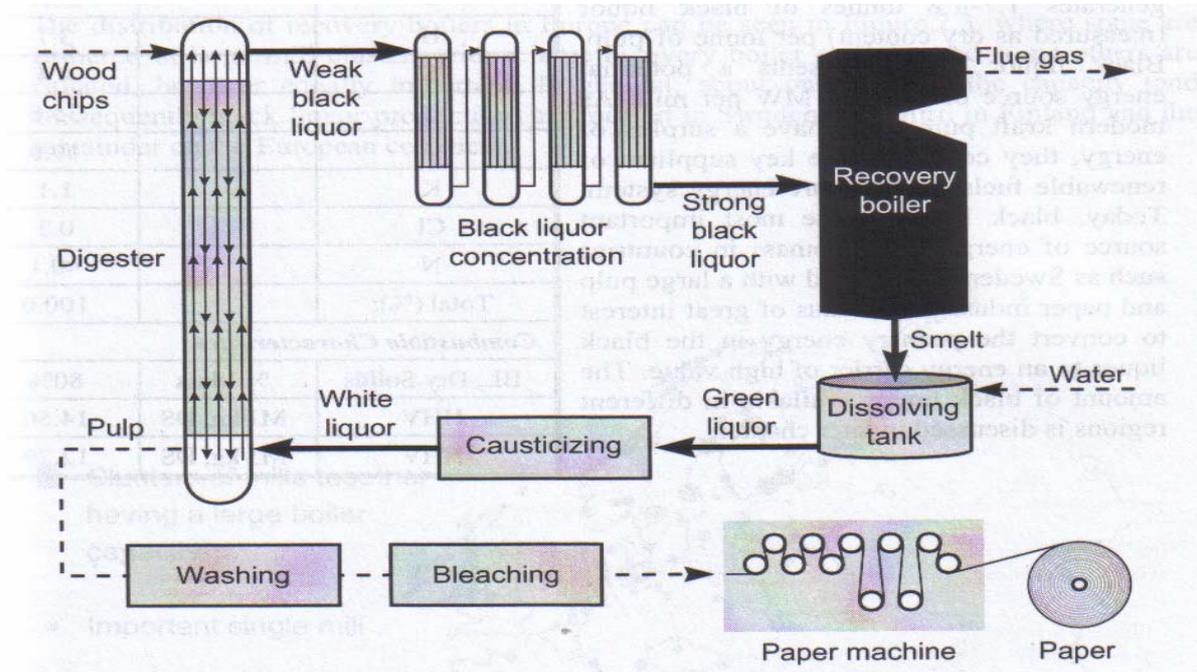
In 2002 there were more than 1260 pulp and paper mills in Europe, producing about 91 million tonnes of paper and board (with an annual turnover of more than 400 billion Euros). A pulp mill that produces bleached craft pulp generates 1.7 to 1.8 tonnes of black liquor (dry content) per tonne of pulp. The black liquor represents a potential energy source of 250 to 500 MW per mill. On a worldwide scale, the pulp and paper industry in 2002 processed about 170 million tons of black liquor (dry solids) per year. This amount of black liquor represents a total energy content of 2 EJ, which makes black liquor a significant biomass fuel not only in Sweden, but also worldwide. [14]

As a modern craft pulp mills has a surplus of renewable energy, they could become permanent suppliers of renewable energy in the energy system, but then the energy first has to be converted into a form that suits the existing energy system (preferably electricity) or an energy form suitable for automotive use (liquid or gaseous).

The estimated black liquor production -including a projection to 2025 based on the previous 35 years of annual production records- is shown below for Europe and for the world, according to FAOSTAT 2001 [14].

Table 7 Estimated world black liquor production
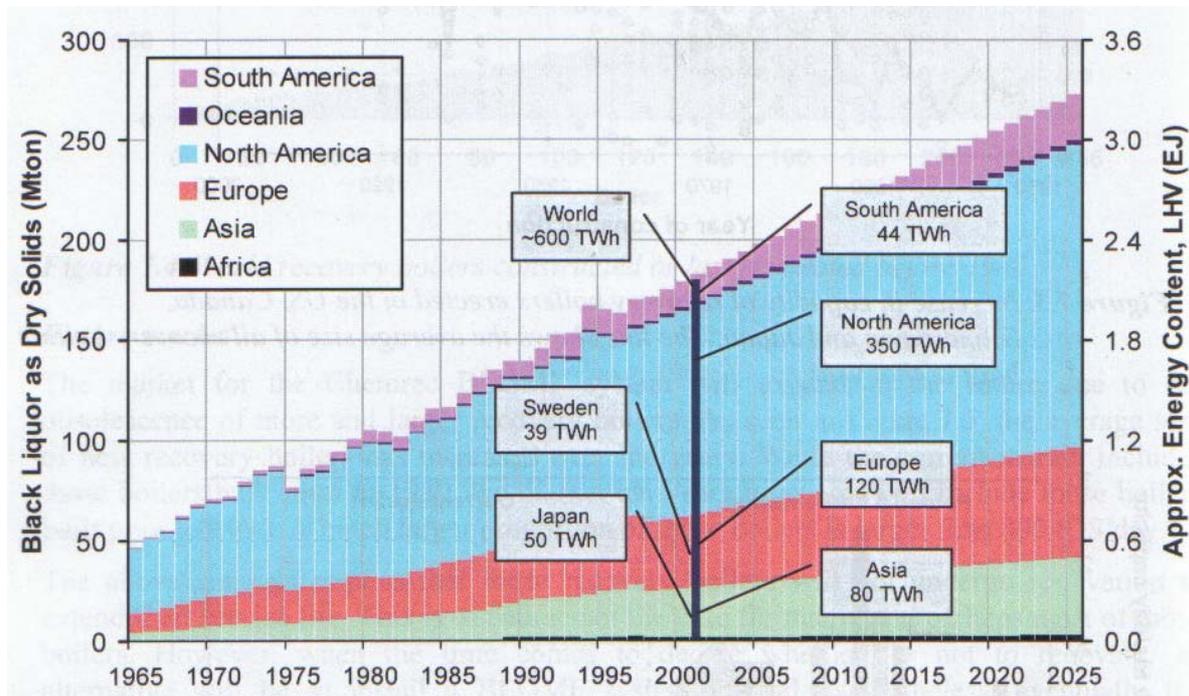
Table 8 Estimated EU black liquor production
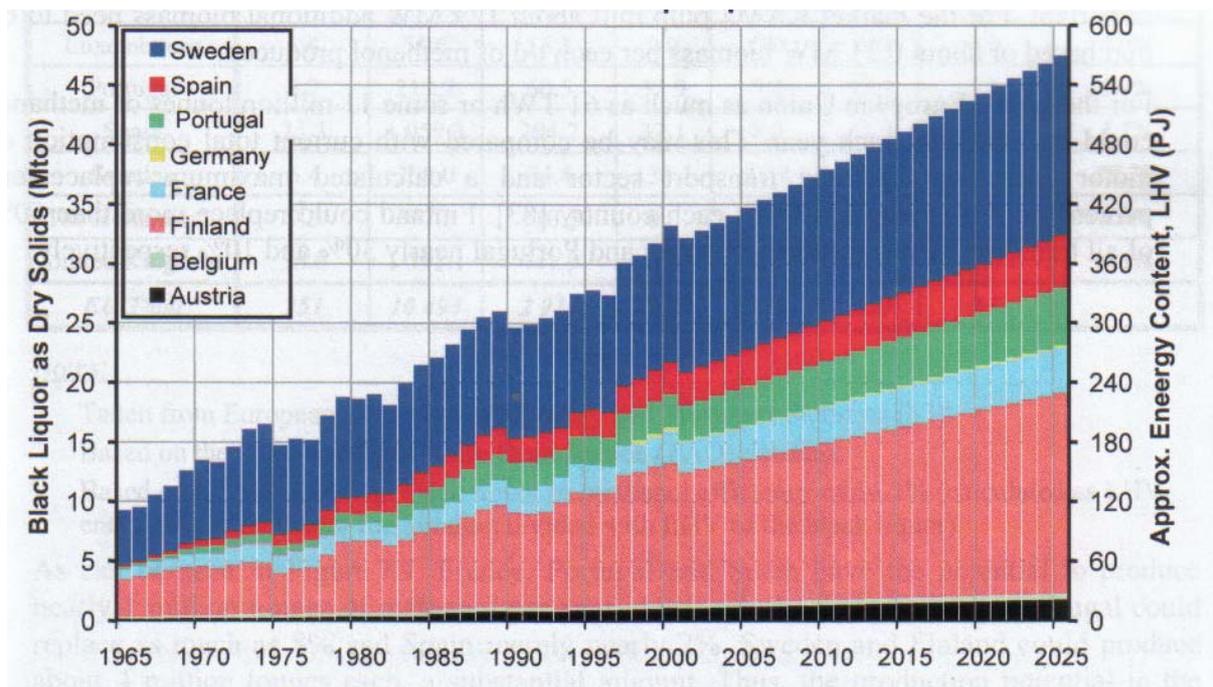
If it would be possible to convert the primary energy in the black liquor into a high value energy carrier such as electricity or a liquid or a gaseous vehicle fuel, this would certainly increase the possibility to recover much more of the energy content in the black liquor and it would contribute substantially to the total supply of energy. This conversion could be done by gasifying the black liquor, followed by use of the gas in a gas turbine for electricity production or use of the gas (after cleaning, shifting and reforming the raw gas to a synthesis gas) for production of vehicle fuels such as dimethyl ether (DME), methanol, synthetic gasoline or synthetic diesel oil. At the same time, there would be a certain possibility to increase the total production capacity of domestic produced bio based vehicle fuels.

3.2.3.2 Black liquor gasification (BLG)

Black liquor gasification as an option to produce gas for gas turbines or synthesis and later also for the production of automotive use/vehicle fuels has been investigated in Sweden for a long time. Bergholm developed the first systems for gasification in 1963.

In the BLG system the recovery boiler is replaced with a gasification unit and the evaporated black liquor is gasified in a pressurised reactor under reducing conditions, and the generated gas is separated from the inorganic smelt and ash. Further the gas and smelt are cooled and separated. The smelt is dissolved and used to form green liquor, while the raw fuel gas is further cooled, water vapour is condensed and the heat release from this step is used to generate steam. After cleaning the gas is a dry fuel gas that is almost sulphur free and that mainly consists of carbon monoxide (CO), hydrogen (H_2) and carbon dioxide (CO_2).

Black liquor gasification combined Cycle (BLGCC)

In a BLGCC system the synthesis gas is used in a gas turbine. The hot flue gas from the gas turbine is used to generate steam in a waste heat boiler and the generated high-pressure steam is used in a steam turbine for additional power generation [1].
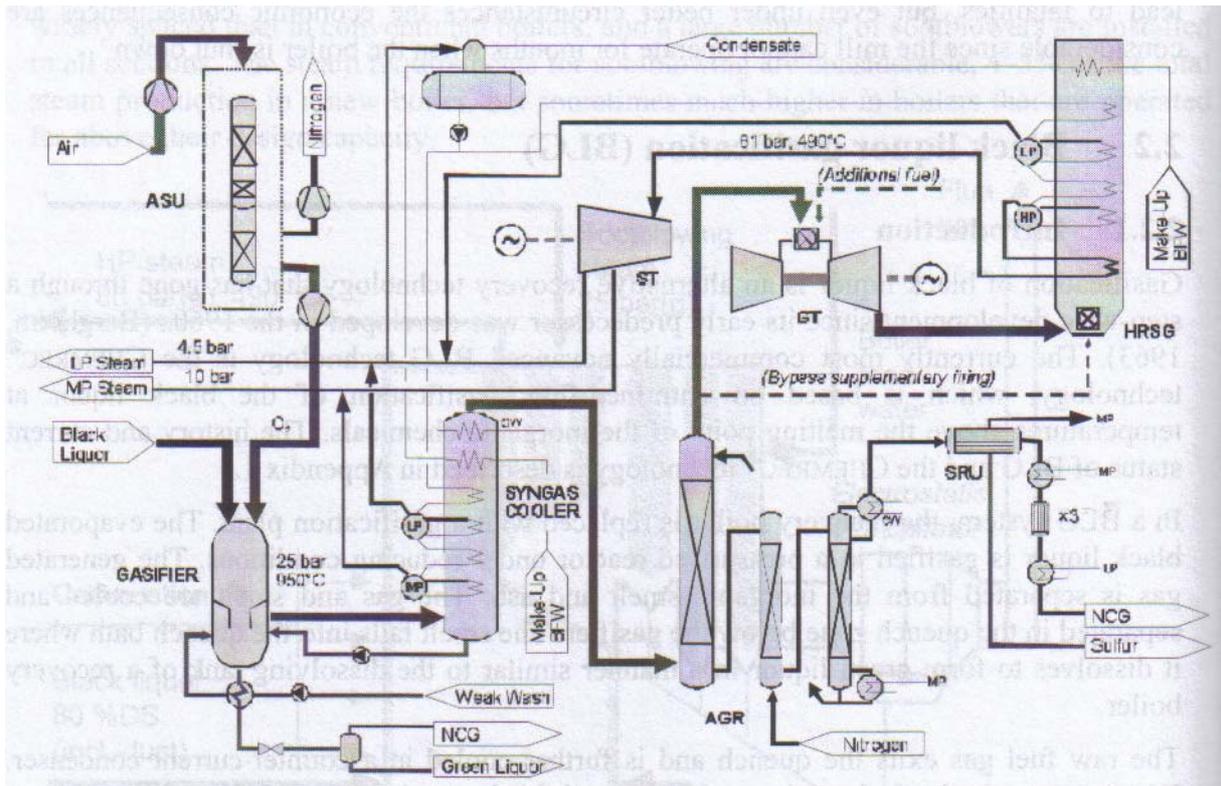
Figure 10 BLGCC concept

The use of a BLGCC compared to a recovery boiler system increases the potential to generate power and reduces the heat surplus of the craft mill.

Research and development on black liquor gasification has been an item of interest in Sweden for a long time. Since 2001 there is a national research program in Sweden, which is co-ordinated by ETC and funded by the Swedish Energy authority, MISTRA, Vattenfall, the regional county Board in Norrbotten and different forest industry actors. The main goal of the research program is to:

- Eliminate knowledge gaps that might prevent a large-scale introduction of the technology.
- Provide underpinning know-how that creates confidence in the technology.

Crucial research topics have been defined as:

- Conversion of all organic carbon
- High quality green liquor production
- Durable materials for contaminant
- Gas cleaning
- Pulp mill integration
- Up scaling

At the Smurfit Kappa craft pulp mill in Piteå in the Northern part of Sweden, a research plant on black liquor gasification has been built and started operation in September 2005. The capacity of the DP 1 plant is 20 tDS/24 hours.

3.2.3.3 Black liquor gasification with motor fuel production (BLGMF)

BLGMF is a system for processing black liquor and intended to replace the conventional recovery boiler combined with the production of a synthesis gas that is suitable for the production of different automotive fuels.

The black liquor together with oxygen is gasified to produce a raw gas and a molten salt smelt. The gas and the smelt are cooled and separated and the smelt dissolves to form green liquor, while the raw gas is cooled, water is condensed and the heat from that step is used to generate steam. After this step the gas is cleaned from sulphur and other contaminants and, if necessary after shifting and reforming, the gas is pressurised and used for the production of synthetic fuels.
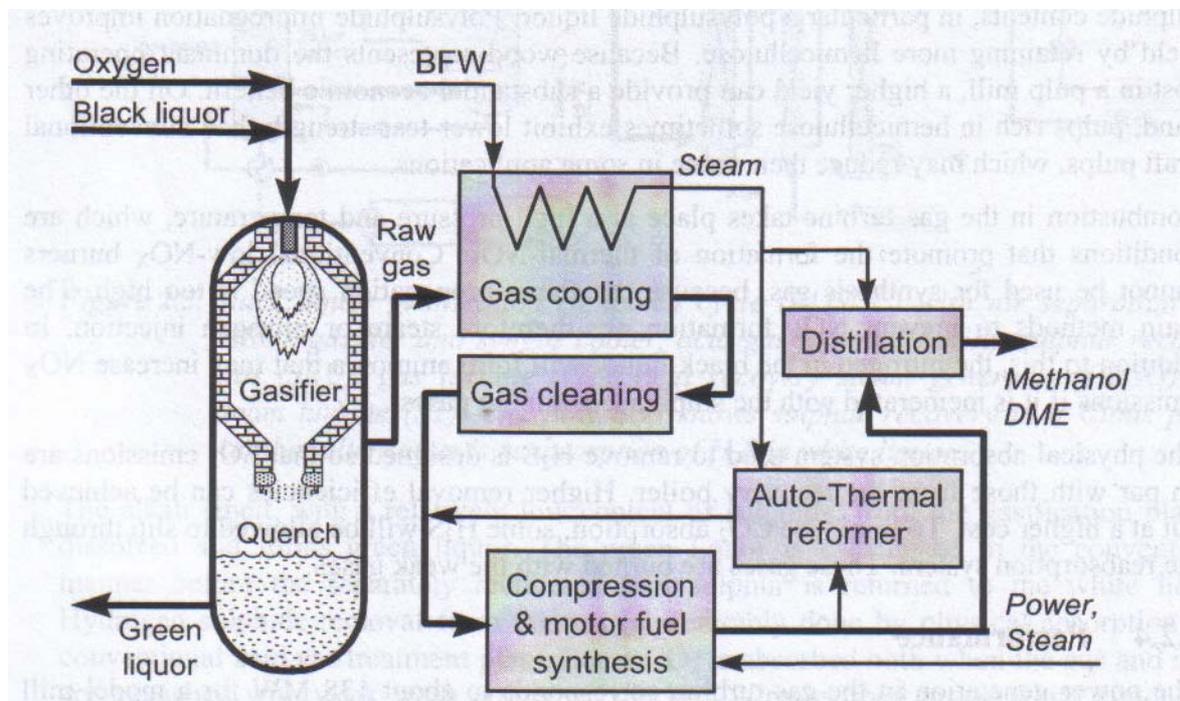
Figure 11 Black liquor gasification with motor fuel production (BLGMF)

3.2.3.4 BLGMF project 1, Sweden

In 2001 a project to investigate black liquor gasification combined with motor fuels production was initiated within the EU ALTENER II programme, contract No. 4.1030/Z/01-087/2001. The project "Black Liquor Gasification With Motor Fuels production" BLGMF was started in February 2002. Behind the project was a consortium of industries, research institutes, oil distribution companies, automotive manufacturers and consultant companies such as Nykomb Synergetics, Chemrec, Methanex, OK/Q8, Volvo and Ecotraffic. In December 2003 the results of the project were reported [1].

The main short-term goal of the project was to establish preliminary engineering and cost estimates for calculating the economically preferred technical option for a BLGMF system.

Some other goals of the project were to:

- Study the process integration of black liquor gasification with a motor fuels production system, with an existing and a future modern ecocyclic pulp mill (where all energy and by-products are recovered with today's most efficient technology) for the production of renewable energy sources in the form of CO_2 neutral fuels for automotive use.
- Study technical and economical feasibility of black liquor gasification integrated with production of DME and methanol as fuels for automotive use.

The results of the project are based on a comparison with a reference mill with a capacity of 2000 Adt/day of pulp and with a modern recovery boiler producing electricity for export.

As a result of the investigations it was inter alia concluded that:

- The biomass/black liquor logistics are extremely simplified when the raw material for fuel production is handled within the ordinary operations of the pulp and paper plant.
- The process is easily pressurised, which enhances fuel production efficiency.
- The produced synthesis gas has a low methane content, which optimises the fuel yield.
- The pulp mill economy becomes less sensitive to pulp prices when the feedstock is diversified with another product.
- Gasification capital costs are shared between recovery of inorganic chemicals, steam production and synthesis gas production.

In the project production of two possible automotive fuels was investigated: dimethyl ether and methanol. The resulting biomass-to-fuel energy efficiency -when only biomass is used, as an external energy source- was as high as 66 % for methanol and 67 % for DME.

Tabel 9 Summary of consumed and produced energy products (BLGMF project)[**14**]

Fuel options	Methanol	DME
Biomass consumption	414 MW	408 MW
Black liquor consumption	487 MW	487 MW
Fuel production	273 MW	275 MW
Energy efficiency (LHV)		
Black liquor to fuel	56 %	56 %
Biomass to fuel	66 %	67 %

The plant also generated additional electricity for internal use.

It was concluded in the project that in 2002 there were 236 recovery boilers in the world that had not yet been rebuilt during the last 20 years, and thus might be suitable for replacement with gasification technology. However, since the majority of these recovery boilers had a capacity less than 500 to 600 tDS/day, they are not suitable for a replacement of the recovery boiler with gasification technology on which the study has been based, the tDS/day Chemrec BLGMF technology.

In 2003, the actual market for replacement of old recovery boilers with a capacity over 800 tDS/day was 57 boilers, about half of which were situated in the USA and the majority of the remaining ones were located in either Canada or Japan.

In the project report it was further concluded that for the whole European Union approximately as much as 61 TWh -or some 11 million tonnes- of methanol could be produced per year. On a national basis it was calculated that in 2002 as much as 50 % of all transportation fuels in Finland, 30 % of all transportation fuels in Sweden and 10 % of all transportation fuels in Portugal could be replaced by bio fuels (methanol) produced with black liquor as feedstock. Sweden and Finland could produce about 4 million tonnes each in 2002.

For each tonne of methanol produced, about 1.5 tonnes of carbon dioxide could be saved with an average value of 85 % carbon in 1 tonne petrol and with energy content of 11.626 MWh.

Outside Europe, Canada had in 2002 a production potential of more than 7 million tonnes of methanol, which at that time was equal to a reduction potential concerning diesel oil and petrol of approximately 7 %.

The 2002 figures for the USA were calculated to be 28 million tonnes of methanol and 2.2 % replacement of diesel oil and gasoline. The low replacement figure is a result of the high gasoline consumption in the USA.

3.2.3.5 BLGMF project 2, Sweden

As an additional and second step to the BLGMF project described above, and as a result of the growing interest in synthetic fuels, in a follow up of the first EU-ALTENER project the possibility to produce FT-fuels from gasified black liquor has been studied.

The study has been carried out partly under the framework of the Swedish Energy Agencies program on alternative fuels (FALT), with NYKOMB Synergetics as project manager. A consortium including NYKOMB Synergetics, Structor Hulthén & Stråth, STFI Packforsk and Statoil Lubricants carried out the work. The project was started in May 2003 and completed in December 2005.

In the BLGMF 2 project, the biomass to fuel efficiency calculation for DME and methanol from the BLGMF 1 project was supplemented with calculations for a Fischer-Tropsch diesel production with naphtha as by-product. The calculations for the FT-fuel were based on the same black liquor capacity as for the calculation for DME and methanol. The results of the BLGMF 2 project are also based on a comparison with a reference mill with a capacity of 2000 Adt/day of pulp and with a modern recovery boiler producing electricity for export.

The resulting biomass to fuel energy efficiency -when only biomass is used as an external energy source- was estimated to be 43 % for the FT-diesel and 65 % for all FT-products (diesel fuel + naphtha).

Table 10 Summary of consumed and produced energy products (BLGMF 2 project)

Fuel options	Methanol	DME	Ft-Diesel
Biomass consumption	414 MW	408 MW	378 Mw
Black liquor consumption	487 MW	487 MW	487 MW
Fuel production total	273 MW	275 MW	244 MW
Fuel production total	410 600 t/year	286 000 t/year	109 700 t/year (+ 56 200 ton naphtha per year)
Energy efficiency (LHV)			
Black liquor to fuel	56 %	56 %	33 % diesel + 17 % naphtha
Biomass to fuel	66 %	67 %	43 % diesel + 22 % naphtha

The calculated BLGMF 2 plant generates steam, which can be used in the pulp mill. Falling bark and purchased biomass as well as off gas from the FT-process/reactor are burnt in the power boiler, which was assumed to be sized to meet the complete steam need of the BLGMF 2 plant and the pulp mill (that generates the black liquor that is used). In the calculations the power boiler also produces electricity. In the methanol and DME cases calculated in the BLGMF 1 project this electricity covered the electricity need in the BLGMF 1 plant. However, in the FT-diesel (BLGMF 2) plant, additional electricity has to be added to meet the need of the plant. In all three cases, external "green" electricity must be purchased to cover the electricity need of the pulp mill.

It is important to notice that the calculations for the FT-diesel production are considerably more complicated and also based on assumptions, rather than the vendor's calculations that are used for the methanol and DME cases. Furthermore it is important to notice that these figures might have been different if the product mix would have been optimised for naphtha/gasoline. Also the choice of reactor type and catalyst might influence the total energy output.

4. Cleaning

Synthesis gas can be produced by gasification of solid material and by reforming of natural gas. Synthesis gas from shifted and reformed natural gas is mostly very clean, while synthesis gas from gasification of coal and biomass contains different kinds of contaminants such as:

- Particulates
- Alkali compounds
- H_2S
- HCL
- NH_3
- HCN
- Tar

 [15].

Such contaminants can poison the catalyst and consequently they can reduce the efficiency of the FT-process. Some of the contaminants are also poisonous to catalysts that are used in the shift and reforming processes.

Tars (which could be described as larger hydrocarbons) can -if allowed to- condensate on the system (downstream) coat surfaces and they may enter pores in filters and adsorbents.

To avoid these problems the synthesis gas has to be cleaned from contaminants and the concentration of the tars must be below the condensation point of the tars at the pressure in the FT-synthesis reactor.

Below, some approximated maximum levels of contaminants in synthesis gas to be used in Fischer-Tropsch reactors that can be found in the literature [11].

Table 11 Contaminants in synthesis gas

Contaminant	Maximum concentration PPB
Particulates	0
Tars	0
HCN+NH_3	20
H_2S+COS	10
HCL	10
Alkalis	10

To reach these levels, gas from gasified biomass often has to be cleaned with an efficiency of more than 99.9 %.

For example the average particle load in the gas from gasified woodchips is about 500 mg/Nm^3. When gasifying woodchips, the particulates in the gas contain predominantly sub

micron soot (>90 %), while the remainders are biomass /wood residues and traces of ash (3 %).

A number of technologies can be used to clean the gas. The two most important production technologies are:

- Wet low temperature gas cleaning
- Dry hot gas cleaning

Wet low temperature gas cleaning, which is the most commonly used technology, can be described by the schematic set up below [15, 16].

| Tar Cracker | $\Rightarrow$ | Cyclone | $\Rightarrow$ | Bag filter | $\Rightarrow$ | Scrubbers NaOH H_2SO_4 | $\Rightarrow$ | ZnO Guardbe |

Wet gas cleaning can be said to be the conventional way of cleaning synthesis gas for use in gas turbines.

However, when the synthesis gas is to be used for FT-synthesis, there will be much more stringent requirements concerning contaminants, see the table above.

Wet and dry gas cleaning may be used to reach these levels when it is combined with extra cleaning steps, such as active coal filters.

Dry hot gas cleaning consists of several filters and separation units and is a technology in which the high temperature of the synthesis gas can at least partly be maintained throughout the cleaning process. This will result in higher energy efficiency and it may sometimes also result in lower operation costs. The maintained high gas temperature will be an advantage when the gas is to be shifted or reformed, since this operation requires high temperature gas. However, if the gas is to be fed into the FT-synthesis reactor, the gas has to be cooled down to a temperature of about 200 ^{o}C, which results in less advantage using this technology. Currently there are probably no dry hot gas-cleaning units in commercial use in the world.

This technology can further be combined with tar removal or tar cracking. The tars contain a lot of potential CO and H_2 and can preferably be cracked into smaller hydrocarbons, but since the tars themselves have a value on the market they can also be sold after they have been removed from the gas.

There are mainly three methods for tar removal/cracking [17]:

- Thermal cracking
- Catalytic cracking
- Scrubbing

At temperatures above 1100 ^{o}C, tars are more or less destroyed without a catalyst. Usually this is done by the addition of steam and oxygen. Some drawbacks of this technology are material problems, soot production and low thermal efficiency.

Catalytic (dolomite or Nickel) cracking seems to be best applied in secondary beds and has none of the problems that will occur in thermal cracking.

At low temperature, the tars can be removed by advanced scrubbing using an oil-based medium [18]. The tars can further be stripped from the scrubber oils to be re-burned in the gasifier.

5. Reforming

Reforming is the process in which methane (CH_4) is converted into carbon monoxide (CO) and hydrogen (H_2), with the help of steam. CH_4 is one of the by-products when processing synthesis gas into synthetic fuel by Fischer-Tropsch technology, but the output of CH_4 can be reduced to a rather low level depending on reactor design and feedstock. The need of a separate reforming process can then be reduced to a very low level.

However, when natural gas is used as feedstock the gas preparation will certainly consist of reforming processes.

The key reactions in steam reforming are:

(1) $CH_4 + H_2O \leftrightarrow CO + 3H_2$

(2) $CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$

(3) $CO + H_2O \leftrightarrow CO_2 + H_2$

(4) $C_nH_m + nH_2O \leftrightarrow nCO + (n + {}^m/_2)H_2$
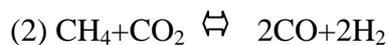
Before starting the reforming step, the gas has to be "cleaned" from impurities such as higher hydrocarbons, high content of CO_2 and different sulphur compounds. It is important to reduce the amount of sulphur components as far as possible, since they are poisonous for the FT-catalysts later in the FT-Synthesis process.

After gas purification there are different technologies that can be used to reform the natural gas to a FT-synthesis gas.

Pure steam reforming is perhaps not the best choice for a large gas to liquid process plant using FT-technology, since steam reforming tends to have a poor scale economy compared to other processes based on partial oxidation and air separation. Besides that, in the steam reforming process the energy need is high and it may result in a gas with a too high (for the FT-synthesis process) H_2/CO ratio (2:1 is preferred).

This is the main reason why in general the adiabatic oxidative reforming technology is preferred. In the adiabatic oxidative reforming the heat for the reforming reactions is supplied by internal combustion. The benefits of using adiabatic oxidative reforming instead of steam reforming are inter alia that the H_2/CO ratio will be closer to the optimal value and that much larger single stream units are possible. Additionally, adiabatic oxidative reformers are rather compact units compared to other types of reformers.

However, different types of steam reforming or pre-reforming might play a role in optimised gas to liquid plants. The most commonly used technologies in this case are:

- Adiabatic pre-reforming
- Fired tubular steam reforming

- Heat exchange steam reforming

Adiabatic pre-reforming has been used in modern synthesis gas production for more than 25 years. Today this technology is used in the chemical process industry for example. In the process higher hydrocarbons, when in contact with a relevant catalyst, are converted by reaction number 4 above. The optimal operating conditions in an adiabatic pre-reformer depend on the type of feedstock as well as on the application. The pre-reforming process is exothermic for heavy feedstocks such as naphtha, while being endothermic for lighter feedstocks such as natural gas [6].

The catalyst for the adiabatic pre-reforming process is often based on nickel. A low operation temperature requires catalyst with a high surface area, which has to be taken into account when designing the catalyst.

A gas to liquid plant tends to be operated at a low H_2O/C ratio to obtain optimal economics of the process. However, that will increase the risk of formation of carbon on the catalyst in the pre-reformer, which has to be taken into account when designing the plant in combination with the reforming step.

Steam reforming is -when it comes to full-scale industrial use- mainly carried out in fired heaters with catalyst filled tubes. But also so called 'heat exchange reformers' may be used. Heat exchange reformers are heat exchangers with catalyst filled tubes. In both cases heat is added to generate the process.

The main issues when constructing a steam reformer are the design and adaptation of the:

- Tubes and burner arrangement
- Inlet and outlet systems
- Tube design
- Burner characteristics

When it comes to design there are a number of different main types. For example the burners may be side-, top- or bottom-fired. Also when it comes to the in- and outlet systems as well as the burner design etc., there is a number of different solutions, depending on the special conditions that apply in each case.

A heat exchange reformer is a steam reformer where the heat required for the reaction is predominantly supplied by convective heat exchange, which can be supplied from any kind of available hot gas. This is mostly hot process gas.

Heat exchange reformers can be divided in three different types that are available on the commercial market:

- Straight through tubes
- Bayonet tubes
- Mixing of heating and product gas before heat exchange

The last type can of course only be used when the desired product gas is a mixture of the heating gas and the product gas from the catalyst in the heat exchange reformer.

When using heat exchangers that are heated by process gas one problem is how to avoid metal dusting corrosion on the heat transfer surface.

Other reforming technologies for the preparation of synthesis gas are inter alia:

- Homogeneous partial oxidation (POX)
- Heterogeneous catalytic partial oxidation (CPO)
- Auto thermal reforming (ATR)

In POX the oxidant and the hydrocarbon feedstock are mixed in a reactor where they, at a high temperature, can react homogeneously. Even though the technology can be used for different types of feedstock, natural gas seems to be most commonly used.

In CPO the oxidant and the hydrocarbon feedstock are premixed in a mixer before they enter the catalytic bed. Even though different types of feedstock can be used, the literature tells that natural gas seems to be the first choice.

ATR is a combined combustion and catalytic process carried out in an adiabatic reactor. In ATR, after a pre-reformer treatment, the feedstock gas goes to the adiabatic oxidation reformer. However, in ATR it is not possible to produce synthesis gas for FT-synthesis directly. The composition of the produced gas has to be adjusted before entering the FT-reactor by removal of carbon monoxide or by adding hydrogen.

5.1 Steam reforming catalyst

In an adiabatic pre-reformer it is highly desired to have a catalyst with high activity and a high active surface area. This is to give the catalyst a good resistance against deactivation and poisoning.

However, in primary reformers and heat exchange reformers the reactivity is not as important as the reactor design. Worth to mention is that for example the volume is predominantly determined by heat transfer and mechanical criteria. In these cases the catalyst activity is normally much higher than what is needed. Instead, the catalyst is designed for maximum heat transfer and minimum pressure drop [6].

According to the literature, nickel tends to be the most used catalyst metal for steam reforming. Many other metals -such as cobalt and rhodium- have higher catalyst activity but they are seldom used since they are also much more expensive.

Typical catalyst carrier materials are aluminium, magnesium and zirconium.

Steam reforming catalyst will show reduced activity over time for reasons such as:

- Sintering (loss of active surface area)
- Sulphur poisoning
- Alkali and silica metals poisoning
- Carbon formation

6. FT production technology

6.1 Basics

The full FT-process from "cradle to grave" consists of three main process steps:

- Production of the synthesis gas (including cleaning, reforming and shifting).
- The FT-synthesis.
- Product upgrading/cleaning.

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                                              ┌──────────┐
                                              │  IGCC    │  ⟹  Power
                                              └──────────┘
                                                   ⬆ Off Gas
                          ┌──────────┐        ┌──────────┐
Raw ⟹  ┌──────────┐  ⟹   │ Gas:     │  ⟹     │ FT-      │
Material│Gasification│     │ Cleaning │        │ Synthesis│
        └──────────┘      │ Reforming│        └──────────┘
                          │ Shifting │             ⬇ Liquid hydrocarbons
                          └──────────┘        ┌──────────────────┐
                                              │ Upgrading/Cracking│
                                              │ Recovery          │
                                              └──────────────────┘
                                                 ⬇              ⬇
                                          ┌────────────┐  ┌────────────┐
                                          │ C5 – C9    │  │ C10 – C20  │
                                          │Naphta/Gasoline│ Diesel     │
                                          └────────────┘  └────────────┘
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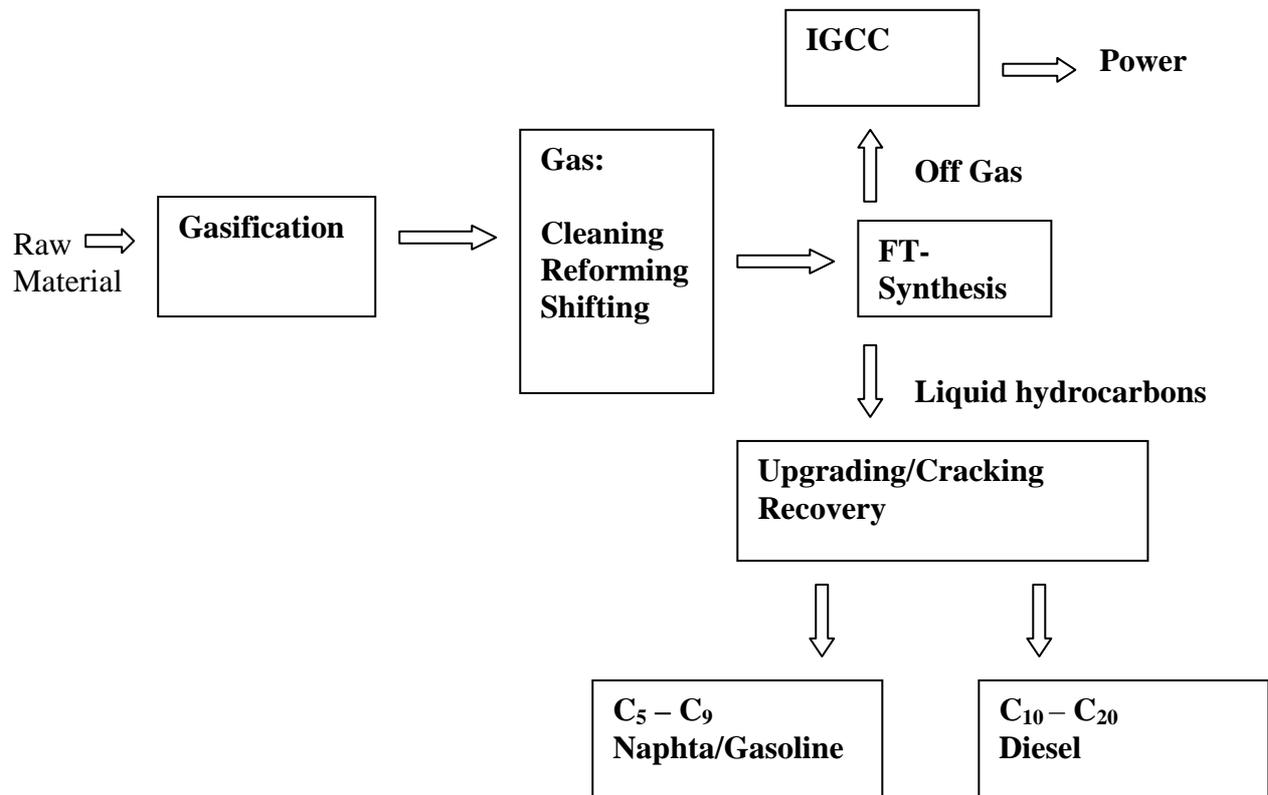
The possibility to produce high value hydrocarbons in large amounts depends of course on the type of FT reactor, reactor dependent technical solutions and the choice of the catalyst.

Of course the result will also be depending on the after-treatment of the product mix. For example:

- Naphtha can be converted into lower olefins by steam cracking,
- Olefins and paraffin's can be converted to alkylate and high value co-monomers such as C_6 and C_8 that can be recovered from the product mix.

6.2 Raw material

As already mentioned before, synthesis gas can be produced from almost all kinds of carbon containing materials. Besides carbon it is also desirable that the feedstock material contains hydrogen. The optimum H_2: CO ratio in the synthesis gas for FT-processes is 2:1.
If there is a lack of hydrogen in the feedstock, the gasification process has to be complemented by adding hydrogen by splitting water and steam, which is a very energy intensive process.

So far, coal is the most important feedstock for FT-syntheses or rather for the production of a synthesis gas for the FT-synthesis. However, coal is not rich in hydrogen and it has to be gasified together with water and steam. The reaction products when gasifying coal are mainly hydrogen, carbon monoxide and carbon dioxide.

A second feedstock for synthesis gas production that is becoming more and more common is natural gas. Natural gas (or rather methane) does not have to be gasified, but it has to be reformed to transform methane (CH_4) into carbon monoxide (CO) and hydrogen (H_2). Generally this is a much cheaper process than gasification of coal. This is mainly caused by lower investment costs. Even though the resulting components are the same as for synthesis gas, the amount of carbon dioxide from coal is much less from reforming than from gasifying. About 25% of the carbon in natural gas is converted to CO_2 compared to 50 % when coal is used as feedstock for synthesis gas production. Using natural gas instead of coal has also another clear advantage since treating and gasifying of coal is a rather "dirty" process that has a not negligible negative impact on environment and health.

The thermal efficiency when producing liquid fuels from natural gas have been estimated to be around:

- FT-Gasoline 60-62 %
- FT-Diesel 63-66 %

Concerning gasification of biomass, this is not a new technology but compared to gasification of coal there are still a number of issues that need to be further developed. The knowledge today concerning gasification of biomass mainly concerns air blown gasification at atmospheric pressure. This results in a gas with a high amount of nitrogen (N_2) that is suitable for use in an IGCC, but it is not suitable for production of FT-Fuels.

If the gas will be used for fuel production, it is most likely that the gasification process has to be pressurized and oxygen blown. Biomass gasification in most cases seems to result in a significantly lower H_2: CO ratio in the synthesis gas, so a shift reaction to adjust the ratio may be necessary. Of course, this depends on the moisture content in the biomass. High moisture ("fresh") biomass would certainly reduce the need for a shift reaction.

Besides that, biomass is not a homogeneous raw material. Biomass can vary between al kinds of bio-based carbon containing materials, for example well-defined woodchips or a dry mix of garbage and wastes. This implicates that gasification of biomass has to be built on a broad range of different types of gasification technologies/gasification equipment.

6.3 Reaction chemistry and process efficiency

The chemistry in the FT-synthesis is a heterogeneous catalytic reaction, in which carbon monoxide (CO) and hydrogen (H_2) react with each other to form a "liquid" fluid of hydrocarbons of variable chain length of the molecules.

The main FT-reaction mechanism is:

$CO + 2H_2 \implies - CH_2 - + H_2O$
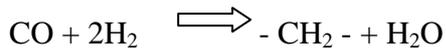
The " - CH_2 – " group is a building block for longer hydrocarbon chains.

From a thermodynamically point of view the dominating product of the FT-synthesis should be methane. However, in practice the synthesis products tend to be higher hydrocarbons.

One important performance characteristic of the FT-synthesis is the liquid selectivity of the process. The liquid selectivity is the mass fraction of hydrocarbons with a chain length of 5 atoms or higher C_{5+} (S_{c5+}). S_{c5+} is determined by the chain growth probability alpha (α), which is a figure describing the probability that a hydrocarbon chain is extended with another –CH_2- group instead of terminating.

A high liquid selectivity is desired for the production of synthetic fuels. While a low liquid selectivity (C1 – C4) is desired when the gas will be used in an Integrated Gas Combined Cycle for power (heat and electricity) generation.

The relation between the yield of hydrocarbons and the chain growth probability can be described by the so-called Andersson-Schultz-Flory distribution formula/relation (ASF) [19, 20, 21]. This ASF formula describes the molar yield of each hydrocarbon fraction as:

$C_n = \alpha^{n-1} * (1-\alpha)$

α = Chain growth probability
C_n = Linear hydrocarbon yield, where n is the number of carbon atoms
$1-\alpha$ = The chance that the chain-growth terminates.

The first figure below shows the hydrocarbon yield in wt % of product in relation to the α-factor.

The second figure shows the relation between the α-factor and the "product" selectivity.

*Figure 12 FT-Product Distribution*

α = Probability of chain growth
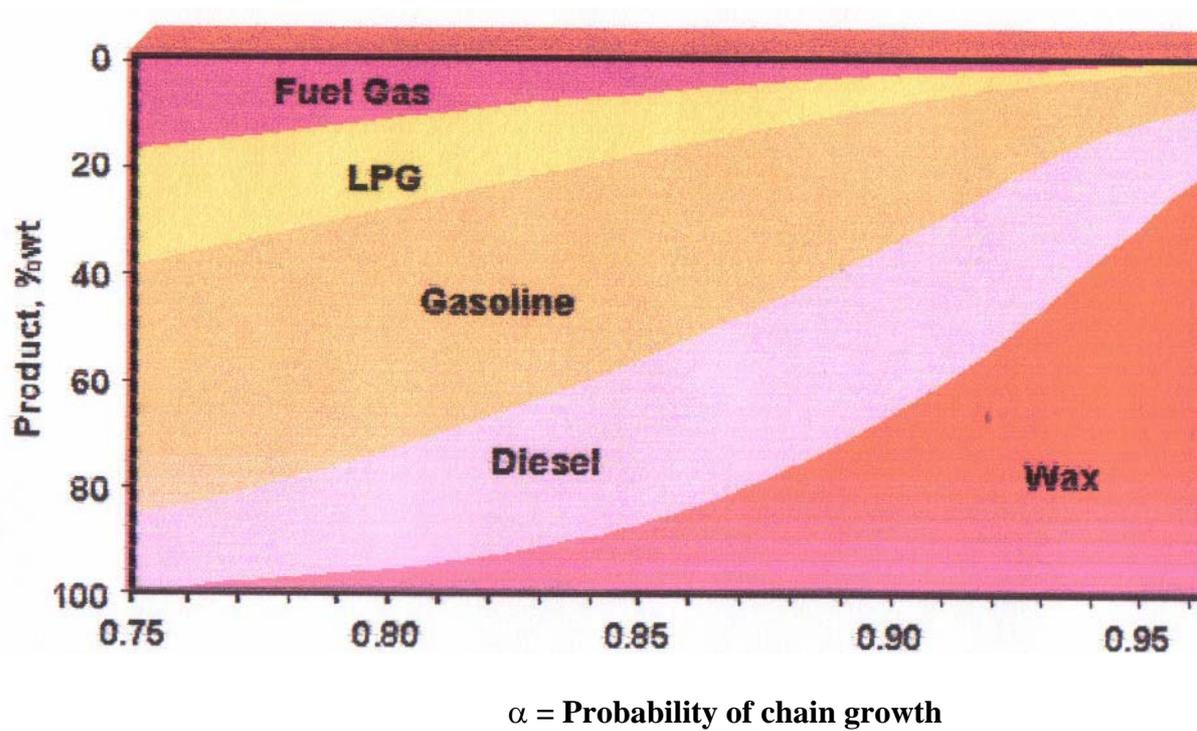
Figure 13 The Schultz-Flory distribution
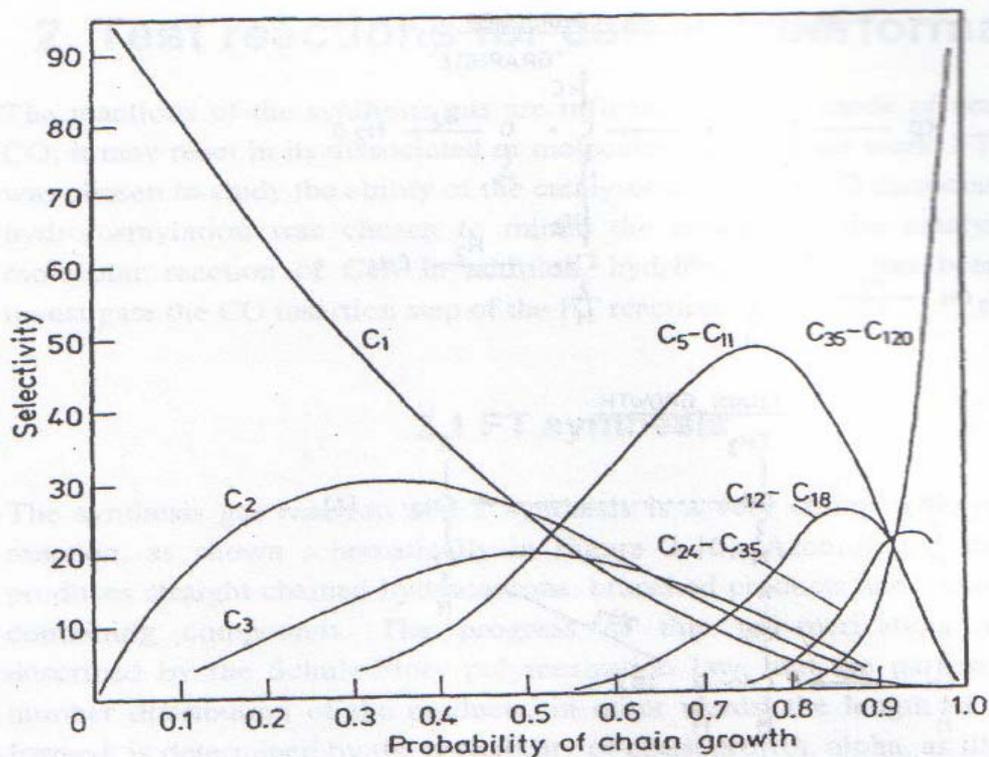
From the figures it can be seen that an α of almost 1 will give mainly waxes as a result of the FT-reaction, while a α of almost 0 will result in mainly methane as the product. From the figures it can also be seen that it is impossible to get "diesel fractions" as the main product from a FT-process. If diesel fuel is the required final product, it is better to aim for a high α and then hydrocrack the waxes to shorter hydrocarbon chains. However, at an α of approximately 0.75 the yield of hydrocarbon chains suitable for refining to synthetic gasoline will be at the maximum (almost 50 %), while still hydrocarbons that are suitable for the production of diesel fuel (15 – 20 %) as well as waxes that can be hydro cracked to diesel fuel compounds will be produced.

The α factor -and because of that the selectivity- is influenced by a number of factors. These factors are either, as mentioned above, catalyst dependent or non-catalyst dependent.

Examples of catalyst dependent factors are for example:

- Type of catalyst metal
- Type of catalyst support material
- Preparation preconditioning and age of catalyst

Examples of factors that are independent of the catalyst are:

- The H_2/CO ratio in the feed gas/synthesis gas
- Gas/reactor temperature
- Partial pressure of the reactants and inerts
- Reactor residence time
- Gas recirculation
- FT-technology

The optimum H_2/CO ratio is -as already mentioned- 2:1 for the FT-synthesis, depending on the selectivity. If for example the H_2/CO ratio decreases, the α-factor will increase and the products will tend towards waxes.

Concerning temperature and pressure, the FT-process normally operates at pressures ranging from 20 – 40 bar and temperatures ranging from 180 – 250 ^{o}C.

All the factors mentioned above are more or less interrelated.

Changing these factors will cause desirable as well as undesirable effects concerning both the final products (for example length of carbon chains as well as branched or straight chains) and the quality of the by products (for example chemical composition, by product gas composition and energy content, heat or steam). A higher partial pressure of H_2 and CO will for example lead to higher liquid selectivity S_{c5+}, while more N_2 or CO in the synthesis gas will decrease the partial pressure of these compounds, and because of that it will also reduce the liquid selectivity.

6.4 Carbon conversion chemistry

Conversion of carbon to olefinic hydrocarbons can be described by the following equation:

Gasification: 1.5 C + 2 H_2O $\Longrightarrow$ CO + 2 H_2 + 0.5 CO_2

FT-synthesis: CO + 2 H_2 $\Longrightarrow$ (-CH_2-) + H_2O
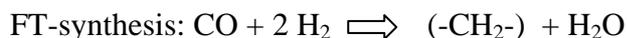
Giving a carbon efficiency of 67 %.

However this reaction is thermodynamically impossible.

If the gasification is modified by adding oxygen to try to make it thermodynamically feasible, the gasification equation will change to the following:

1.77 C + 2 H_2O + 0.27 O_2 $\Longrightarrow$ CO + 2 H_2 + 0.77 CO_2

Still, this reaction would be thermodynamically impossible and in this case the carbon efficiency is reduced to 56 %.

The most effective way to provide heat for endothermic reactions is by combusting additional carbon with oxygen. That would lead to the following equation:

$$2\,C + 2\,H_2O + \tfrac{1}{2}\,O_2 \quad \longrightarrow \quad CO + 2\,H_2 + CO_2 \quad \longrightarrow \quad (\text{-}CH_2\text{-}) + H_2O + CO_{2\,+}\,Heat$$

Now the carbon efficiency is reduced to 50 %.

Decreasing the steam feed to the gasifier can increase the amount of heat produced by the reactions. However, this will further decrease the carbon efficiency to 47 % [6].

6.5 Carbon losses

Carbon losses in the FT-process have an impact on the total gas to liquid efficiency and can be identified for three different cases.

The first case is carbon losses that are associated with the hydro processing of the primary Fischer-Tropsch products. These hydrocarbons can be recovered and further used as fuel gas. The potential to reduce these carbon losses is very limited.

Secondly, there is a loss of light and oxygenated hydrocarbons, mainly in the reaction water. These losses can be decreased by improving the selectivity of the Fischer-Tropsch catalyst. However, light hydrocarbons such as methane can be used as fuel gas in the process.

The third case includes carbon conversion inefficiencies and losses of non-reacted carbon monoxide (tail gas), unconverted reformer methane and reformer carbon dioxide. In many cases, these losses can be avoided by process improvements. To avoid carbon losses in the form of the tail gas CO, more effective separation technologies to separate CO and H_2 have to be developed. Another possibility is to add hydrogen rich gas to the reactor and reacting it with the remaining CO gas.

6.6 Catalyst

The FT-process as well as the reforming process have to be supported by a catalyst. The type of catalyst will have a certain impact on the efficiency and the hydrocarbon selectivity of the processes. In this chapter the FT-process catalysts will be discussed, while the steam reforming catalyst will be discussed in the reforming chapter.

Today existing catalysts having any commercial importance for the FT-synthesis tend to be:

- Fused Iron
- Precipitated Iron
- Supported Cobalt

Each class of catalysts has its own application as well as room for further improvement concerning the decrease of undesirable catalytic effects and an increase of desirable effects, such as better product selectivity and enhanced catalytic effect. Besides these main catalyst groups, it also seems possible to use ruthenium -either or not in combination with cobalt- as catalyst.

Iron catalysts are mostly used in high temperature two phase fluidised bed reactors (HTFT) and in low temperature three phase slurry reactors (LTFT). The fused iron catalyst is used in HTFT reactors, while the precipitated iron catalyst is used in LTFT reactors.

Supported cobalt catalysts are also used in low temperature three phase slurry reactors.

See below for more information about reactors.

The reasons for choosing a certain catalyst in combination with a reactor type are of course depending on the choice of feedstock for the synthesis gas and they are for example depending on the risk of catalyst toxification. The final product/hydrocarbon mix that is required also plays an important role.

In the synthesis reactor the catalyst tends to revert producing to its initial form before processes to promote and enhance the catalysts efficiency and selectivity as well as its stability.

The result is reduced catalytic activity and selectivity over time, and finally the catalytic particles might for example swell and break. This implicates that the catalyst material has to be exchanged by continuous or periodical loading and reloading.

The fused iron catalyst is made from iron oxide. Alkali may be used to promote the activity and selectivity of the iron oxide. Also different types of structural promoters may be used to increase the catalyst surface area.

In the FT-reactor high alkali levels are considered to be positive since they may decrease the formation of methane. However, too high alkali levels may, besides increasing methane levels, also contribute to the formation of heavy hydrocarbons in the liquid phase and to increased levels of organic acids in the final hydrocarbon product mix. This may in turn give rise to corrosion problems. The liquid hydrocarbon that are formed with the help of fused iron catalysts are to a high extent olefinic, which makes this technology suitable for the production of hydrocarbons that are to be used in the petrochemical industry.

In order to further decrease the catalytic selectivity for methane, precipitated iron can be used as catalyst in a slurry reactor. The best methane selectivity that can be reached today is 3 %, compared to 7 % for fused iron catalyst used in a fluidised bed reactor. However, this requires a lower operation temperature and in parallel with that it also requires decreased reaction rates. To compensate for the lower reaction rates, catalysts with higher catalyst surface area should be considered.

When preparing the precipitated iron catalyst, iron as metal and not iron oxide is required. Like for the fused iron catalyst, promoters are used to promote activity and selectivity. Alkali is one important promoter, like for the fused iron catalyst. In the further treatment of the precipitated iron catalyst, extrusion technologies have to be chosen to provide the catalyst with properties that will give the best result in relation to the type of reactor where the catalyst will be used.

The supported cobalt catalyst consists of cobalt deposited on a carrier material, often a pre-shaped refractory material. The carrier material is often an oxide of silica, alumna titan or

zinc, but also zirconium, La and Ce can be used. Also combinations of these oxides can be used.

Pre-shaping of the carrier material includes activities to obtain maximum particle size distribution, pore size and strengthening (heat treatment). After that the pre-shape treatment of cobalt is done together with promoter metals such as platinum, palladium and rhenium, which are placed on the carrier material. Finally, the carrier with cobalt placed on it is dried and then treated with hydrogen at high temperature to reduce it. An important factor with an impact on the selectivity and effectivity is the distribution of cobalt crystalline size on the carrier material.

While the iron catalysts pre-dominantly produce olefins, the cobalt catalysts tend to produce paraffin's. This makes cobalt catalyst a good choice for the production of diesel fuel.

The best methane selectivity that can be reached with the cobalt catalyst today is between the fused iron and precipitated iron catalysts and in the range of 5 % selectivity.

Cobalt catalysts are not suitable for reactions with coal-based synthesis gas, since the risk of catalyst poisoning from different kinds of impurities that are present in coal might occur. Instead, cobalt catalysts may be used for production of the "cleaner" natural gas based synthesis gas. When using coal as raw material for the synthesis gas production, it is advisable to use an iron catalyst in the FT-synthesis since the iron catalyst is much cheaper than the cobalt catalyst.

6.7 FT-reactors

When designing a FT-reactor it is important to take all the above-mentioned aspects and their interrelations into account. Furthermore, there is also a strong interaction between the design of the reactor and the technology to provide the synthesis gas into the reactor, taking into account separation technology and recycling of certain process streams.

When designing a FT-reactor as well as the components in the whole production chain -from raw material via gas production and treatment to the final products- it is important to have a good picture of the energy consumption and energy supply. The FT-synthesis is a quite energy intensive process/technology and it is important to minimize the energy demand. It is also important that of the energy that is supplied, as much as possible can be utilized in the process or recovered as by-product, both from an economical point of view but also from an environmental point of view.

There are three main types of FT-reactors:

- The fluidised bed reactor
- The fixed bed reactor
- The slurry phase reactor

According to the literature, the fixed bed and the slurry phase reactors seem to be the most promising alternatives. There is still not enough information available to give any indication if one of these two alternatives has any particular advantage when using biomass as raw material. However, it seems clear that the slurry phase reactor is less sensitive to inert in the

gas, and inert may to a greater extent be present in some biomass-derived synthesis gases. One disadvantage of using the slurry phase reactor is that there will be a continuous need for catalyst and wax separation.

When discussing different types of FT-reactors and catalyst, there are at least four types of reactor and catalyst combinations that should be mentioned [6]:

- High temperature Fischer Tropsch (HTFT) two phase fluidised bed reactors (iron catalyst)
- Low temperature Fischer Tropsch (LTFT) three phase slurry reactors (iron catalyst)
- LTFT three phase slurry reactors (cobalt catalyst)
- LTFT tubular fixed bed reactors for special circumstances

These four categories could be further divided into sub-types, etc.

The choice of reactor and the combination of reactor and catalyst will of course depend on the feedstock for the synthesis gas production and on the final products to be produced by the FT synthesis.

It might be difficult to make absolute comparisons of different reactor types and reactor type/catalyst combinations, since the design of the reactors as well as the development of the catalysts have developed and improved over the years (among others concerning performance in the field of efficiency and selectivity) and that this new knowledge often is proprietary to individual companies.

However, what initially can be concluded is that:

- Fluid bed reactors have an advantage concerning the heat transfer coefficient.
- Fluidised bed reactors may be two-phase (gas catalyst) or three-phase (gas with catalyst suspended in a hydrocarbon) slurry (slurry reactor). These types of three phase reactors have a heat transfer coefficient for the cooling surface that is five times higher than for a fixed bed reactor [6].
- A fluidised bed reactor has a much higher capacity (barrel per day) than a fixed bed reactor.
- The FT reactor is not a dominant cost component in the overall plant cost.

It is also a fact that certain technologies "compete" for application with the same feedstock.

The table below shows some possible combinations and locations where they have been or might be commercialised.

Tabel 12 Examples of FT-Applications worldwide

Feedstock	FT-Technology	Primary products	Applications
High ash coal	Synthiol (HTFT)	Gasoline	Secunda South Africa
High ash coal	Iron catalyst (LTFT)	Waxes, paraffins, LPG, hydrogen	Sasolburg South Africa
Low ash coal	Synthiol (HTFT)	Diesel and electricity	Proposed China
Associated Gas	Co-catalyst (LTFT)	Diesel	Escravos Nigeria
Natural gas	Iron-catalyst	Waxes, paraffin's, LPG	Sasolburg South Africa
Natural gas	Synthiol (HTFT)	Gasoline	Mossel Bay South Africa
Natural gas	Co-catalyst	Waxes, Paraffin's, diesel, naphtha, LPG	Bintulu Malaysia
Natural gas	Co-catalyst	Diesel	Ras Laffan Qatar

Furthermore it may be concluded that:

- The iron catalyst based LTFT-process seems to offer a higher concentration of olefins than the Co-catalyst based LTFT-process.
- The HTFT-process contains more branched hydrocarbons than the highly linear product compounds produced by the LTFT-synthesis. This makes it suitable for gasoline production.

Still, the HTFT-process seems to be used more and more to produce olefinic high value chemical products. If these olefins ($1\text{-}C_5$ and $1\text{-}C_8$) are extracted from the product/gasoline mix, this does not bring a severe disadvantage since these compounds (linear ones) have low octane numbers.

It is also important to notice that:

- Even with the HTFT-process considerable refining of the product mix is still required to obtain synthetic gasoline.
- The HTFT-process is not only suitable for gasoline production but it is also well suited for the production of paraffin/synthetic diesel oil. This is done by oligomerisation of the high olefins C_5 to C_9 together with the hydro processing of straight run diesel chains.

When designing a FT-plant it is important to not only consider the most suitable technology with respect to the possible feedstock and product mix, but also investment and operational costs as well as co-product mix and value in relation to the desired product mix must be considered. It is also important to look for economy of scale benefits, to investigate the possibilities to integrate the various technologies that will be used, and to see if the technologies that will be applied can be associated with utility systems.

Probably all commercial applications of FT-Technology include recycling of some of the tail gas. The gas and vapour outlet is cooled first to condensate the hydrocarbon product mix and the reaction water, and to separate them from the tail gas. Some of the tail gas is then recycled to the FT-reactor with the purpose to contribute to the optimisation of the process. This recycle stream is known as internal recycling.

The remaining tail gas is often further processed to provide a gas that may be recycled to the FT-reactor (external recycle) or the methane reformer, or it may be used as a fuel or it may even be used to produce hydrogen. The gas process scheme is known as the gas loop. To avoid accumulation of inert gases (nitrogen) in the gas loop, there must always be some gas outlet from the loop. When this outlet is kept to the minimum level that is required to avoid accumulation of inert, the loop is defined as a closed loop. When gas is taken out as a product that will be used (for example as fuel or as raw feedstock for hydrogen production), this is known as an open gas loop.

The gas loops are important steps to maximize the production of fuels. This technology is known as full conversion FT-process. Another possibility is the 'once through' concept, which combines the FT-process with firing in a natural gas based gas turbine. This concept without gas loops produces less FT-Fuels but more tail gas, which can be used for firing. In such a case it is not necessary to include reforming and CO_2 removal, which results in lower capital costs and somewhat higher total energy (FT-fuels + energy) efficiency.

The reactor type and the feedstock are important parameters when discussing and designing the gas loops in a "full" reactor concept.

Further parameters influencing the need for a gas loop are for example:

- Reactor temperature
- Gas H_2/CO ratio
- Acceptable CO_2 level
- CO_2 -removal capacity
- Stoichiometric ratio in relation to product/hydrocarbons and by-products

Besides the parameters above, the different types of gas loop are also depending on/connected to:

- The desired final product mix
- Co-product marketing/value
- Type of gasifier

Examples of such gas loop combinations are:

- HTFT-reactor - Sasol-Lurgi fixed bed coal gasifier for conversion of high ash coal. (Can be used both in open or closed versions.)
- HTFT-reactor- Entrained flow gasifier for conversion of low ash coal.
  LTFT-reactor with natural gas feed (Cobalt catalyst).

7.   Upgrading - refining

The refining of Fischer-Tropsch products (including fuels) is quite different from crude oil refining. This relates to the composition of the feedstock but it also concerns the product focus and the heat management. However, since FT-products are not yet widespread on the commercial market, specific refining technologies have not yet been developed. Instead, the basic technologies of crude oil refining have been adapted for the refining of FT-products. The choice of refining technologies depends of course very much on the final product mix that is wanted, and so far the production has been focused on fuels that have not influenced the refining technologies.

The upgrading of FT-products may often start with removal of light hydrocarbons and dissolved gases to facilitate storage of the remaining products at atmospheric pressure. Further olefins may be removed by fraction- and extractive distillation, for separate use as a chemical feedstock or to be hydrogenated to petrol and kerosene. The remaining stream of chemical compounds is often -after distillation- hydrogenated to naphtha (that might be reformed to petrol) and/or paraffin that might be fractioned into petrol, kerosene and diesel.

The refining technology of FT-fuels can be split into two separate main refining technology lines called High Temperature Fischer Tropsch Fuels refining (HTFT-Fuels refining) and Low Temperature Fischer Tropsch Fuels refining (LTFT-Fuels refining).

Primary fuel refining steps in HTFT-Fuels refining, as already mentioned above to some extent, are:

- Oligomerisation for shifting products to higher boiling material
- Hydro cracking for shifting heavy products to lighter boiling material
- Aromatisation and isomerisation for improving octane and density
- Hydrogenation for removing unwanted oxygenates, olefins and dienes

Sometimes also technologies such as thermal cracking, alkylation and etherification are added to these refining steps.
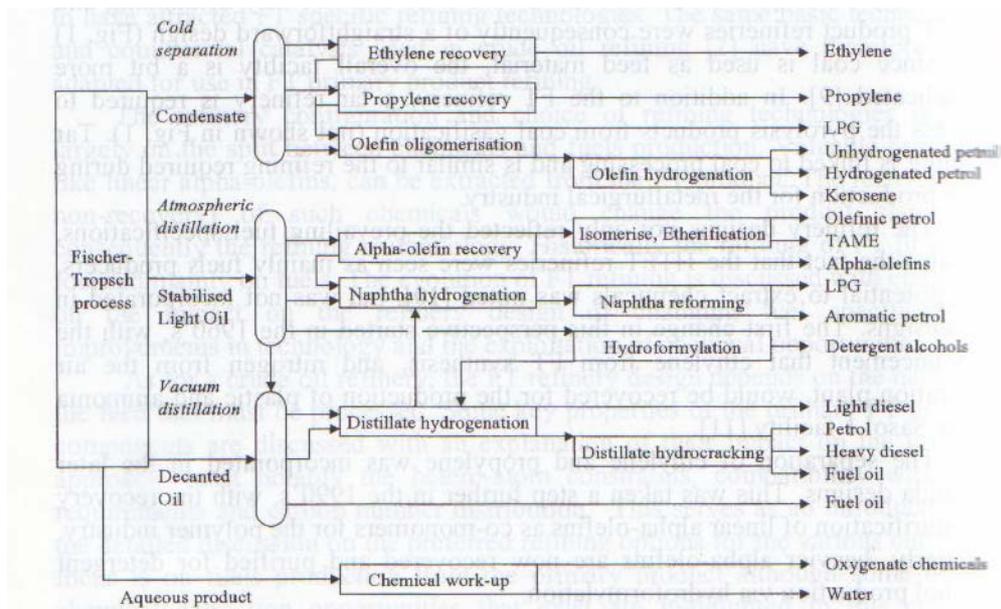
Figure 14 The 2004 design of the HTFT refinery used at Sasols plant Secunda, South Africa [6].

In the hydro cracking process, hydrogen is added to remove double bonds in hydrocarbons. After that treatment, the hydrocarbon liquid is catalytically cracked with hydrogen. The overall efficiency in the hydro cracking step is often above 98 % [6].

The hydro cracking step is a very important process step, especially if diesel fuel is aimed for as the main product, since -as already described above- the FT-process itself (especially the HTFT-process) has a low sensitivity for direct production of diesel hydrocarbons.

Hydro-isomerisation is used to convert straight chain hydrocarbons to branched hydrocarbons. One reason to do this is to improve the cold flow properties of the synthetic diesel oil.

The petrol components in an HTFT-Fuel mix do often have a rather low octane number. This is something that has to be dealt with by different kinds of after-refining and upgrading, as mentioned above. It is also important to take into account that measures that are bad for the octane number of the product can be good for the cetane number. Low aromatic content and little branching results in a high cetane number. But little branching also results in poor cold flow properties.

Low Temperature Fischer Tropsch Fuels products are ideally suited for upgrading (LTFT-Fuels refining) to middle distillates such as diesel oil, with naphtha as a by-product. The lighter and heavier fractions are usually undesirable due to low prices and a limited market. However, the option to produce waxes or to hydrocrack waxes to diesel compounds can also give these fractions a substantial value.

Overall, the FT-synthesis is well suited to produce synthetic gasoline as well as synthetic diesel oil. Since the FT-products (including FT-Fuels) are free from sulphur, nitrogen and metals like nickel and vanadium, and further the levels of naphthenes and aromatics are very low, FT-products are very well suited for use as vehicle fuels from an environmental point of view. Future market demands will determine if synthetic diesel oil or synthetic gasoline will

be produced. For example today the production in Sasols production plants in South Africa (Secunda and Sasolburg) is mainly designed (concerning fuels) to produce synthetic gasoline. However, some may have the opinion that today gasoline composition in Europe and in the USA is already environmentally optimised, while there is much more to do on the diesel side. Such an opinion may also lead to the conclusion that the production of sulphur free and low aromatic diesel oil will be much more advantageous for the environment than choosing to produce synthetic gasoline. Furthermore, the higher energy efficiency of a diesel engine compared to a gasoline engine may from a greenhouse gas emission point of view also favour the use of diesel engine/diesel oil compared to gasoline engine/gasoline.

8. Environmental Aspects of FT Diesel

8.1 Literature Review

In order to get an overview of the papers and articles concerning emissions from engines and vehicles powered by FT fuel, a literature review was carried out. Several Internet search engines were applied in an extensive search for any kind of publication concerning emission data. Only results dating 5-6 years back are included in this search and references were limited to the following languages: English, Danish, Swedish, and to some (modest) extend French.

The results of the search are typically data found on the basis of chassis dynamometer tests. Some though were found by portable measuring equipment and others by engine test benches.

8.1.1 Results of the Review

There wasn't anything at all published concerning emission from engines running on FT gasoline products, among the reviewed literature. All results presented in this section are tests of FT diesel fuels and knowledge on FT diesel fuels.

Not all of the results were usable but the usable results counted: 13 SAE Papers, 12 website presentations and 8 website publications.

FT Gasoline has been produced for commercial use only in South Africa. The limitation in production seems to be due to economical reasons and/ or the nature of FT process itself. Emission measurements have therefore been carried out at The Technical University of Denmark in order to investigate the potential of FT gasoline. The emission performances of FT diesels are relatively well documented at this point and measurements have therefore not been necessary.

Both heavy-duty (HD) and light-duty (LD) engines and vehicles are represented among the results. Various exhaust after treatment devices have been fitted to engines and in different configurations. Cold versus hot start tests, low sulfur vs. high sulfur issues, blends of FTD and regular diesel studies and tests with different driving cycles are amongst the results.

8.2 Important FT Diesel Fuel Properties

FT diesel usually has another chemical composition than that of conventional diesel fuel. Diesel consists of hydrocarbons, mainly alkanes, alkenes and aromatics. Conventional diesel consists of approximately 25% aromatics [46]. The hydrocarbons are chained and are usually a blend of iso-, cyclic- and normal-structures (branched and straight chains). FT diesels mostly consist of normal-paraffins and this is probably the main reason for the difference of fuel and combustion properties and consequently emissions. Iso-structures and aromatics are less willing to ignite than n-paraffin and the result is different combustion reactions inside the engine cylinder compared to those of conventional diesel. FT diesels can consist of up to almost 100% pure n-paraffin.

The high n-paraffin content causes a high cetane number, low density and poorer lubricity and cold flow properties. The properties of a fuel, in particular the content of sulfur and aromatic hydrocarbons, have in many cases been shown to have an impact on the emission and FT diesels generally have a much lower content of sulfur than conventional diesels. An exception is Swedish MK1 diesel that has the same low content. Another is FTCOD (Conversion of Olefins to Distillate) from Petro SA that has a high aromatic content of 10%.

Besides the appearance of PAHs in the exhaust gas, the aromatics influence the combustion process of the engine and therefore the emission of other pollutants. The following is an attempt to summarize the information concerning consequences of fuel properties, found in the literature included in this review.

8.2.1 Sulfur

Up to 2005 the upper limit for sulfur content in diesels sold in the EU, the USA and in some Asian countries was 350-500 ppm. Other countries have a limit of 2000-5000 ppm.
USA and EU regulations require a limit as low as 50 ppm in 2005 and 15 ppm in 2007.AAn even more stringent level of sulfur, 10 ppm, is required to be marketed or available on an appropriately balanced geographical basis in the EU.

The reason for the low sulfur content in FT diesels is that the catalysts used in the FT production process cannot tolerate sulfur and it is therefore removed from the synthesis gas (syngas) that is used to make FT diesel.

The following is a list of suspected consequences of low sulfur content in diesel fuels:
- Reduction of emission of sulfur oxides.
- Allows various exhaust after treatment systems to function better, and permits higher efficiencies. This applies to Lean NOx, Continuously Regenerating Traps (CRT), Exhaust Gas Recirculation systems (EGR) and Diesel Oxidation Catalysts (DOC). Components in these systems can corrode as a sulfuric oxide combines with water to form sulfuric acids. Issues of unwanted coatings are also possible. Diminishing effects of sulfur in diesel fuel are detected to occur with sulfur levels as low as 3 ppm on a NOx adsorber [23, 24].
- Some modern diesel particle filters (DPF) require fuels with sulfur levels below ~30 ppm [23].
- DPFs and DOCs can convert SO_2 to SO_3 and SO_4 and contribute to an increase in sulfate emission [24], which is measured as increased PM emission.
- Exhaust after treatment systems could in the future be made even more efficient with fuels containing ultra low levels of sulfur thus allowing potentially higher conversion efficiencies and significantly cleaner emissions.
- Can be used in blends with lower quality diesels to make low sulfur fuel possibly with economical benefits [22].

8.2.2 Aromatics

The USA in general limits the aromatic content of diesel fuel to 35 % by volume. California limits the content to 10%. The World-Wide Fuel Charter suggests a limit of 15% for total aromatic content and 2% for [1]PAH content.

FT diesels have dramatically less content of aromatics than conventional diesels. In the reviewed literature conventional diesels have an average of around 17.5% (calculated) and ranges from 2-35%. FT diesels usually have less than 5%, but more often less than 1% content, with the exception of FTCOD (the FT diesel from Mossgas) having a content of 10%. The PAH content can be as high as 10% for conventional diesels around the world, 5% in the EU, where it more often is less than 0.1% for FT diesels.

Suspected consequences of low aromatics content in diesel fuels:
- Less aromatics increase the cetane number, which contributes to NOx and PM reduction [22].
- Some PAHs are suspected to be highly carcinogenic and lower PAH content in fuels results in lower PAH emission.
- Lower aromatic content reduces the in-cylinder flame temperatures during combustion that contributes to lower NOx formation rates. The reason is that aromatics and especially poly nuclear aromatics burn less readily and burn at a higher flame temperature. (Lower aromatic and higher hydrogen/carbon ratio provides less O-radical concentration during combustion that contributes to lower NOx emission [24]).

Figure 15 – H/C ratio and Flame temperature.
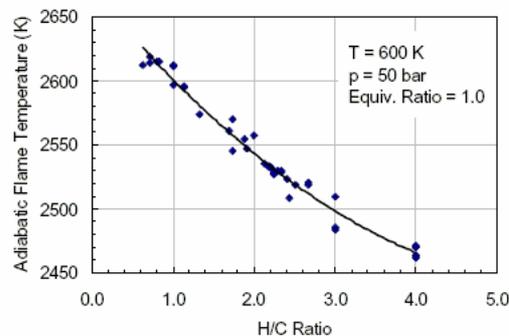
Calculated adiabatic flame temperature as a function of atomic C/H ratio for a variety of hydrocarbon fuels

- Reducing PAH content leads to reduced HC, NOx and PM formation though the effects are modest especially on newer and more modern engines [22, 23].
- A reduction in PM emission of 5-20% has been shown from older engines and even more in modern engines [22, 24].

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[1] PAH = Polycyclic or polynuclear Aromatic Hydrocarbons is hydrocarbons with more than one aromatic ring. Common examples are Anthracene, Phenanthrene and triphenylene. Some PAHs are considered carcinogens.

The adiabatic flame temperature as a function of hydrogen/ carbon ratio (H/C ratio) is linked to the NOx formation ratio. Generally speaking there will be less NOx formation in the engine at lower temperatures. See figure 15.

8.2.3 Cetane number

The cetane number is a measure of how ready the fuel is to auto ignite. With the exception of FTCOD (Mossgas), FT diesels in the literature review have a very high cetane number. Very often the cetane numbers of the FT diesels are reported as >74 on a scale that extends to 100. The cetane number can be determined in a test with a single cylinder cetane engine (ASTM D613). Conventional diesels usually have cetane numbers of 40-50 or higher, i.e. minimum 40 in the USA and minimum 51 in the EU. The reasons for the high cetane number for FT diesels are the high n-paraffin content and a low aromatic content.

Most papers state that a high cetane number imparts following:
- Useful for blending with inferior fuels for upgrading purposes.
- Economic benefits are possible for refinery companies because they can delay the overhaul of aging plants that produces fuel that does not meet cetane and stringent environmental demands. Instead of upgrading the plants FT diesel is blended into the inferior fuel.
- Short ignition delay period from injection to combustion that again imparts a slower pressure rise in the cylinder. This leads to reduced NOx formation rates, though the reduction is moderate (2-5%) [23]. Reductions are more significant at light to medium loads [24].
- A longer and more 'even' burn allows a higher degree of oxidation resulting in lower CO emission.
- Smoother and cleaner cold starts

8.2.4 Density

FT diesels have higher hydrogen to carbon (H/C) ratio compared to conventional diesels that results in a lower density relatively. This is due to the high n-paraffin content in FT diesels.

- The gross heating values are higher for FT diesel than for conventional diesel on a mass basis, but due to the lower density the heating values are lower on a volumetric basis. This can vary and the difference is not significant.
- The lower specific energy content of FT diesels can lead to a minor increase in brake specific fuel consumption even though this fact hasn't been shown with statistical significance. There are contradictory opinions on this subject.
- NOx emission reductions happen due to a lower peak pressure in the cylinder [22].
- CO emission has in some cases been found to increase with decreasing density [24].

8.2.5 Volatility

Increased volatility along with higher cetane number promotes auto-ignition and decrease ignition delay. Due to a reduced pre-mixed combustion, a smoother running engine and a higher output at similar fuel consumption is gained [42]. Shorter ignition delay results can

result in higher soot production rates but not necessarily higher engine-out soot emissions as explained earlier.

8.2.6 Metals

FT diesels are usually low on metals and other ash components that are considered polluting matters.

8.2.7 Additives (lubrication and cold flow properties)

Some polar impurities in conventional diesels contribute to the lubrication of the fuel injection system. Low sulfur diesels and FT diesels are in a way cleaned for those components in the process and for that reason a lubricity additive is in some cases needed to meet standards of lubrication. The effects of additives are not included in this investigation.

Blending fuels can help the problem and some investigations suggest that a blend with FT diesel made from biomass can help this situation. Another investigation suggests that regular biodiesel added in very small amounts, as little as 1%, can bring FT diesels to meet the required standard of lubricity [23].

The cold flow properties of FT diesels can be poor due to the very high n-paraffin content. By producing fuel with a mixture of n-paraffin and branched paraffin, the cold flow properties can be improved. This has been done by both Sasol with SPD (slurry Phase Distillate) and Mossgas with FTCOD (Conversion of Olefins to Distillate).

8.2.7 Nitrogen

FT diesels are generally low on nitrogen that could impart a small reduction of NOx emission, but this has not been investigated in the reviewed literature. NOx formation from fuel nitrogen is not normally considered a problem for transportation fuels though.

8.2.8 FT Diesel Specifications

Table 13 shows typical specifications of FT diesels.

Table 13

	Test Method	Units	Syntroleum S2	Shell GTL	Mossgas COD	Sasol
Specific Gravity	ASTM D4052	kg/l@15degr.C	0.771	0.7845		0.7698
Specific Gravity		kg/l@20degr.C			0.8007	
API gravity	ASTM D287	Degr.	52	54		52.3
RVP	ASTM D323	psi.	0.5			
Flash Point	ASTM D93	degr. C	64	72	100	59
Cloud point	ASTM D2500	degr. C	< -17	3	<-36	-19
Sulfur	ASTM D5453	wt%	*	*	<10	<5**
Viscosity	ASTM D445	cSt@40degr.C	2.1	3.57	2.974	2.08
Aromatics	ASTM D5186				10.1	
Aromatics	ASTM D1319	Vol%	*	0.1		0.7
Olefins	ASTM D1319	Vol%	*	0.1		
Saturates	ASTM D1319	Vol%	>99	99.8		
Cetane number	ASTM D613		>74	>74	51.4	> 74.8
Lubricity	ASTM D6079	mm	<0.37			
Ash	ASTM D482	wt%	<0.001			
FBP	ASTM D86	degr.C	350	338		352
Distillation 95 %					360.8	
HHV	ASTM D240	MJ/kg	47.2	47.2		46.7
LHV	ASTM D240	MJ/kg	44	44		
* Not detectable or below detection level						
** Determined by ASTM D4294, which is not recommended for ultra low sulfur diesel fuel.						

8.3 Emission Performance

Emission performance is a term for the amount of polluting gases and particles released from the engine with or without after treatment device. A good emission performance means a lesser quantity of pollutants. The emission data found in the literature are both of actual emission factor size, often in g/mile, g/km or g/brake horse power (g/ bhp.) but also as comparative sizes i.e. relative reductions of emissions comparing FT diesel to regular diesel. The pollutants in focus are hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx), particulate matter (PM) and polycyclic aromatic hydrocarbons (PAH) also called air toxics.

Due to the variation of the individual vehicle/ engine configuration, comparisons can in practice only be made of emissions from the same running conditions i.e. the same engine, after treatment device, reference fuel etc. Despite this, some overall figures across engine type, year, exhaust after treatment devices, reference fuel etc., and can give an idea of the general possibilities of the fuel.

Looking at the variety of issues examined in the literature, some general trends can be established. Besides the general trend that FT diesel replacing regular diesel reduces PM, HC,

CO, NOx and PAH emissions, the following trends will be dealt with later in this section: Influence of fuel composition, cold vs. hot-start performance, driving pattern, after treatment devices, blending properties and adaptation of engine technology to FT diesel.

8.3.1 Overall Figures

Figures 16 and 17 show the relative reduction in emission of HC, CO, NOx and PM for all tests, comparing vehicles/engines running on FT diesel to those running on conventional diesel. Looking at these figures and table 13, which to some extend shows the variety of test setups, there is evidence that FT diesel produces cleaner emission in almost many cases. The reduction of pollutants is evident in almost any of the test setups. Figures 13 and 14 show results across all the various conditions such as driving pattern, after treatment device such as diesel particle filters (DPF) and EGR, age, technological state or size of the engine etc. This indicates that FT diesel is capable of reducing pollutants in general terms.

Vehicles/ engines are ranging from a light duty 1.9L Golf TDI to a 12.7L DDC S60 heavy-duty vehicle. The vehicle/ engine ages are ranging from model year 1991 to 2002. Exhaust after treatment devices are ranging from none at all, over standard DPFs, to state-of-the-art DNOx heavy-duty systems. Engine technologies ranges from low tech HD bus engine to very modern and FT adapted[2] engines.

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[2] Described later in this section

Figure 16 – Relative reduction of pollutants using FT diesel instead of regular diesel fuel in heavy-duty vehicles/ engines.
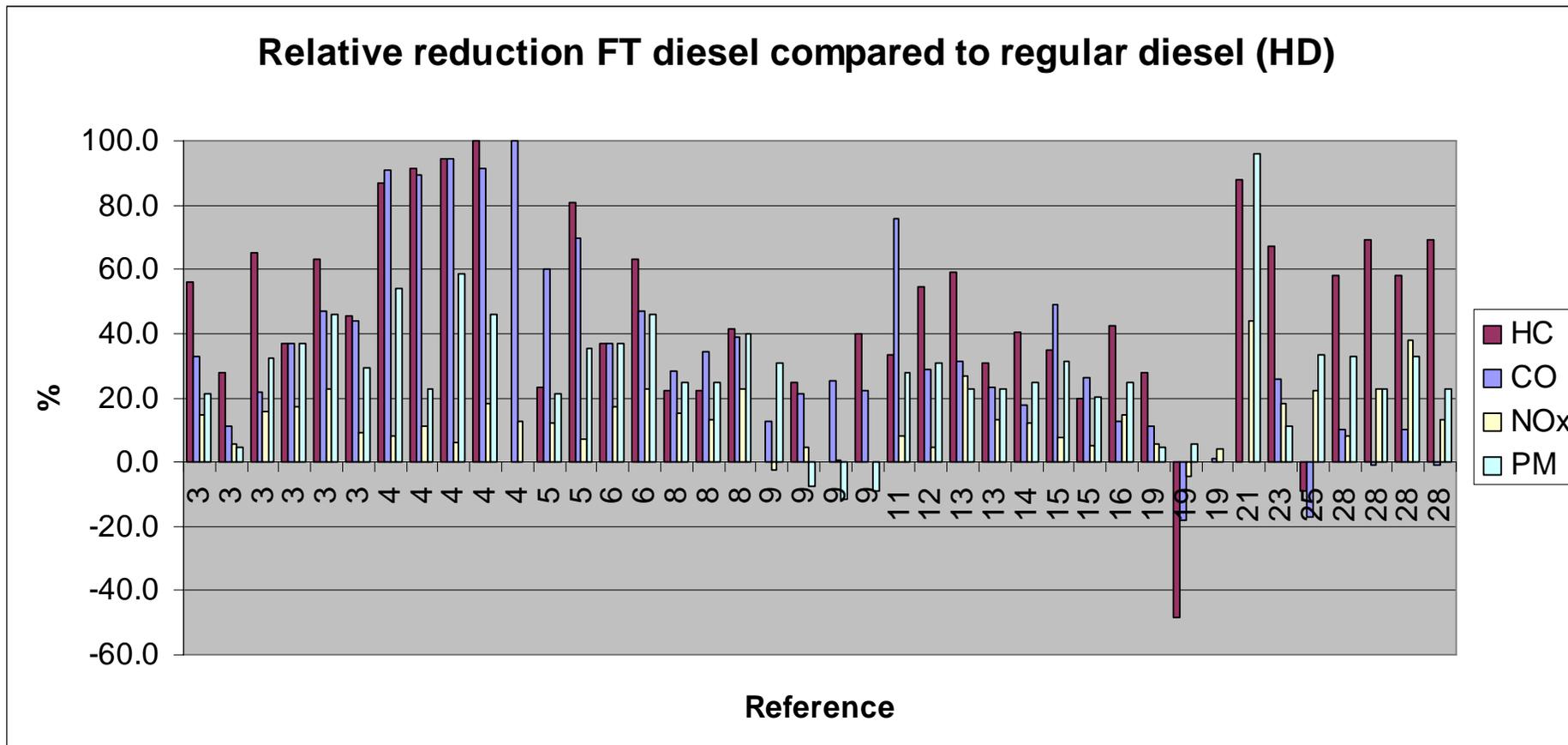
The figure shows that CO and HC emission is reduced significantly with the use of FT diesel, while NOx and PM emission is reduced to a lesser degree. It also shows that emissions are reduced in almost all of the investigated tests with only a few exceptions.

Figure 17 – Relative reduction of pollutants using FT diesel instead of regular diesel fuel in light duty vehicles/ engines.
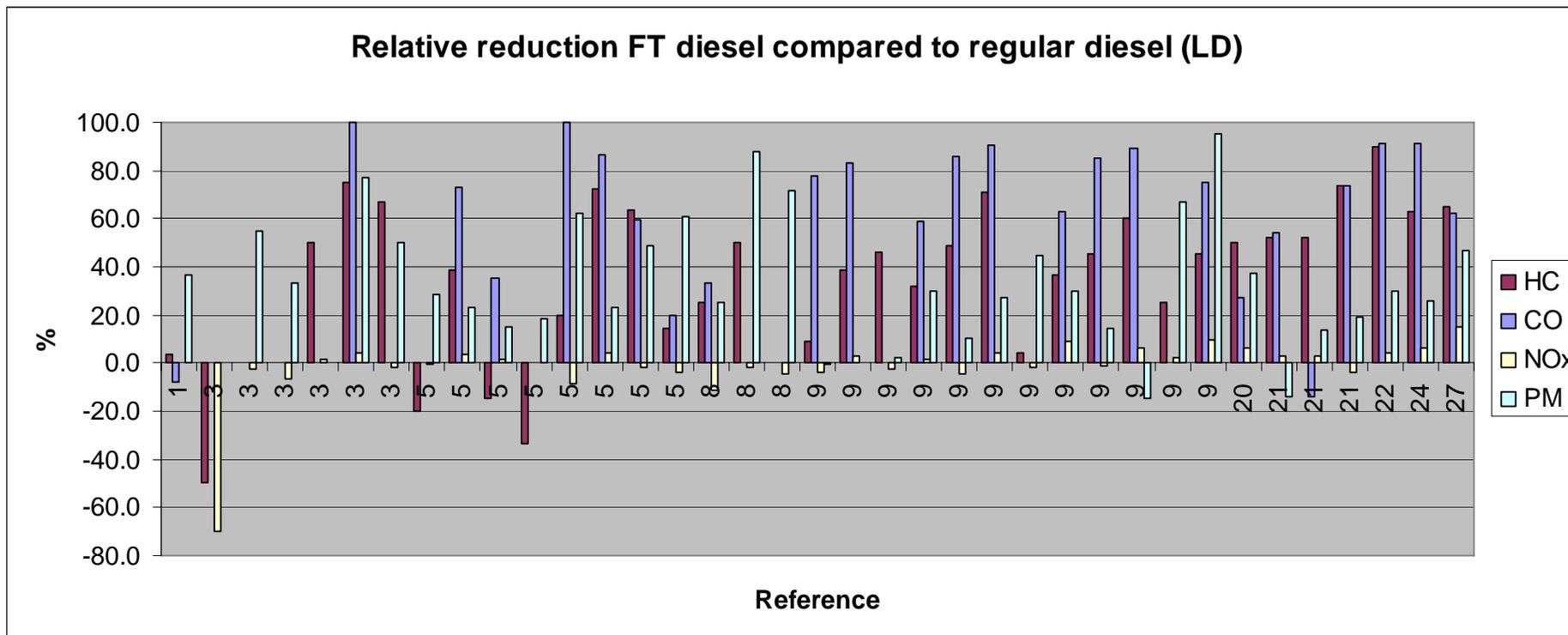
It is seen from the figure that HC, CO and PM emission is significantly reduced using synthetic FT diesel. NOx emission is in many cases not reduced at all. Negative reduction means that FT diesel causes more emission than with conventional diesel.

Table 14 –Table of all vehicles/ engines and test patterns

Ref. #	Vehicle/ engine	Driving cycle/ test pattern	Duty
3	1991 DDC S60, 12,7L , a 1994 Navistar T444E and a 1991 DDC S60, 11,1L	FTP	Heavy
3	1993 Cummins B5,9	Steady state composite result	Heavy
4	International Navistar DT466E 2001 turbo-charged, IC, In-line 6Cyl, 7,6L 230 hp with Ox.Cat. and EGR-DPF	Hot and Cold start FTP	Heavy
5	1998, in-line 5Cyl. 6,634L DI, In-line injection 125kW EGR WITH Ox. Cat	The Japanese 13 mode HD test cycle	Heavy
5	SUV in-line 4 Cyl. DI, TC with IC, 3L Cooled EGR, Common rail fuel injection, var. Boost turbo, with ox. Cat.	Japanese 10-15 + modes 2, 5 and 8 Tokyo cycle	Light
6	In-line 6Cyl. 12,7L Turbocharged – 321kW	FTP	Heavy
7	Cummins ISM 6 cylinder 10.8 liter heavy duty diesel engine MODIFIED by Ricardo with EGR	FTP	Heavy
8	1999 Cummins 5.9L and a Dodge Ram 2500, 5.9L	EPA, FTP and US06	Heavy
8	1999 VW Golf GL TDI 1.9L	FTP, US06, HFET	Light
9	'EURO 4' 6cyl. 11L - with CRT and a 'EURO 5' 6cyl. 12L - SCR + urea	ESC, ETC	Heavy
9	Car A "EURO 3" 2002 1.9L 4 cyl. Ox. CAT. And a Car B "EURO 3" 2001 2.2L 4 cyl. Add. DPF	NEDC	Light
11	HD "Euro 2" with DNOx	ESC	Heavy
11	Skoda Fabia	ECE 83.05 similar to NEDC	Light
12	Rebuilt 1991 DDC series 60, 12.7L and a 1991 DDC S60 Heavy Duty	FTP	Heavy
13	1991 DDC series 60	FTP	Heavy
14	Heavy duty GMC truck, powered by a 1996 Cat 3176B 10.3l engine	WMU 5-mile	Heavy
15	1991 Bus with Detroit Diesel 2-stroke engine 6V92, 6 cyl. 9.05L With and without CAT	CBD, described in SAE J1376	Heavy
16	2001 Cummins ISL 8,9L I-6 turbo, odometer 3348miles	EPA UDDS	Heavy
19	Navistar T444E V8 7,3L	?	Heavy
20	Daimler Benz OM 611 engine, 4Valves/cyl, turbo, aftercooling, variable swirl tuning	EPA 13-mode steady state	Light
21	DaimlerChrysler OM611 CIDI engine	FTP, US06 and ECE	Light
22	Mercedes E 220 CDI 2,2L 4Cyl. Turbo-charged with IC, with EU3 hardware status (EGR + Ox.CAT)	NEDC	Light
23	1991 DDC Series 60 HDD engine installed in a transient-capable test cell	Hot-start transient emissions FTP	Heavy
24	VW Golf TDI 100hp	On road	Light
25	Advanced technology truck engine hardware generating ~ 2002 emissions	Selected FTP patterns, transient & steady state	Heavy
27	1999 Mercedes A-170	FTP-75 and NEDC	Light
28	International DT466, year 2000, 6cyl. With and without CCRT	CSHVR, NYCB	Heavy
29	1991 DDC s60 6cyl 11.1L turbo charged after cooled Direct injection	FTP and NEDC	Heavy

Driving patterns, vehicle/ engine type and other info was not always available in the literature. As seen in the table not many tests have similar conditions regarding fuel, driving pattern, engine etc. and direct comparisons are therefore not possible.

The average reduction is for light duty (LD) and heavy-duty (HD) vehicles/engines can be seen in Tables 15 and 16.

Table 15 – Table of relative emission reduction for HD engines and vehicles.

	HC	CO	CO2	NOx	PM
Average %	43.1	34.8	3.2	13.0	26.7
StDev.	31.5	29.7	2.3	9.8	19.4

Table 16 – Table of relative emission reduction for LD engines and vehicles.

	HC	CO	CO2	NOx	PM
Average %	34.4	43.1	3.9	-1.1	32.0
StDev.	33.0	39.8	2.2	12.7	27.2

The tables show that the HC, CO and PM emissions are significantly reduced. NOx emission is reduced to some degree for HD engines and CO_2 to a lesser degree. The tables also show that there are differences especially regarding NOx between HD and LD tests.

Looking at the reduction of the CO_2 emission one has to consider the fuel consumption too. Though an investigation of fuel consumption is included in many of the references, the results are most often categorized as 'a trend towards lower consumption'. The size of the reduction matches the reduction of CO_2 emission in most cases. There are examples of up to 10% lower brake specific fuel consumption though. [38].

There is a fairly large deviation in the sizes of reduction and in a few cases FT diesel causes larger emission factors than running on conventional diesel.

8.3.2 Trends

This section deals with the trends in emission performance that can be seen when focusing on specific conditions or aspects of the emission test. These include reference fuel composition, cold or hot start, driving pattern, after treatment devices, blending FT diesel with conventional diesel, PAHs and adaptation of the engine to suit the unique properties of FT diesel in order to get more efficiency and less pollution.

8.3.2.1 Influence of fuel sulfur and aromatics

The reviewed literature suggests a connection between fuel composition and emission performance. There is a general agreement in the reviewed literature on the subject of sulfur and aromatics and their contribution to air pollution.

The distributions of sulfur content in the reference fuels are shown in table 17, figure 18 and figure 19. It is seen that most of the fuels contain between 0 and 500 ppm sulfur for both HD and LD tests. The calculated[3] average content of sulfur and aromatics in the tested fuels is shown below.

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[3] Where sulfur and aromatics were not documented, numbers were assumed on the basis of other sources documenting a similar fuel.

Table 17 – Table showing the overall average sulfur and aromatic content in reference fuels compared to the synthetic fuels tested.

|	Sulfur[ppm]	Aromatic [%]
Baseline fuels	205	17.3
FT diesels	0.9	1.3

The table shows that the difference between regular and synthetic fuels is quite significant both regarding sulfur and aromatics.

Figure 18 – Content of sulfur in the reference fuels, HD tests.
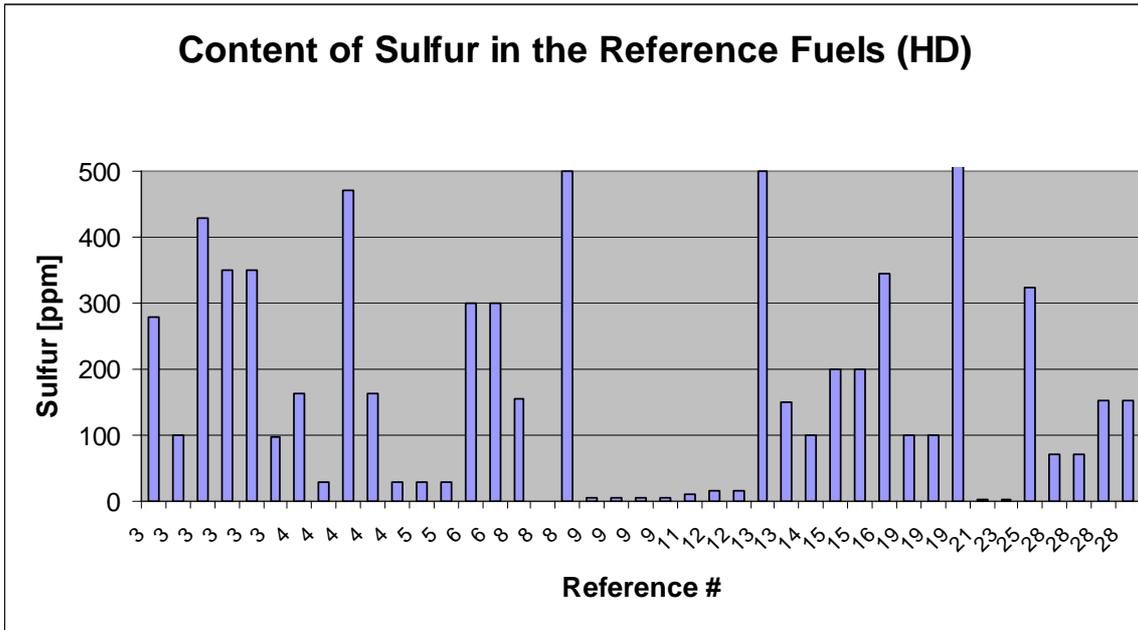
(Ref # 19 has a test of with a fuel with a sulfur content of 3500 ppm.)

*Figure 19 – Content of sulfur in the reference fuels, LD tests:*
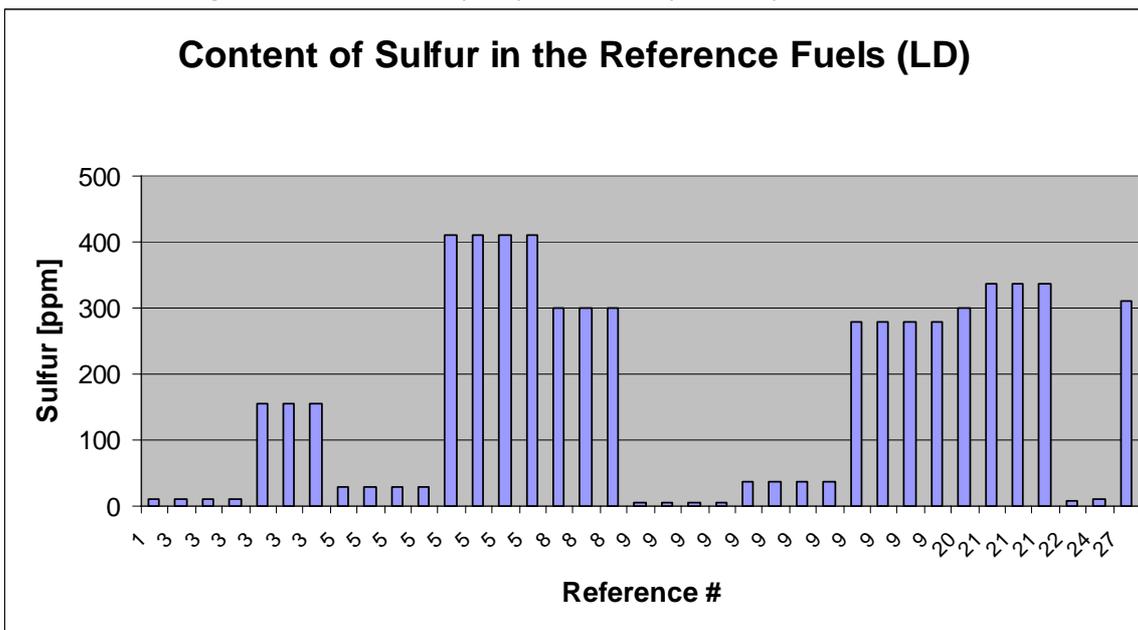
The figures show a large difference in sulfur content across the tests.

Comparing the emissions from running on conventional diesel with those from running on FT diesel there is almost in any case a reduction. Charts showing this reduction relative to the sulfur and aromatic content for all tests reviewed can be seen in figures 20-31. The trend lines are calculated with the least squares fit method.

Figures 20 – 23 Relative reductions of pollutants NOx, CO, HC and PM relative to sulfuric content of reference fuel for all tests.

**Reduction of PM relative to sulfuric content of reference fuel**
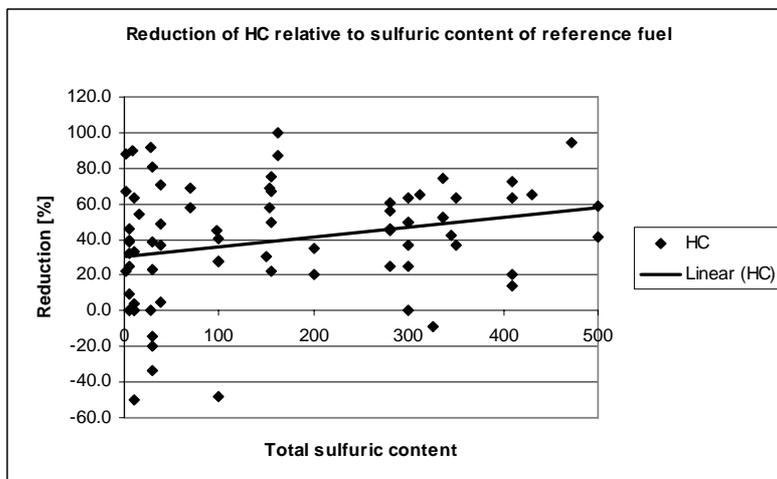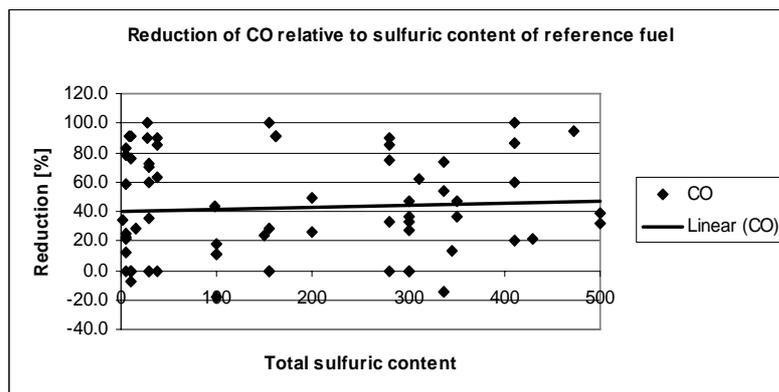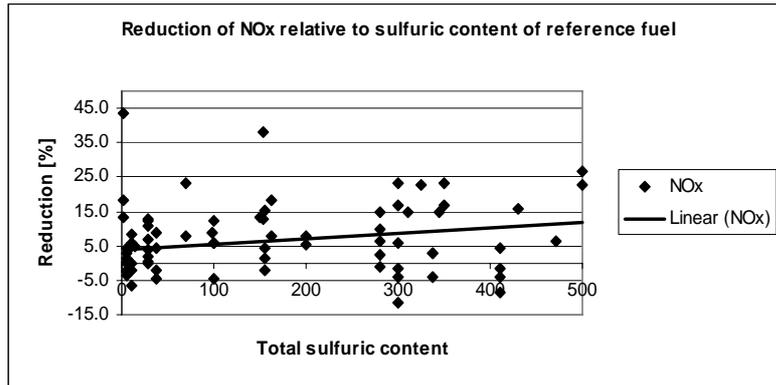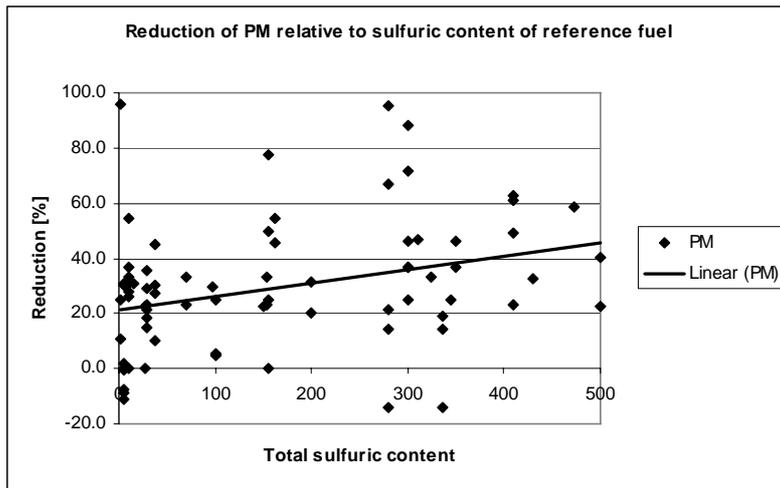
A result is omitted to enhance the appearance of the trend lines and graphs: [33] test of 49-state diesel with 3500ppm sulfur and FTCOD[4]

For the NOx figure one result of -69% [24] is omitted for the sake of appearance.

Figures 24 - 27 – Relative reductions of pollutants NOx, CO, HC and PM relative to aromatic content of reference fuel for all tests.

Reduction of NOx relative to aromatic content of reference fuel

Reduction of CO relative to aromatic content of reference fuel

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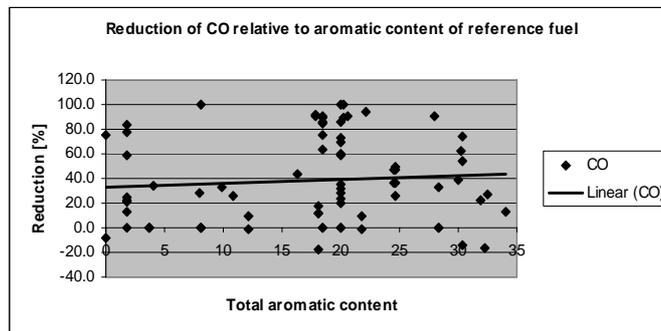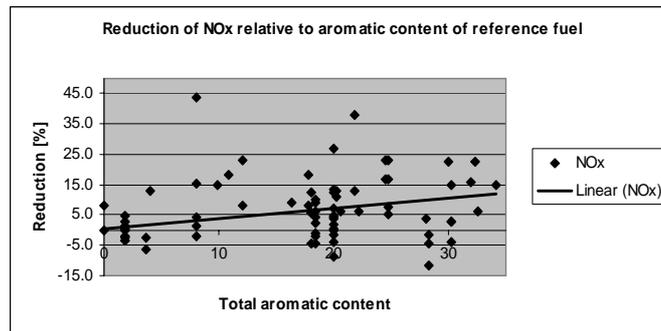
[4] FTCOD = FT Conversion of Olefins to Diesel.

Reduction of HC relative to aromatic content of reference fuel

Reduction of PM relative to aromatic content of reference fuel
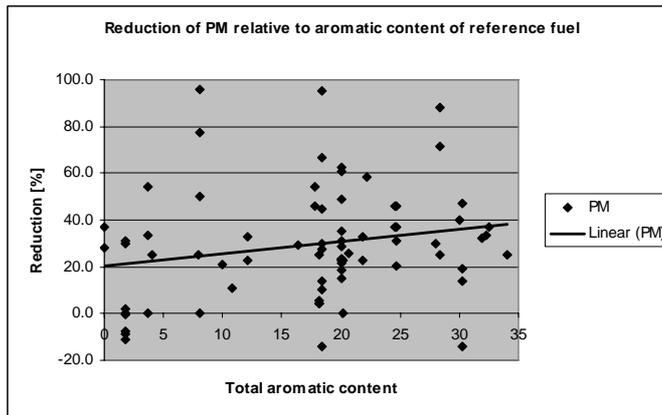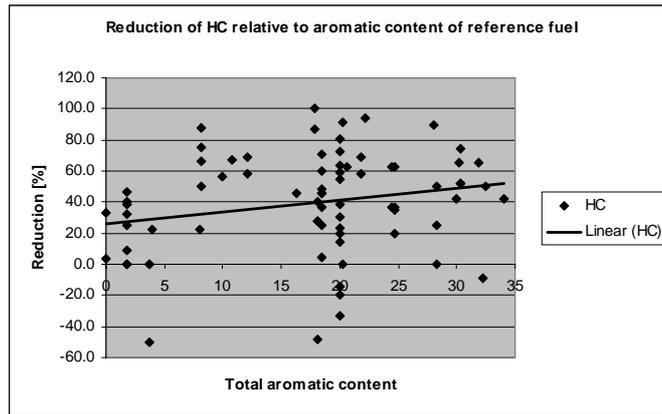
Figures 28 – 31 Relative reductions of pollutants NOx, CO, HC and PM relative a normalized aromatic and sulfuric content.

Reduction of NOx relative to aromatic and sulfuric content of reference fuel

Reduction of CO relative to aromatic and sulfuric content of reference fuel

Reduction of HC relative to aromatic and sulfuric content of reference fuel

Reduction of PM relative to aromatic and sulfuric content of reference fuel
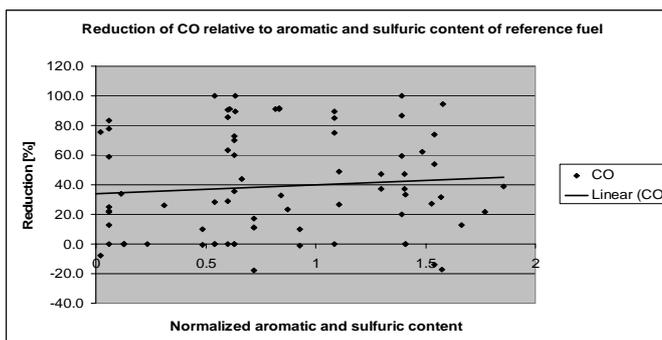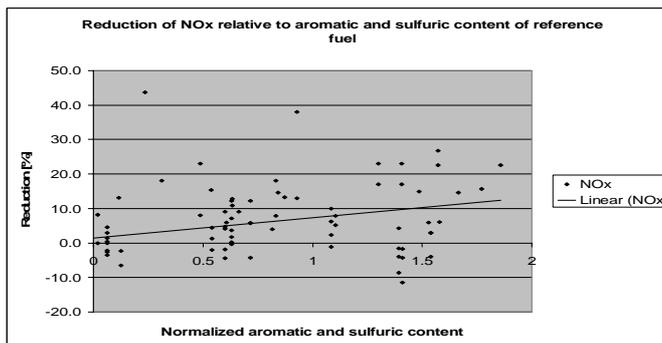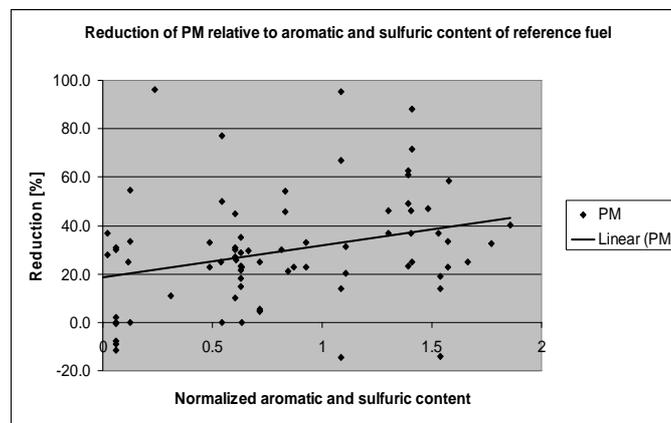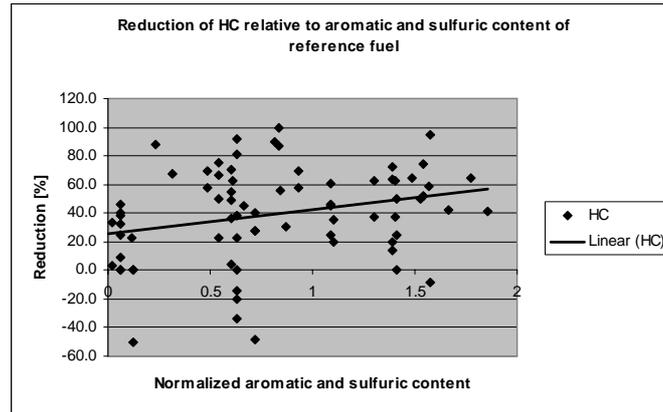
Looking at these figures there are indications of a connection between aromatic and sulfur content and relative reduction of emission comparing conventional diesel to FT diesel.

The figures also show that across the various different conditions such as fuel, engine, driving pattern and exhaust after treatment device there are significantly better performance with FT diesel even if it is compared to high quality low sulfur low aromatic diesel fuels.

In order to examine the contributions of sulfur and aromatics the data was normalized by dividing sulfur content (ppm) with 500 and aromatic content (%) with 35 and then combined. Charts can be seen in figures 28 - 31.

The figures also show that across the various different conditions such as fuel, engine, driving pattern and exhaust after treatment device there are significantly better performance with FT diesel even if it is compared to high quality low sulfur low aromatic diesel fuels.

The difference of reduction in % of the trend line going from 0 to maximum content can be seen in table 18

Table 18 – Table of differences in the trend lines.

	NOx	HC	CO	PM
Sulfur 0-500 ppm	8,0	27,0	7,0	24,0
Aromatics 0-35%	12,0	26,0	11,0	18,0
Normalized combined	11,0	32,0	12,0	26,0

The numbers in the table and the figures support the suggestion of an influence of aromatics and sulfur looking at the literature generally. It can also be seen from the combined data that sulfur and aromatics both have a contribution that to some limited degree adds up. Note that the numbers are based on a relatively small amount of data and are as such only indications of these trends.

Reductions of PM with lower fuel content of sulfur are well known in the literature. Reductions of HC and CO with lower sulfur could be due to higher conversion efficiencies in the exhaust gas catalyst. NOx reductions with lower sulfur can not be explained at this time but the trend could be due to the fact that fuels with low sulfur content usually also has low aromatic content, since they fall in to the category of high quality or environmentally friendly diesel fuel.

Reductions of PM with lower fuel content of aromatics are also well described in the literature. NOx is reduced with lower aromatic content since the combustion temperature is lower.

8.3.2.2 Cold vs. hot start

The largest part of the polluting tailpipe emission is produced while the engine is running cold, i.e. immediately after the start-up. There is therefore a difference between testing a driving pattern when the engine or vehicle starts being cold or hot. It is mentioned in some of the reviewed literature that the emission performance with FT diesel is believed to be even better relatively when the engine makes a cold start, but there is not enough evidence among the references to generally support this point. It is shown in [27] though that cold start emissions are improved even more than hot start emission comparing FT diesel to conventional diesel.

8.3.2.3 Driving Pattern

Figure 32 – FTP75 Driving Pattern
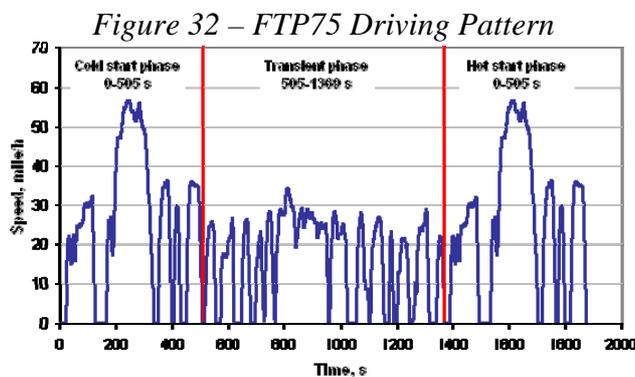
A driving pattern is a graph of time over speed of the car to be tested. The purpose is to simulate real life driving and to have a common standard in order to be able to compare tests.

There are many standard driving patterns but the most commonly used are the Federal Test Procedure (FTP) and the European Driving Cycles (EDC). As the need for simulation of more diversified driving situations, new patterns have been put into use. US06 is a driving pattern that is aggressive, has higher speeds and more rapid speed fluctuations, and was developed as a supplement to the FTP75 cycle. HFET is a fuel economy test protocol for highway driving. See figures 32 - 34 [47].

Figure 33 – HFET Driving Pattern
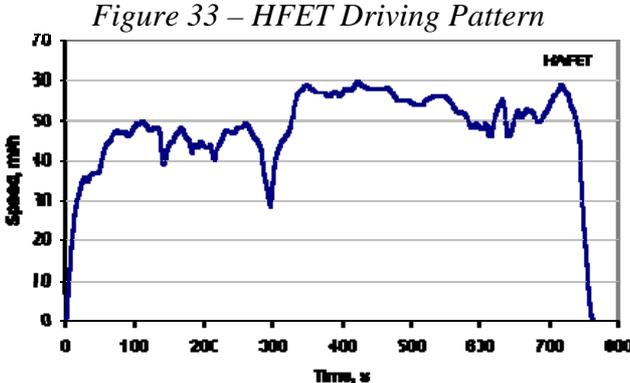
In [35] test results suggest a larger relative reduction in emissions with a more aggressive test cycle (US06 compared to NEDC and FTP).

In [20] it is shown that FT diesel improved the efficiency of the oxidation catalyst during the most urban driving like parts of the test cycles. The same was concluded in [39].

8.3.2.4 After treatment devices

Exhaust after treatment devices are devices or systems designed to remove or convert pollutants from the engine before it is emitted through the tailpipe. Some of the most common in the reviewed literature are: Diesel Oxidation Catalysts (DOC), Diesel Particle Filter (DPF) and Exhaust Gas Recirculation systems (EGR).

Figure 34 – US06 Driving Pattern
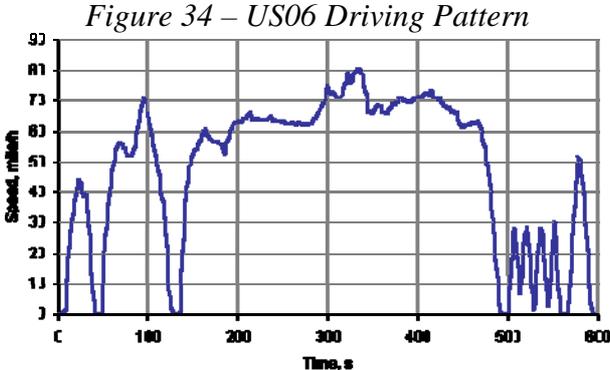
It is concluded in [25] that engine out[5] emission from modern engines does not benefit from a reduction of sulfur at levels below 150 ppm. It concludes though that fuel sulfur reduction makes a positive difference regarding PM emission using a DOC because of higher oxidation rates. This point is supported by [26]. The study also concludes that after treatment devices have a significantly higher effect on emissions than alternative diesel fuels have, and that neither after treatment devices nor alternative diesels have any effect on emission of CO_2. That fact is disputed by [30].

DOC efficiency is significantly higher with FT diesel than conventional diesel at lower operating temperatures according to [20].

In [30] it is stated that when using a DPF the only fuel property influencing PM emission is fuel sulfur content. The report also concludes that many after treatment devices designed to reduce NOx emission will potentially benefit from ultra low sulfur fuels. This point is acknowledged in [35] where after treatment devices such as DPF, NOx adsorber and DOC respond very positively to fuel sulfur levels lower than 30 ppm.

8.3.2.5 Blending properties

Blends of conventional diesel and FT diesel have been shown to improve emission performance compared to the performance of neat conventional diesel. This has been shown in [23], [27] and [34]. In blend studies it has been shown that the emission performance is over-linear with the blend fraction in a positive way. This means that the emission is cleaner than the fraction would indicate.
In [23] it is stated that a 30/70 FT diesel/conventional diesel blend performs as good as a 50/50 blend with respect to certain emission factors. An over-linear emission response is showed [132]. In [36] a 50/50 blend performs almost as good as the neat FT diesel. An over-linear response is also shown where a 20% fraction FT diesel gives 40% of the total FT diesel emission benefit. In [37] there is an over-linear emission response to NOx emission. More than half the obtainable FT diesel NOx emission benefit was gained by a 33% FT diesel fraction.

8.3.2.6 PAHs – Air Toxics Emission

Some PAHs (polycyclic aromatic hydrocarbons) are categorized as being carcinogenic and are as such unwanted substances in the environment. PAHs are a part of a larger group of molecules called aromatic hydrocarbons or just aromatics. The conventional diesel fuels in the review contain up to 34% fuel aromatics and hereof up to 5% PAHs. The average aromatic content of the reference fuels in the reviewed literature is 17% where the number is 2.1% for the FT diesels. FT diesels from most of the fabricants have near zero aromatic content except the diesel fuel from Mossgas called Fischer-Tropsch Conversion of Olefins to Distillate (FTCOD) that has a content of 10%. Regulations of the aromatic content in diesel fuels can be expected in the future.

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[5] Emission output directly from the motor head, i.e. before any aftertreatment device.

Reference [23] contains studies that show a reduction of 35% and 50% reduction of exhaust gas PAHs using FT diesels compared to conventional diesels, even though some of the conventional diesels are very clean fuels (low on sulfur and aromatics). In [26] this is supported without giving percentages. In [29] results of 17% PAH exhaust emission reduction is obtained using FT diesel instead of the ultra clean Swedish Class 1 diesel. 27% is obtained compared to other inferior fuels. A reduction of exhaust PAHs of 45% was found in the [31] study. This gives an average PAH emission reduction of 35% compared to an average quality of conventional diesels.

8.3.2.7 Combustion and Adaptation of the Engine to FT Diesel Fuel

FT diesel has a different chemical composition that leads to different fuel properties and therefore a different combustion process, compared conventional diesel. These properties and their consequences are described later in this section.

It has been tried to alter an engine to utilize the different FT diesel properties in a way that leads to cleaner emission and lower fuel consumption. Not many studies of the adaptation of engines has been done yet, but as engines get more and more flexible the benefits of FT diesel should be obtained to some degree 'automatically'.

Figure 35 – Adapting to FT fuel.
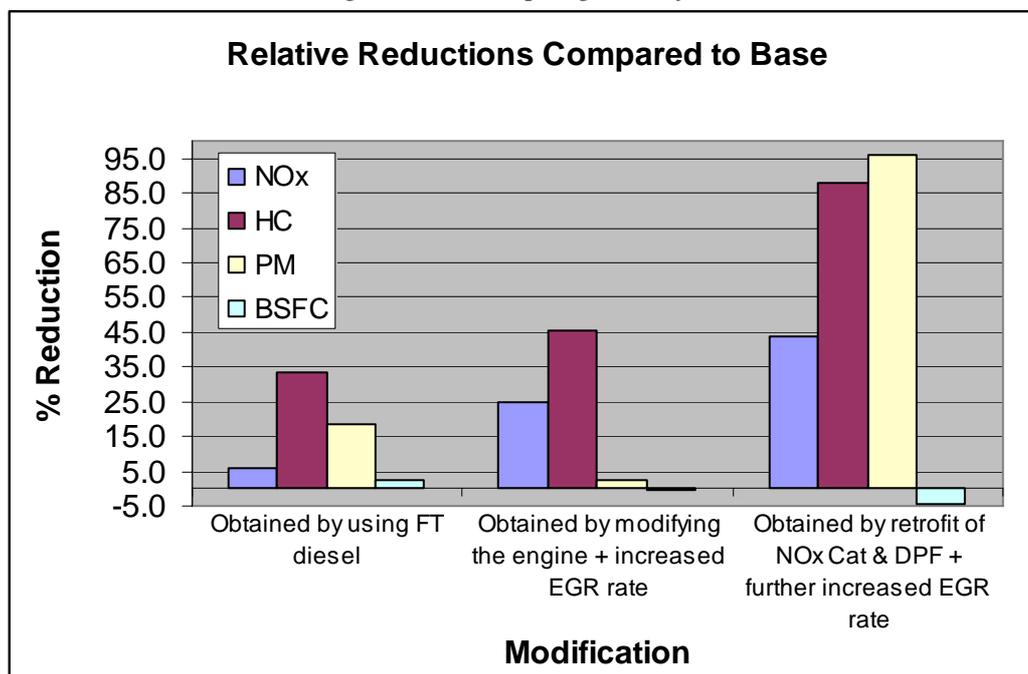
A presentation [28] of emission data comparing emissions from a 2002 Cummins ISM heavy duty engine with EGR fueled by a high quality baseline conventional diesel and a FT diesel. The conventional diesel had 8.1% aromatics and The FT diesel had less than 0.1%. Both were very low on sulfur. The reductions caused by changing fuel were 5.5, 33.4 and 18.7% for NOx, THC and PM respectively. A modification of the combustion bowl of the piston was

then made in order optimize the combustion process. An improvement of NOx and HC emission of around 20% was gained but the drawback was 20% higher PM emission. A lean NOx catalyst and a DPF was then fitted and compared to the baseline configuration (a reference fuel with 8% aromatics and 2ppm sulfur + EGR). The result was a reduction of 44, 87 and 96 percent for NOx, THC and PM emission respectively. See figure 36.

A more in-depth report focused on the combustion studies of a FT diesel called SunDiesel™ is described in [38] and [41]. SunDiesel compared to a regular diesel has a higher volatility and produces shorter pre-mixed combustion than conventional diesel that generally would increase soot. In fact soot decreased due to different soot oxidation characteristics later in the combustion cycle. In plain this means that though more soot is produced early in the combustion cycle with SunDiesel, more soot is also 'burnt' later in the cycle and the end result is less soot compared to conventional diesel. It is stated in [38] that 'Chemistry mechanisms dominate fluid mechanics for overall soot reduction.'

A Mercedes OM646 engine were used to test SasolChevron GTL diesel, EU2005 sulfur free diesel (reference fuel) and two blends of 80/20 and 50/50 (%) GTL/ EU diesel fuel. [36]. The GTL fuel showed almost zero emission of HC and CO during warm-up phase. The reason was believed to be that the very low raw (engine out) emissions allowed the catalyst to convert the emission though it wasn't at optimum operative temperature. The 50/50 blend showed almost the same properties as the neat GTL fuel, that is a large reduction of soot emission and a higher EGR tolerance (facilitating higher NOx reduction) compared to the reference fuel. The combustion was examined and the ignition with the blend fuel was early, like the GTL but unlike to the 80/20 blend and the reference fuel.

In reference [36] it is described how a software modification of the Electronic Control Unit (ECU) can lead to soot and NOx emission reductions of 35% (compared to a reference).

Figure 36 – Blends and ECU recalibration [22]
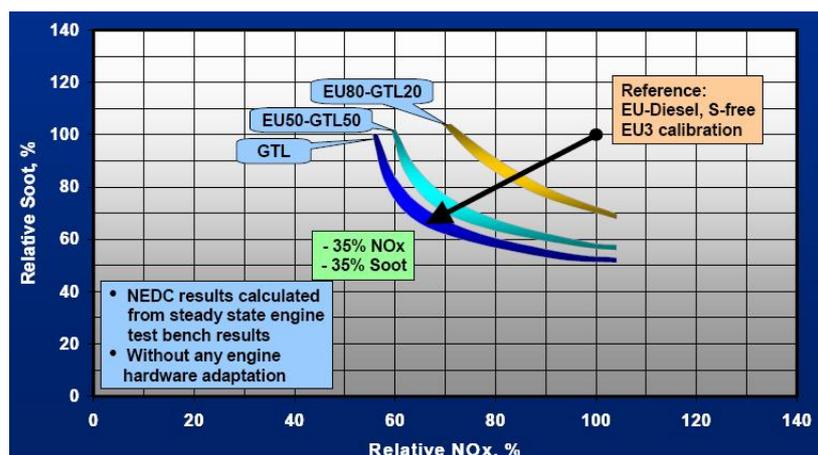
Soot and NOx emission reductions (compared to the reference) of 35, 30 and 15% for neat, 50/50 and 80/20 fuels respectively were obtained by recalibration and optimization of the ECU. See figure 29. It was concluded that blends of EU and GTL diesel might show reductions significantly larger than the blending ratio. 40% of the emissions benefit of GTL may be obtained in a 20% GTL blend and up to 85% may be obtained in a 50% blend.

Single cylinder optical engine tests were carried out and the tests showed better vaporization characteristics and more uniformly distributed flame structure of the neat GTL compared to that of the reference fuel. It showed that main combustion occurs at approximately 3 degrees crank angle earlier for GTL than for the EU diesel.

8.4 Discussion

In the reviewed literature it has been shown that the use of FT diesel instead of conventional diesel can reduce polluting emission from diesel engines/ vehicles significantly. It has also been shown that the degree to which FT diesel reduces pollutants, compared to conventional diesel, depends on the chemical composition of the conventional diesel. There are indications of a diminishing advantage of FT diesel as conventional diesels get cleaner, i.e. the content of sulfur and aromatics lower. On the other hand there are also indications of a the fact that FT diesel shows advantages almost no matter the conditions, for example with an older or a more modern engine technology, exhaust after treatment system, comparing with high quality diesel, etc.

The emission performances of FT diesels are closely connected to their unique chemical composition. There are exceptions but in general FT diesels are almost pure n-paraffin, straight chained hydrocarbons, which leaves no room for other and less optimal types of hydrocarbons such as aromatics. The unique chemical composition leads to unique combustion properties that have been briefly described earlier. In general it is said that FT diesel ignites earlier due to the high cetane number and the combustion runs more smoothly than with conventional diesel. The conclusion seems to be that the combustion of FT diesel runs over a longer period, the flame is more uniform and the in-cylinder pressure curve is more even and therefore there is a gain that is cleaner emission.

The (brake specific) fuel consumption reduction running on FT diesel has in the reviewed literature been measured extensively but has very often been found insignificant ±5%. Some cases though show up to 10% lower fuel consumption and CO_2 emission accordingly. It seems that there are possibilities of adapting diesel engines to take advantage of the combustion properties even more and in that way obtain not only lower emissions but also lower fuel consumption.

Evidence has been shown to prove that much of the benefit of FT diesel can be obtained with blends of conventional diesel and FT diesel. By blending products there seems to be an immediate way to introduce FT diesels in to the market on a larger scale. In the literature it has been suggested that substandard diesel fuels mixed with FT diesel could be sold with an economical benefit. FT diesel has already been introduced to some limited extend and will probably be more popular as the demands for low pollution emission gets ever more stringent.

Many times it has been mentioned in the reviewed literature that the FT production method itself has some advantages. Because FT diesel can be made from almost any kind of material that is rich on hydrocarbons, gas, coal, biomass or even waste, there are major future possibilities. FT diesel can reduce dependency of fossil crude oil to some degree. FT diesel can be a CO_2 neutral fuel and a sustainable alternative to fossil fuel. FT diesel can be used as a way to utilize remotely located or low quality gas resources.

Because of the many positive aspects of FT diesel it can very well be a transition fuel, going from fossil fuel to sustainable transportation fuels of the future. The fact that FT diesel already is commercially viable to some degree and the fact that the large oil companies are investing in the technology supports this point. It has even been suggested that the FT technology could provide fuels for fuels cell technologies.[43]

8.5 Key Conclusions

Based on the information found in the reviewed literature a number of conclusions can be drawn.

- Various kinds of emission pollutants are reduced with the use of Fischer-Tropsch diesel fuel (FTD) compared to conventional diesel: HC, CO, CO_2, NOx, PM, SOF, VOF and PAHs.

- FTD enables the use of more efficient exhaust after treatment devices.

- FTD has better emission performance than several other alternative fuels.

- FTD are expected to have a potential of even cleaner emission if engines were modified to suit its unique properties.

- FTD has good cold starting properties and cold start versus hot start tests show larger reductions for cold starts.

- More aggressive and more urban-like driving cycle's leads to larger reductions with FTD relative to regular diesel.

- FTD is attractive as component in blends with low quality diesel to upgrade fuels to meet the ever more stringent regulations.

- FTDs can help to decrease the dependence of crude oil through Coal-To-Liquid, Gas-To-Liquid and Biomass-To-Liquid technologies.

- FTD made from a biomass feedstock has the potential of reducing the global outlet of CO_2 (on a well-to-wheel basis) from motor vehicles significantly.

- The option of making FTD from remotely located and/or low quality (flare gas) resources of natural gas are less capital intensive than other methods of exploitation at this point. Since a large part of the known gas resources are remotely located this is a very probable option.

- The FT process is still a relatively expensive technology and requires large-scale production plants/ or further development, in order to be economically viable.

- CO_2 reductions of FTDs can be negative on a well-to-wheel basis when comparing to conventional diesels.

- No engine modifications are needed for using FTDs, and the existing fuel distribution system can be used immediately.

- Some studies suggest a slight increase in fuel consumption, others the opposite. Most studies agree that there is no statistically significant change in fuel consumption.

- Drivers have reported smoother running engines and better exhaust gas odor using FTD compared to conventional diesel.

The conclusions may not represent every aspect of FT diesel fuels or the actual fleet of diesel vehicles around the world.

It must be stated that the conclusions are based on a relatively limited number and variety of engines/ vehicles, but since the tests have shown FT diesels ability to perform better under a variety of conditions there are clear indications of the potential. The limitations of the fuel are also indicated, and it is very possible that shifting to FT diesel or blends of FT diesel and conventional diesel alone is not enough to meet the near future demands for low emission vehicles.

9. Emission Measurements of FT Gasoline

9.1. Introduction

Emissions performance tests were made on a VW Golf 1.6L FSI 2003. With otherwise similar conditions three different fuels and blends of those were tested; a regular Danish octane 95 gasoline, Aspen 4T alkylate gasoline and a South African FT gasoline product. The synthetic Aspen 4T gasoline was brought into the project as a fuel representing FT gasoline as it could be made in its most ideal form.

The goal of the project is to examine the emission performance of Aspen and FT gasoline including pollutants such as hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NOx) and particulate matter (PM). An analysis of the soluble organic fraction (SOF) of the PM regarding carcinogenic polycyclic aromatic hydrocarbons (PAH) is also included.

9.1.1. FT gasoline

The FT gasoline product tested is a rather complex blend of natural gas derived products. Natural gas is via a high temperature Fischer-Tropsch process made into liquid fuel. After the FT process naphtha is treated by ordinary refinery methods such as hydro treating, alkylation, isomerisation and platforming. Olefins originating from the FT process are treated by the Conversion of Olefins to Distillate (COD) process. The final product consists of several types of molecules such as normal and branched alkanes, cycloalkanes, alkenes and aromatic hydrocarbons. It is oxygenated with ethanol and MTBE (Methyl-Tertiary Butyl Ether). Other ingredients such as xylene, benzene and toluene are present too. The product is categorized as unleaded RFG (Reformulated Gasoline). The tested gasoline is actually only 70% FT gasoline blended with regular South African gasoline. The aromatic content is 32% by volume. The FT gasoline tested is one of many possible formulations and is not necessarily representative for all FT gasoline fuels.

9.1.2. Aspen 4T

Aspen Petroleum AB, distributes a product called Alkylate Gasoline, Aspen 4T, made from petroleum crude oil based gas, not via the FT process. The Aspen product is widely distributed in Sweden intended for use in boats, chainsaws and lawnmowers but is not an approved transportation fuel for gasoline cars. (The VW Golf ran very well on the fuel though.)

Figure 37 – 2,2-dimethylpentane.
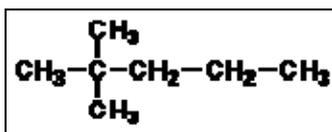
In general alkylation is a process related to polymerization. Reactants in the alkylation process are an alkene and an alkane, for example iso-butane (C_4H_{10}) reacted with propylene ($CH_3CH:CH_2$ or C_3H_6) which both are gases. The product is liquid motor fuel alkylate with an

octane number of 90-115. The product is a mixture of 60-80% 2,2-dimethylpentane, 10-30% 2-methylhexane and ca. 10% 2,2,3-trimethylbutane (triptane)

The Aspen product is claimed to be very low on sulfur, aromatics, benzene and cracked components. The product is similar to what, at best, can be expected of a gasoline fuel made via the FT process, although many different forms of FT gasoline are possible. Since it hasn't been possible to obtain any literature on FT gasoline this cannot be verified at this point.

Figure 38 – Schematic of alkylate production, **[44]**
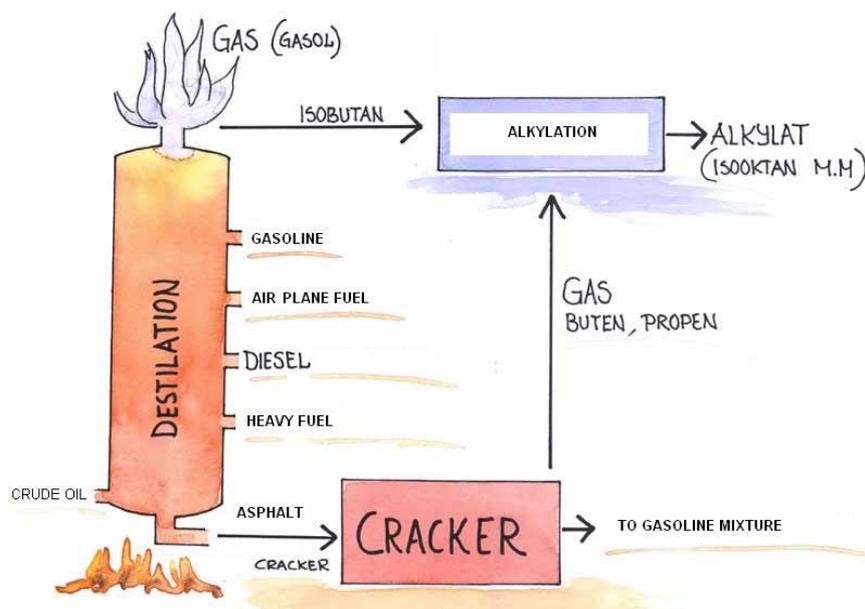
Alkylate gasoline from Aspen, Sweden is made via a process of synthesizing iso-paraffin's by combining light olefins with iso-paraffin's.

Table 19 – Table of Properties, Aspen, FT gasoline and regular gasoline

Property	Regular Danish	Method	FT gasoline	Method	Aspen 4T	Method
Aromatics, vol%, max.	35	EN 14517	32		0.5	ASTM D 5443
Olefins, vol%, max.	18	EN 14517			0.5	ISO 3837
Benzene, vol%, max	1	EN 14517	4.9		0.1	ASTM D3606
Oxygen, wt%, max.						
Sulfur, ppm, max.	5	EN ISO 20846			0.002	ASTM D5453
RVP, kPa	70-95	EN 13016-1	36-63 @ 20C		55-65	ASTM D5191
Lead, mg/l, max.	5	EN 237	0.079		2	ASTM D 3237
Octane, RON, min.	95	EN ISO 5164	95		94.1	ASTM D2699
Octane, MON, min.	85	EN ISO 5163			92	ASTM D2700
Final boiling point, degr. C			192		186.2	ASTM D86
Flash point, degr. C			-43		<0	
Ignition point, degr. C			>280		>250	
Density, kg/m3	755 @ 15C	EN ISO 12185	743 @ 20C		690-710	
LHV, kJ/kg	43900	Calculated			44000	Calculated
Naphtenes, %vol, max.					0.5	ASTM D5134
Boiling range	30-210		39-200			

9.2. Experimental

The emission analysis system consists of three separate units; the Chassis Dynamometer, the Constant Volume Sampling (CVS) Dilution System and the Analysis Test Bench. The system is designed to perform according to international standards for measuring emissions performances of light duty vehicles.

The analysis bench consists of the following instruments: A hydrogen flame ionization detector (HFID) HC analyzer, a chemiluminescent NOx analyzer, CO and CO_2 non-dispersive infrared absorbance (NDIR) analyzers and an oxygen analyzer.

The systems setup was made according to the FTP75 protocol through both FTP75 and NEDC tests.

Every test both NEDC and FTP75 was started with a cold engine. The vehicle was placed in the workshop over night to temperate between tests and the room temperature was 20°C.

The test regime and abbreviations for tested fuels can be seen in table 20.

Table 20 – Test Regime

Test#	Pattern	Fuel	Abbreviation
6	NEDC	Regular	R
7	FTP	Regular	R
8	NEDC	Regular	R
9	FTP	Regular	R
10	NEDC	Regular	R
11	FTP	Regular	R
12	NEDC	Regular/ Aspen 4T	R/A
13	FTP	Regular/ Aspen 4T	R/A
14	NEDC	Regular/ Aspen 4T	R/A
15	FTP	Regular/ Aspen 4T	R/A
16	NEDC	Aspen 4T	A
17	FTP	Aspen 4T	A
18	NEDC	Aspen 4T	A
19	FTP	Aspen 4T	A
20	NEDC	FT	FT
21	FTP	FT	FT
22	NEDC	FT	FT
23	FTP	FT	FT
24	NEDC	Regular/ FT	R/FT
25	FTP	Regular/ FT	R/FT
26	NEDC	Regular/ FT	R/FT
27	FTP	Regular/ FT	R/FT

When shifting fuels the car was run dry and then ½ liter of the new fuel was filled into the tank of the car. The car was then run dry again. This was repeated four times running two liters through before actual testing.

Particulate matter was collected in a separate unit with a Ø293mm quartz fiber filter. PAH analysis was done by obtaining the soluble organic fraction (SOF) of the PM by Soxhlet extraction, and then analyzing the SOF with High Performance Liquid Chromatography (HPLC) fluorescence equipment. The HPLC is capable of analyzing 15 different PAHs.

9.2.1. Test Vehicle

The test vehicle was a VW 2003 model Golf 1.6L FSI. The odometer reading was approx. 48.000km before the first test. According to Carfolio, [45], it has a kerb weight of 1184kg, a 1600cc displacement, 4 cylinders with 4 valves each, a max output of 84.3 kW, a nominal CO_2 emission of 168 g/km, a compression ratio of 12:1 and a direct fuel injection system.

9.3. Results

An overall average of gaseous emission factors running FTP75 and NEDC tests is shown in figure 30. Looking at HC emissions they are reduced using Aspen and FT gasoline relative to regular. Emission of CO is also reduced using Aspen and FT compared to the reference fuel. NOx emission seems a bit reduced with Aspen 4T and CO_2 emission too, but they are increased when using FT gasoline. HC emission when running on a blend of regular an FT gasoline seems rather high, in fact the emission is doubled, which is peculiar.

Figure 39 – Average gaseous emissions using different fuels.
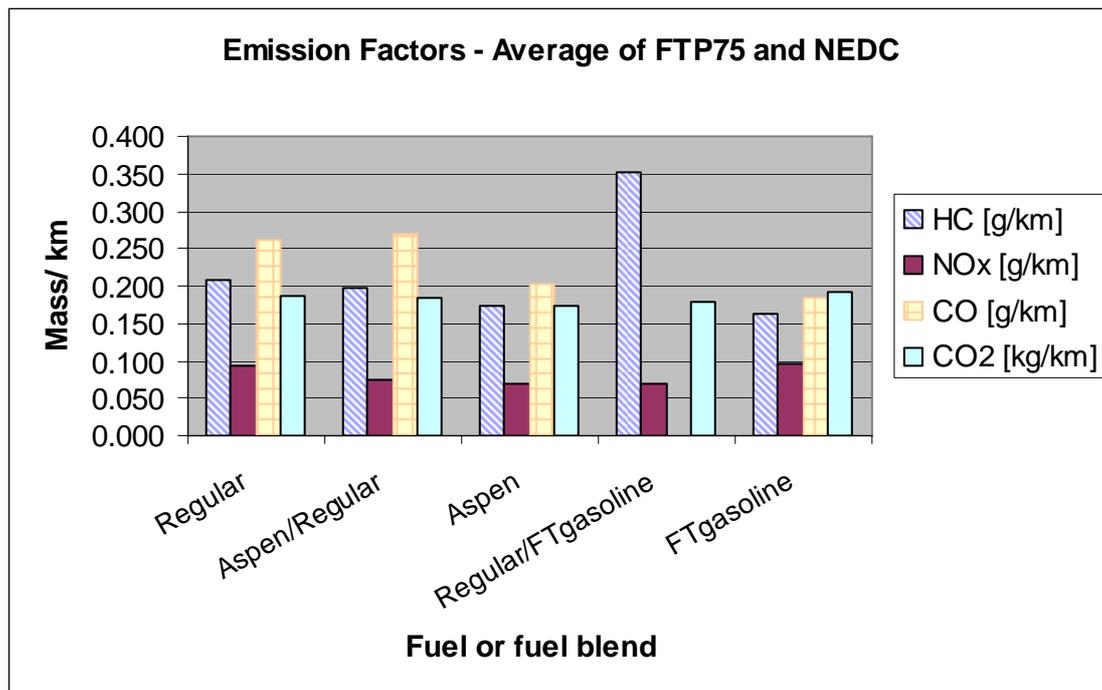

Figure 30 shows the overall average of particulate emission for the tested fuels. It is seen that the reference fuel produces the most PM and the FT gasoline the least. The blends are seen to produce PM according to the expectations i.e. somewhere between the tests using neat alternative fuel and reference fuel.

*Figure 40 – Average of particulate matter emitted.*
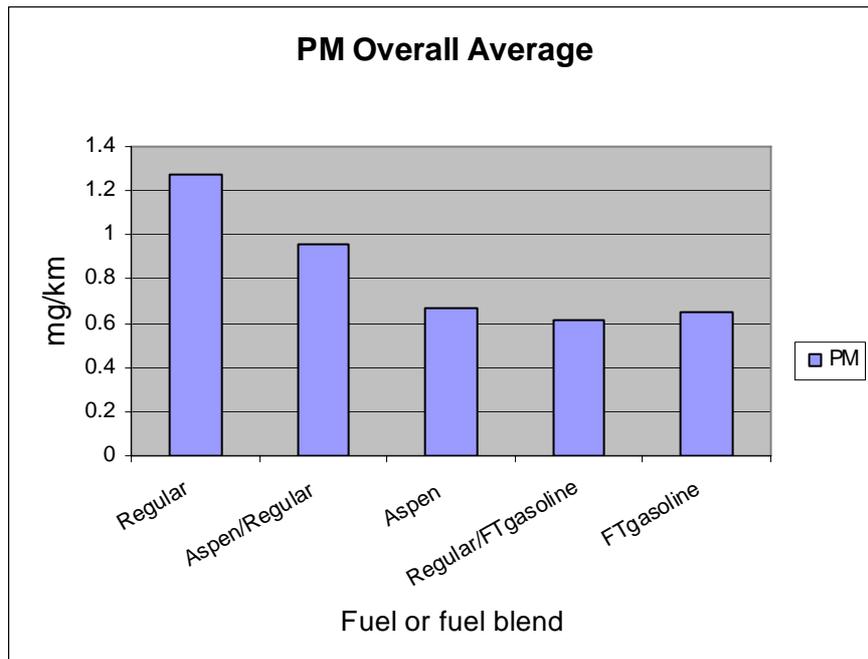
Figure 9.5 shows the average reduction of emission factors comparing the alternative fuel to the reference fuel. HC is reduced about 20% with Aspen and FT. NOx is also reduced about 20% except for neat FT that is peculiar. CO is reduced 20-30% with Aspen and FT. It is seen that PM is reduced to a quite significantly i.e. in the area of 25-50%. The CO_2 emission is reduced by ca. 9% with Aspen fuel and 5% with the R/A blend. This is quite significant given the fact that the effect delivered by the car, due to the driving patterns, is the same. The reduced CO_2 emission gives reason to believe that the brake specific fuel consumption of the car is decreased accordingly. CO_2 is increased with neat FT gasoline.

Figure 41 – Reduction of pollutants compared to the reference fuel.
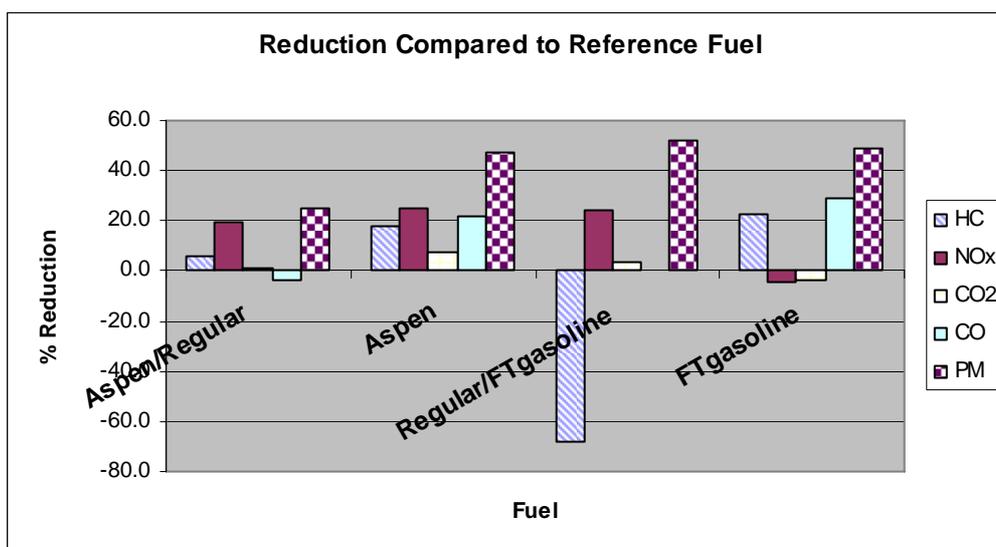
No CO measurements were conducted on R/FT due to technical problems.

There are differences in emissions running the NEDC or the FTP75 driving cycle. Most significant is HC, NOx and CO emission with a difference of 61, -29 and 34% respectively, comparing FTP75 to NEDC on average.

9.3.1. PAH Analysis

Quite significant trends can be seen on figure 9.6. Compared to the regular Danish unless the use of Aspen 4T results in significantly reduced emission of carcinogenic compounds. The mixture of Aspen and regular produces a similar trend. Looking at FT gasoline and the blend the results are that FT produces more emission of PAHs. Figures 34 - 46 show the emission of each individual PAH measured.

The relative PAH emission reductions are 33, 54, -4 and -56% comparing reference missions to R/A, A, R/FT and FT respectively. (Negative reduction indicates increased emission.)

Looking at the figures the overall trend showing relatively low PAH emission for Aspen, high for R/FT and even higher for FT repeats itself for the individual PAHs. The amount of Indeno (1,2,3,-cd) pyrene and Dibenzo (a, h) anthracene is most significantly higher for R/FT and FT. The analysis shows that of the 15 PAHs that possibly could be detected by the HPLC all 15 was found in Aspen, FT and regular Danish Gasoline. The amounts of the individual PAHs vary with the used fuel, but are at the same order of magnitude for many of them.

In the following figures abbreviations R, R/A, A, R/FT and FT are Regular gasoline, 50/50 blend of Regular and Aspen, Neat Aspen, 50/50 blend of Regular and FT gasoline and FT gasoline respectively.

Figure 42 – Total PAH emission, average of all tests.

PAH Total - Average of FTP and NEDC
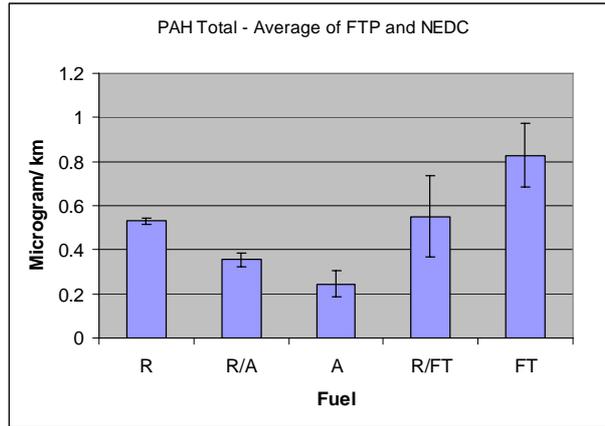
Figures 43 - 54 – Individual PAH emission.

Napthalene Emission Overall Average

Pyrene Emission Overall Average

Benzo(k)flouranthene Emission Overall Average

Phenanthene Emission Overall Average

Benzo(a)anthracene Emission Overall Average

Benzo(a)pyrene Emission Overall Average

Chrysene Emission Overall Average

Dibenzo(a,h)anthracene Emission Overall Average

Flouranthene Emission Overall Average

Benzo(b)flouranthene Emission Overall Average

Benzo(g,h,i)perylene Emission Overall Average

Indeno(1,2,3,-cd)pyrene Emission Overall Average

9.4. Discussion

The most significant conclusion drawn from this investigation is that Aspen's Alkylate gasoline 4T produce cleaner emissions than the other fuels. The pollutants CO, NOx, CO_2, PM and PAH are reduced. Especially the PAH analysis shows a difference between the fuels. These results are as expected when looking at the aromatic content of the fuels. FT gasoline has a better emission performance than regular with regards to emission factors HC, CO and PM, but has higher PAH emissions.

Regarding the gaseous emission Aspen reduces NOx emission with over 20% compared to regular gasoline. This fact plus the fact that CO_2 is reduced by ca. 9% indicates that the combustion of Aspen is a bit different to that of regular and FT gasoline. The following will discuss some factors that could contribute to these results.

One reason could be related to different hydrogen/ carbon (H/C) ratios. The effects of H/C ratio have been discussed previously in this report. Regarding CO_2 a higher H/C ratio would result in lower emissions since there is relatively less carbon in the fuel. The H/C of gasoline is usually 1.8-1.9 [48] and it is somewhat higher for Aspen according to the fuel description chapter 9.1.2. Having roughly the same heating value and higher H/C ratio will lead to lower CO_2 emissions. This is probably the main reason for the lower CO_2 emissions.

Aspen contains only up to 0.5 vol% aromatics where the regular gasoline contains up to 35%. The lack of aromatic content could improve the combustion process compared to regular gasoline combustion. With today's modern exhaust oxidation catalysts the evidence of a less efficient combustion can be hard to detect though, since the catalyst removes unburned products.

A higher H/C ratio has been shown to cause lower combustion temperatures that again lead to lessen NOx formation [40]. When consulting the chemical property tables it reads that the flame temperature of alkylate gasoline is lower than that of gasoline, about 50ºC, which also supports the measured lower NOx emission.

The octane number of the fuel could in a modern engine such as the Golf 1.6 FSI move the engine settings into areas of higher or lower combustion efficiency. The ECU can adjust both injection timing and ignition timing to accommodate different fuel properties such as octane number. Alkylate is normally an octane boosting component in gasoline and Aspen 4T does have a significantly higher motor octane number than the regular gasoline. Since the VW engine has a relatively high compression ratio of 12:1 and is equipped with an advanced knocking sensor and ECU, it is possible that the engine would adjust the ignition in order to gain higher efficiency.

Finally the statistics of the results have to be considered and the conclusion is that there is not enough statistical certainty of these results. 9% CO_2 reduction is a lot and the results should therefore be verified by more tests.

It seems like the Golf engine is capable of utilizing some of the properties of alkylate gasoline in an environmentally positive way. Whether this is the case with the FT gasoline tested is more doubtful. FT gasoline did produce less PM but more PAH which is considered to be more harmful. The eventual benefits of the tested alternatives to regular gasoline are significant though and will likely be investigated further in the future. Compared to FT diesel

the advantages of FT gasoline are not as significant and more tests have to be done to evaluate this.

10.   Life cycle perspective

In environmental calculations for vehicles using alternative fuels, the production method of the fuel itself is very important. Different production methods can give big differences in emissions, particularly of CO_2.

Over the years, a large number of life cycle analyses (LCAs) have been performed on fuels. The German institute IFEU has made an inventory of the life cycle analyses that have been performed, and found more than 800 life cycle studies of fuel production! Admittedly only a few have been performed in accordance with the ISO 14 040 standard, and the majority deal only with energy use and CO_2.

Why then is there a need among so many stakeholders to pay for so many studies that aim to show the advantages and disadvantages of various fuels? In many cases it is public authorities that order analyses and decision data for strategies for future fuel supply. Thus many stakeholders probably do not recognise the environmental performance presented in the analyses and want therefore to publish another picture of the situation. This does not mean that any of them are wrong, but rather that there are many ways in which to produce fuels and also that it is possible to define the production system boundaries in a number of different ways. Different raw materials, different production methods, different degrees of large-scaleness and different assumptions on how possible by-products will be used are examples of reasons why the results of the life cycle studies point towards different results.

The choice of system boundaries and allocation method, time perspectives, and geographical conditions are some of the factors that are of crucial importance for the result of an LCA for fuels. This has been established in a number of reports (Blinge M, 1998), (Jonasson & Sandén, 2004), (Quirin et al., 2004).

LCA as a method is good for producing certain data and certain knowledge, and poor for producing other data and knowledge. The method is being developed continuously, and these advantages and disadvantages are becoming clearer with time. The fact that so many different results can be produced using the LCA method has resulted in the method being questioned from many quarters because "*with LCA you can obtain any result you want*". The criticism is understandable, but it is important to point out that it is not the method's fault that the reality is complex. Nor is there an alternative better method of studying a system's total environmental impact. It is instead a matter of accepting that LCA is a "compass" and that the results must be interpreted in a broader perspective and seen as a jigsaw piece in a complex body of decision data. Not performing an LCA of the entire system and only selecting a small part where it is possible to obtain exact and measurable data on a smaller subsystem is definitely wrong. It is therefore better to be roughly right than to be definitely wrong.

In order to get to grips with the confusion, the recommendation from those researchers who have worked with LCA is that the users of the results must first define what the issues are and the preconditions under which the analysis is to apply. During what period of time is the analysis to apply? What are the volumes in question? What is the geographical scope? Where

were the raw materials sourced and what production method has been used? Once these issues have been clarified, one can search for data and perform those analyses that are credible and that meet the user's conditions.

The scope for this report is to present a feasible set of LCA data on production of Fischer-Tropsch fuels from a global perspective and a large-scale basis. As this scope is comparable to the scope of the studies chosen for this review, a recommendation based on the following five studies can be regarded as fully sufficient and valid for the purpose of this study in question.

10.1 Reviewed LCA:s

The five different life cycle analyses (LCA) of Fischer-Tropsch diesel that are referred to and compared are:

1. *Gas to Liquids Life Cycle Assessment. Synthesis Report. Prepared for: ConocoPhillips, Sasol Chevron, Shell International Gas. Prepared by: Five Winds International. August 2004.*

2. *GM Well-to-wheel analysis of energy use and greenhouse gas emissions of advanced fuel/vehicle systems – a European study. L-B-Systemtechnich GmbH for GM, ExxonMobil, Shell, BP and TotalFinaElf. 27 September 2002.*

3. *Well-to-wheels analysis of future automotive fuels and powertrains in the European context. European Commission Directorate-General Joint Research Centre: Concawe, European Council for Automotive R&D. Version 1B January 2004*

4. *Life-cycle Emissions Analysis of Alternative Fuels for Heavy Vehicles; CSIRO, Australia, 2000*

5. *Vergleichende Ökobilanz von SunDiesel (Choen-Verfahren) und konventionellem Dieselkraftstoff*, PE-Europe GmbH, Leinfelden-Echterdingen, Germany, 2005

A brief description of the scope of the four reports is described below:

- *Gas to Liquids Life Cycle Assessment. Synthesis Report. Prepared for: ConocoPhillips, Sasol Chevron, Shell International Gas. Prepared by: Five Winds International. August 2004.*

This report is based on three different life cycle assessments (LCA)[6] and presents environmental aspects on GTL-fuels as compared to conventional diesel fuels. The three LCA that are compared in the report have been carried out according to ISO standard.

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[6] The studies are:
• *Ultra Clean Fuels Life Cycle Assessment. Nexant Inc.*, (also in conjunction with Penn State University, Cummins Engine Co. and the U.S. Department of Energy's National Energy Technology Laboratory) for ConocoPhillips and US Department of Energy. November 2003.
• *Use of a Life Cycle Approach to Compare the Environmental Implications of Sasol´s*

In the report, the term "GTL technology" is used to refer to the range of liquid products produced by the Gas to Liquids system while the term "conventional diesel" is used to mean the conventional crude oil refinery based system.

All these three LCA studies compare the existing refinery system with an engineering assessment of the GTL technology current at the time the studies were conducted. The GTL data therefore is based on engineering analysis and/or pilot plant operations.

While the two systems, GTL and conventional refining, are not directly comparable, the system boundaries were expanded so that both systems produce the same range of functions. The expansion was performed on the basis of existing complementary technologies. The Shell and Sasol Chevron studies look into the full systems, including all products1 of the two technologies, from electricity generation, space heating to refinery products and transportation fuels. The respective products provided by only one of the systems were compensated by a so-called system expansion, where alternative routes to produce such products were added to the other system so that both systems provide identical services. The ConocoPhillips study used a similar co-product system expansion approach focusing on automotive fuels.

The system expansion approach that was used in these LCA takes a comprehensive view and seeks to ask the question "What are the environmental implications of supplying markets 1, 2, 3 with products from technologies A, B and C?" To answer this question, it is necessary to consider the whole technology system. Specifically for the GTL technology, a system comparison for a complex refinery system included refining, the main products and markets. The three LCA studies intentionally studied the whole technology system and not individual output products from the production system such as only fuel. The system comparisons used here are more comprehensive compared to well-to-wheel studies, since they take the whole suite of products into account. They consider the direct market consequences of applying a new technology.

In the report two production routes have been considered:
• From natural gas (known as Gas-to-Liquids of GTL),
• From woody biomass (known as Biomass-to-Liquids or BTL).

The three studies differ in specific products and services included in the system boundaries. The Shell study for example includes the production of base oils for lubricants, n-paraffin and heavy fuel oil production used for electricity generation in the refinery system. For the GTL system, all studies include the production of diesel, LPG and naphtha for the GTL system. To make GTL and conventional diesel technologies comparable, the service provided by the two systems has been made identical in the LCA. To do this, additional products were added to the respective core product each technology provides. This ensured that overall the same functions can be met even though those functions, such as space heating or electricity generation, are not necessarily provided by the same fuels. The overall environmental impacts

Slurry Phase Distillate Technology with Complex Refinery. PricewaterhouseCoopers LLP (PwC) for Sasol Technology Pty and Sasol Chevron. November 2002.
• *Shell Middle Distillate Synthesis (SMDS). Update of a Life Cycle Approach to Assess the Environmental Inputs and Outputs, and Associated Environmental Impacts, of Production and Use of Distillates from a complex Refinery and SMDS Route*. PriceWaterhouseCoopers LLP (PwC) for Shell International Gas. May 2003.

are measured in reference to the whole system's impact. The results express the total environmental load for all products and services included.

The following describes the system studied in each LCA and specifies which products and services were included. Each study used system expansion so that the products and functions included in the systems became comparable. The LCA's have been carried out from a well-to-wheel approach, thus including also the final step in the chain.

Shell
Refinery system: Production and use of products arising from refining of crude oil.

GTL system: Production and use of products arising from SMDS, plus production (and use) of other products meeting additional (secondary) functions arising from refining of crude oil.

Sasol Chevron
Refinery system: Production and use of products arising from refining of crude oil.

GTL system: Production and use of products arising from Sasol's SPD technology, plus production and use of other products meeting additional (secondary) functions arising from refining of crude oil.

ConocoPhillips
Refinery System: Production and use of products from refining of crude oil.

GTL system: Production and use of products based on a detailed engineering analysis of current and future commercial technologies for GTL production

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- *GM Well-to-wheel analysis of energy use and greenhouse gas emissions of advanced fuel/vehicle systems – a European study. L-B-Systemtechnich GmbH for GM, ExxonMobil, Shell, BP and TotalFinaElf. 27 September 2002.*

This LCA describes the aspects of the Fischer-Tropsch fuel "well-to-wheel". Well-to-wheel studies concentrate solely on transportation fuels. Where a system (such as conventional refining or GTL) produces other products in addition to transportation fuels, these other products are not considered. Those other products are eliminated from the system, by using physical relationships of the co-products and only accounting for the percentage share of the product of interest.

- *Well-to-wheels analysis of future automotive fuels and powertrains in the European context. European Commission Directorate-General Joint Research Centre: Concawe, European Council for Automotive R&D. Version 1B January 2004.* *http://ies.jrc.cec.eu.int/Download/eh.*

This is also a well-to-wheel approach. It has a European perspective and includes an assessment of the future expected improvements for each fuel-powertrain system.

- *Life-cycle Emissions Analysis of Alternative Fuels for Heavy Vehicles; CSIRO, Australia, 2000.*

This review has a well-to-tank approach which is a full fuel cycle-analysis covering from upstream emissions in the production of Fischer-Tropsch diesel, through all steps in the process until delivery to refueling stations. It is not stated in the report whether the LCA was carried out according to ISO standards.

- *Vergleichende Ökobilanz von SunDiesel (Choen-Verfahren) und konventionellem Dieselkraftstoff, PE-Europe GmbH, Leinfelden-Echterdingen, Germany.*

In the search for LCA studies (not only energy and fossil CO2) has only one published report been found. This study is a comparative ecobalance of SunDiesel (Fischer-Tropsch from biomass) and conventional Diesel according to DIN EN ISO 14040 et seqq. PE-Europe GmbH performed this study by order of Volkswagen and DaimlerChrysler. The study was reviewed in terms of ISO 14040 by an independent expert third-party. The German institute IFEU plan to publish another similar report in may 2006.

The scope in the studied report is somewhat different to the others in terms of that it has a scope on evaluating biomass based Fischer-Tropsch production and the fact that it is a "full blown" LCA. It is only available in German and the results from that study is basically a short summary of the report and the results from this report described separately in chapter 11.2.

10.1.1 Sources and manufacturing processes

- *Gas to Liquids Life Cycle Assessment. Synthesis Report. Prepared for: ConocoPhillips, Sasol Chevron, Shell International Gas.*

GTL plants are complex and need to be large to be economically viable. They would normally be sited near a remote gas field in order to have access to a cheap and abundant feedstock. A typical state-of-the-art plant would be designed to produce 2-3 Mt/a of total products, about two thirds of which would be diesel fuel. Gas reserves are available and many potential sites exist but it is generally considered that there will not be more than about 10 worldscale plants in the world by 2020.

The potentially available wood and wood waste could theoretically be used to produce 958 PJ/a of diesel fuel (some 23 Mt/a) i.e. some 11.5% of the forecast total 2010 European diesel fuel demand. Depending on the process significant volumes of naphtha would also be produced. Making these huge quantities of farmed wood available (about 130 Mt/a) would require the development of a completely new farming practice over vast areas of arable land (about 13 Mha, roughly the land area of England) hitherto dedicated to crops such as cereals. Harvesting and transporting wood to the plants would require a vast logistic system and so would the collection and transport of waste wood. The need to feed the plant in a practical and economic manner is likely to call for fairly small plants with capacities in the region of 50 to 100,000 t/a of total liquid product.

Recently a potentially attractive scheme was proposed to integrate synthetic fuels and paper pulp production by gasification of the so-called black liquor (an aqueous solution of the wood's lignine that traditionally serves as an energy source in a pulp mill). There appears to be large synergistic gains between the two processes, potentially significantly increasing the net wood conversion efficiency. This could also make the prospect of producing synthetic fuels more plausible by providing an established industrial environment to do so (there are about 50 paper mills in Europe). Investments are regarded as fairly costly in this LCA.

While the refinery-based system is based on crude oil, GTL uses remote natural gas reserves. The refinery system provides LPG (Liquefied Petroleum Gas), Mogas (conventional

gasoline), diesel, naphtha (a chemical feedstock), light fuel oil and residual oil. The respective uses of the fuels are indicated in Figure 1 and include functions such as transportation fuel, electricity generation and space heating.

The GTL system produces LPG, naphtha and diesel. Here natural gas, coal and kerosene have to be added to the system. While the two systems meet the same functions, they still differ fundamentally in the way the services are being provided. Heavy fuel oil for example is an economically less attractive product from the refinery system. It is mainly used in electricity generation. It has high sulphur content and achieves significantly smaller energy efficiency yields as compared to the natural gas alternative in the GTL system.

The ConocoPhillips LCA used a very similar method where co-product emissions were attributed to the primary product or products in the fuel production stage. Those co-products were then compared with alternative products in downstream applications and the net consumptions or releases are assigned as either credits or debits to the primary products. As a result this study compares different transport fuels. The study expresses the results for the different fuel types in units of consumption or releases per unit of distance traveled.

All studies use sensitivity and uncertainty analysis to better understand the influences from variables and assumptions. Key assumptions have been assessed to the extent they can influence the overall results. The analysis showed that the study results are stable and do not significantly change when altering assumptions and variables.

- *GM Well-to-wheel analysis of energy use and greenhouse gas emissions of advanced fuel/vehicle systems – a European study. L-B-Systemtechnich GmbH for GM, ExxonMobil, Shell, BP and TotalFinaElf. 27 September 2002.*

This study covers several fuels from several sources. Two of them are FTD from remote source (natural gas based) and FTD from residual wood. For the first, the study the energy content of the natural gas in the gas field was considered and for the latter, the study traced the energy use back to the energy content of the crop.

The analysis is focused on a base vehicle, an Opel Zafira minivan from 2002. The components in each powertrain analysed were sized to meet a set of vehicle performance requirements typical for European consumers such as launch performance, 0-100 km/h acceleration time, and top vehicle speed. The energy management and control strategies were optimized over the European Driving Cycle. The characteristics of the different powertrain technologies studies were based on efficiency and performance consistent with Euro IV emission standards. Cold start performance was not included nor issues regarding cost and packaging needs due to their surrounding uncertainties.

The main fuel production pathways that were investigated and compared were:
- Crude oil based pathways
- Natural gas based pathways including the following two FTD products and scenarios: FTD synthesized from European Natural Gas Mix at a centralized EU FTD plant, distributed by pipeline, inland ships or railroad trailer to a depot and transported by truck 150 km to the refueling station; or FTD from Remote Gas – here the FTD is shipped to Europe over sea and transported 500 km by truck to the refueling station.
- Electricity based pathways

- Biomass based pathways – including the following FTD product and scenario: Hydrocarbon Liquids from Residual Woody Biomass, where the biomass is collected and transported 50 km to a biomass processing plant. Then the biomass is converted to HC-liquids by gasification to synthetic gas and FT synthesis. The resulting HC-liquids are transported 150 km by truck to a fuel station.

The GTL and BTL processes can produce a variety of products. When focusing on the diesel fuel product from these processes, one is confronted with the issue of allocation of production energy. Although diesel fuel often is the main product in volume terms, its fraction in the total product will not, in practice, exceed 75% (higher yields may be achieved by recycling lighter products but at a considerable cost in energy). Naphtha takes the largest share of the balance and can hardly be considered as a by-product being of the same nature as diesel fuel and usable in applications where it also would displace petroleum products. It has therefore been considered that each product is produced independently, with the same energy efficiency.

The combined process of primary energy conversion and FT synthesis is energy-intensive, more so for wood than for natural gas. This is mainly because the overall process is more straightforward and more energy efficient for gas. Also future GTL plants are expected to be very large and highly heat integrated. This is likely to be less so in smaller wood conversion plants where the size may be dictated by the raw material availability/collection and such complexity may not be economically justified.

- *Well-to-wheels analysis of future automotive fuels and powertrains in the European context. European Commission Directorate-General Joint Research Centre: Concawe, European Council for Automotive R&D. Version 1B January 2004.*

By synthetic diesel fuel this report means the products made by Fischer-Tropsch (FT) or DME synthesis from "syngas" the mixture of carbon monoxide and hydrogen obtained by partial oxidation of hydrocarbons or wood or by steam reforming of natural gas. The products of this process scheme are long-chain paraffins or DME, both free of sulphur.

This Well to wheel study has taken into account some scenarios for alternative use of biomass.

The first case is a "maximum ethanol" scenario. Ethanol is produced from surplus sugar beet and wheat, from extra wheat grown on set-asides and from straw and wood waste. In the second and third cases liquid diesel fuel is produced from oilseeds and wood by changing the use of the set-aside and of an area of cultivated land corresponding to the cereal surplus. The second case shows maximum oilseeds and the third maximum wood. It is assumed that sugar beet and straw are still used for ethanol. The fourth case is a variant of the third where DME is produced instead of synthetic diesel fuel.

In the study it is estimated that ethanol and FAME, Fatty Acid Methyl Esters, produced in the conventional way, could supply a maximum of around 5% of the total road fuels (including heavy duty) or up to 8% of the passenger car transport demand (based on the energy content of the biofuels, i.e. not accounting for the fossil energy required for their manufacture). For ethanol this is based on projected cereal surpluses, sugar beet yield increases and the use of set-asides. For FAME the figure is based on increasing use of oilseed rotations to counter the

projected EU-25 cereals surplus, as well as set-asides (there is a synergistic effect in this case as oil seed crops used as break crops increase cereal yields in subsequent years).

"Wood" is considered here as a proxy for cellulose material, the largest potential sources being farmed wood and perennial grasses, wood waste from forestry and wheat straw. The potential for farmed wood is estimated to about 1640 PJ/a if replacing surplus cereals, to which some 650 PJ/a could be added by planting short rotation forests on set-aside land. Waste wood from forestry could add 365 PJ/a to this tally.

The wood routes produce the highest amount of fuel, because of the high yield of wood and the good conversion efficiency of the underlying process. Wood processing would also produce naphtha in ratio of about 1 to 3 to diesel fuel. Even larger volumes of DME can be produced because of the slightly higher conversion efficiency but also because 100% of the wood is turned into DME, without any co-product.

The FAME route appears marginally better than the pure ethanol one mainly as a result of the synergistic effect of oil seed plants as enhancers of wheat yields.
These four alternatives are of course extremes and a mixture of the three is more likely to occur in reality. The "all wood" scenarios in particular is not very likely and it would require vast tracks of land to be permanently turned into short rotation forests, with a large impact on the countryside, as well as a complex logistic system to collect and transport all this wood to the processing plants.

There are clear differences between the four scenarios in terms of CO2 avoided. The wood pathways have very low fossil energy consumption which combines with the higher efficiency of the Diesel engines to make the diesel fuel substitution routes are much more favorable than the ethanol route. This is particularly so for synthetic diesel fuel whereas the FAME options are penalized by high N2O emissions. The DME option benefits from higher wood conversion efficiency and DME represents 100% of the product (whereas some naphtha is produced in the synthetic diesel fuel case).

- *Life-cycle Emissions Analysis of Alternative Fuels for Heavy Vehicles; CSIRO, Australia, March 2000.*

FTD is here supposed to be produced from natural gas at a plant in Australia that has large natural gas deposits in the North West Shelf.

Upstream emissions expected from producing FTD from natural gas would be from the recovery and processing of the natural gas, from the syngas and Fischer-Tropsch processes, upgrading plant, transportation to the major cities and distribution to retail outlets.

The report sums up data from different full fuel cycle analyses including the three steps of production of FTD: syngas production, hydrocarbons synthesis and product upgrading; transportation of FTD via ocean tankers, storage at port terminals and transportation via pipelines, railcars, barges and/or trucks to the refueling stations.

10.2 LCA on F-T from biomass – the PE-Europe study

In terms of this study SunDiesel is a fuel produced by the gasification of wood residues followed by the Fischer-Tropsch synthesis according to the Choren-procedure. This study is a life cycle analysis i.e. all processes of the value-added chain from the raw material production to the usage of the fuel are taken into account.

The data of the Choren-procedure is based on the design parameters of the 43 MW plant in Freiberg, which is currently under construction. In addition measuring data of the existing pilot plant has been considered. The data of the fuel use phase is based on a modern Diesel Euro 4 car. The potential for reducing emissions of a SunDiesel powered car has been determined by the project partners Volkswagen and DaimlerChrysler. Data for wood production and transports has been taken from literature. For the reference system "conventional diesel" PE-Europe has performed a detailed life-cycle model.
This study evaluates three scenarios with varying parameters:

- The "**Base-Autarkic-Scenario**" represents the current status of plans for the Choren-procedure in the plant in Freiberg. The required hydrogen and electric power as well as the gases oxygen and nitrogen are produced internally by the input-biomass. In this way no external energy or other substances have to be added. Thus, the plant works autarkic.

- In the "**Future-Scenario**" the required electric power as well as the gases hydrogen and oxygen are produced externally based on renewable energy. In this way the yield of SunDiesel per processed kg wood can be increased considerably. This scenario is a realizable option for the future.

- The "**Partly-Autarkic-Scenario**" is another option that can be realized already today. The hydrogen is produced internally, while oxygen and nitrogen are obtained externally from conventional production and the electric power is supplied from the German grid. This scenario is deemed as technically and economically equal to the base-autarkic-scenario.

10.2.1 Results

The essential boundary conditions are presented in Tabel 20

Table 20: Boundary conditions and results of the three scenarios

	Sceario		
	Future	Base-Autarkic	Partly-Autarkic
Wood transport Forest > Choren-plant	50 km		
Fuel transport Choren-plant > filling station	50 km		
Sensitivity analysis	Biomass input: 100% trunk wood Transport distance forest > Choren-plant: 200km Transport Choren-plant > filling station: 100km		
Mass relation Biomass [kg] to Diesel [kg]	3,4 : 1 (35% H2O) 2,2: 1 (atro)	9,3 : 1 (35% H2O) 6 : 1 (atro)	7,5 : 1 (35% H2O) 4,9 : 1 (atro)
Efficiency factor Choren-procedure [%] (Hu Output / Hu Input)	64%	45%	55%
Climate impact potential with regard to convetional diesel	-91%	-87%	-61%

Besides the climate impact potential additional environmental impacts are evaluated in an ecobalance. Figure 1 presents the environmental potential of SunDiesel compared to conventional diesel in the impact categories climate change, summer smog, eutrophication and acidification. Negative values demonstrate ecological advantages of SunDiesel compared to conventional Diesel. The "Base-Autarkic-Scenario" and the "Future-Scenario" show big reduction potentials in all categories, especially in the categories climate change and summer smog. The "Partly-Autarkic-Scenario" shows big reduction potentials in these categories as well while the reduction potentials in the categories eutrophication and acidification are limited.
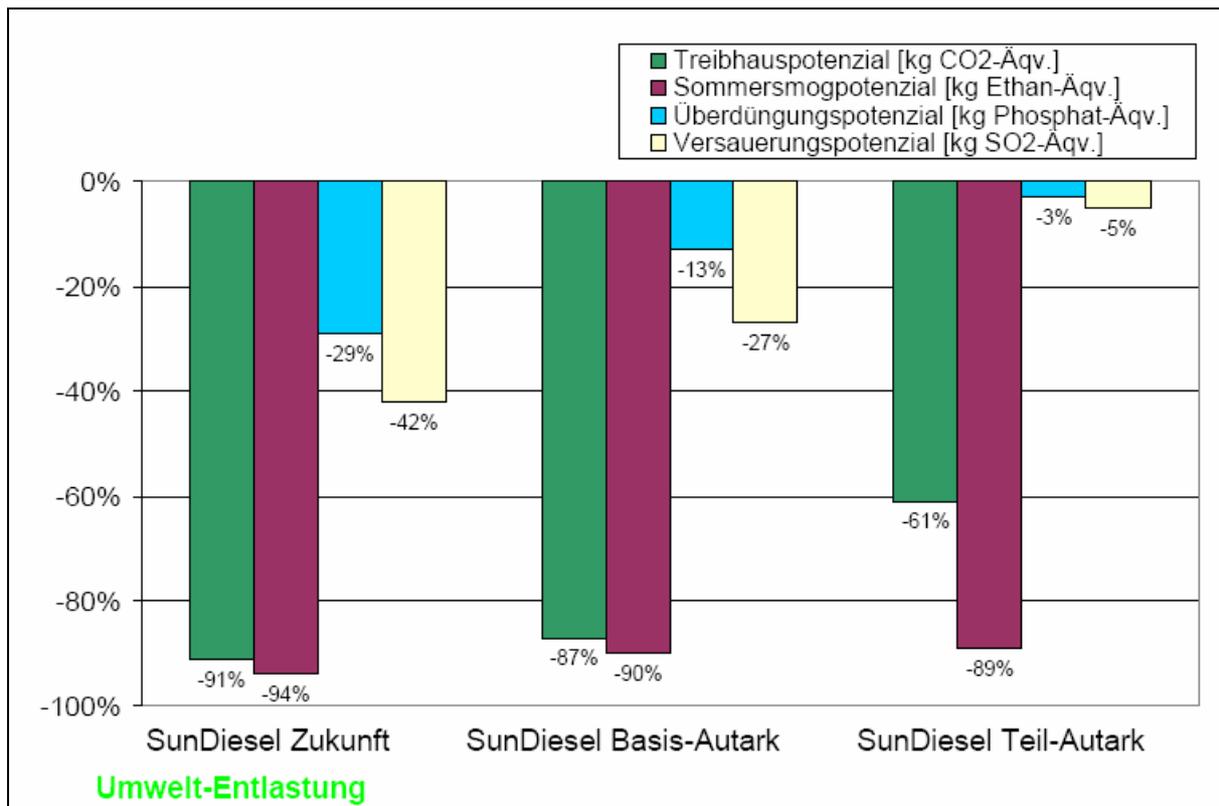
Figure 55: Reduction potentials of environmental impacts of different technology scenarios compared to conventional diesel

It turned out that the results are dominated by the use phase (burning the fuel in the motor) as well as by the provision of electric power, oxygen, and nitrogen and in particular hydrogen. The role of the Choren-process is comparatively limited due to only little emissions.
The study shows that SunDiesel according to the Choren-procedure possesses room for environmental improvements taking current boundary conditions for wood gasification as well as transport distances into account. This is valid for all scenarios.

The reduced environmental impact in the category **climate change potential** can be traced back to the usage of wood as raw material for the SunDiesel production. The wood provision represents a CO_2-drain since wood absorbs CO_2 in the photosynthesis during the growth phase.

The reduced environmental impact in the category **summer smog potential** can be traced back to two effects:

- The non-existence of NMVOC-emissions, which occur in the crude oil provision and refining to conventional Diesel products[7].

- The reduced NMVOC-emissions in the use phase of SunDiesel in internal combustion engines. The reduction can be realised with Diesel cars that are currently in operation without any adjustments. The smaller NMVOC-emissions of this study are based on Diesel cars that fulfil the Euro 4 emission standard.

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[7]A certain uncertainty has to be considered since the values of the NMVOC emissions vary a lot depending on the source of information and database. However, this study shows that the trend of reducing the summer smog potential persists even if the uncertainties are taken into account.

Diffuse NMVOC emissions of the Choren plant have been neglected. This data gap has been accepted since it is assumed to be relatively insignificant.

The environmental advantages in the categories acidification and eutrophication are generally less obvious. They are also more sensible to changes in the supply of external energy and substances as well as to variations of transport distances and type of wood.
Furthermore, changes of the results have been evaluated in the case of:

- An increase of the transport distance for the transport of the wood from the forest to the Choren-plant

- The usage of trunk wood instead of wood residues, i.e. the environmental impact of the wood cultivation is allocated completely to SunDiesel.

The effects on the different scenarios are in detail:

Assuming current boundary conditions for transport distances and type of wood as well as renewable power production, the **Future-Scenario** shows the biggest reduction potentials in all analysed impact categories. Even in case of bigger transport distances (48) or the usage of trunk wood (49) the environmental impact of SunDiesel is still smaller as the one of conventional Diesel. Bigger transport distances or usage of trunk wood cause only very slight changes in climate change and summer smog impact.

Assuming current boundary conditions for transport distances and type of wood, the **Base-Autarkic-Scenario** shows much smaller environmental impacts in all analysed impact categories compared to conventional diesel as well. In case of a transport distance from the forest to the Choren plant of more than 120 km or a share of trunk wood of more than 60%, the environmental impact of SunDiesel is still smaller. However, at this break-even point the eutrophication potential is slightly higher. The environmental impact of SunDiesel compared to conventional diesel in the impact categories summer smog and climate change is still bigger than 80% even if transport distance or wood type are changed.

The **Partly-Autarkic-Scenario** shows still significant advantages compared to conventional diesel in the categories climate change and summer smog potential as well. On the other hand the eutrophication and acidification potential are only slightly smaller. In case of a transport distance from the forest to the Choren plant bigger than 70 km or a trunk wood share of more than 20% the environmental impacts eutrophication and acidification will be higher compared to conventional diesel. In case of variation of the transport distance and type of wood, the environmental reduction potential of SunDiesel compared to conventional Diesel accounts for the climate change potential 57% and for the summer smog potential 83%.
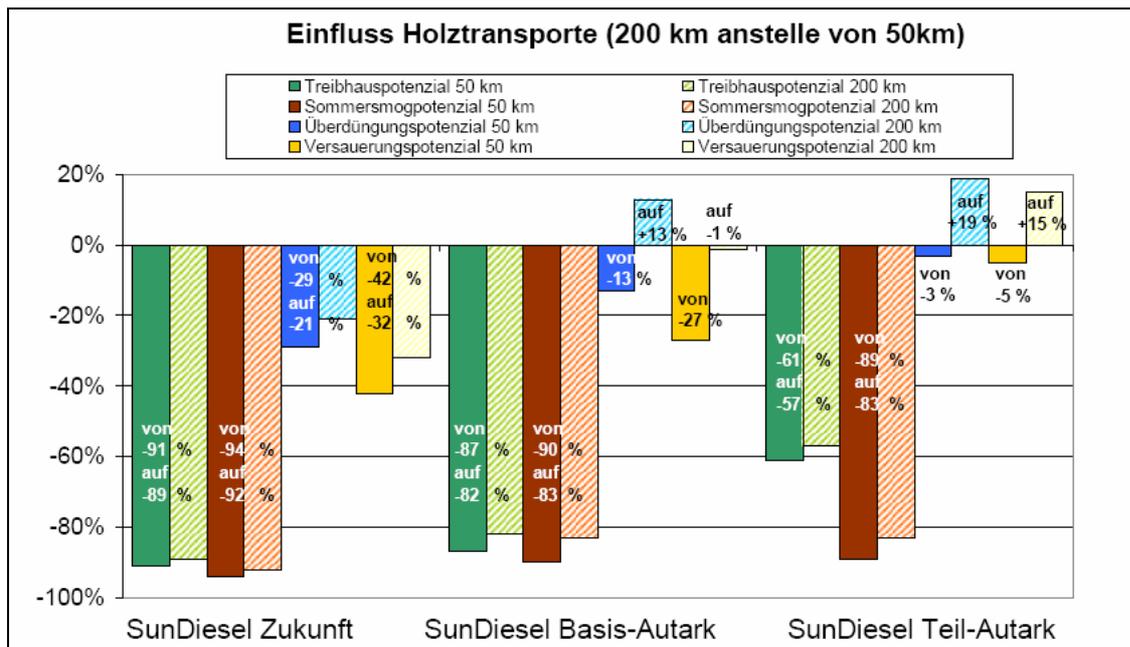
Figure 56: Influence of transport distance (200 km instead of 50km) - Change of impact potentials
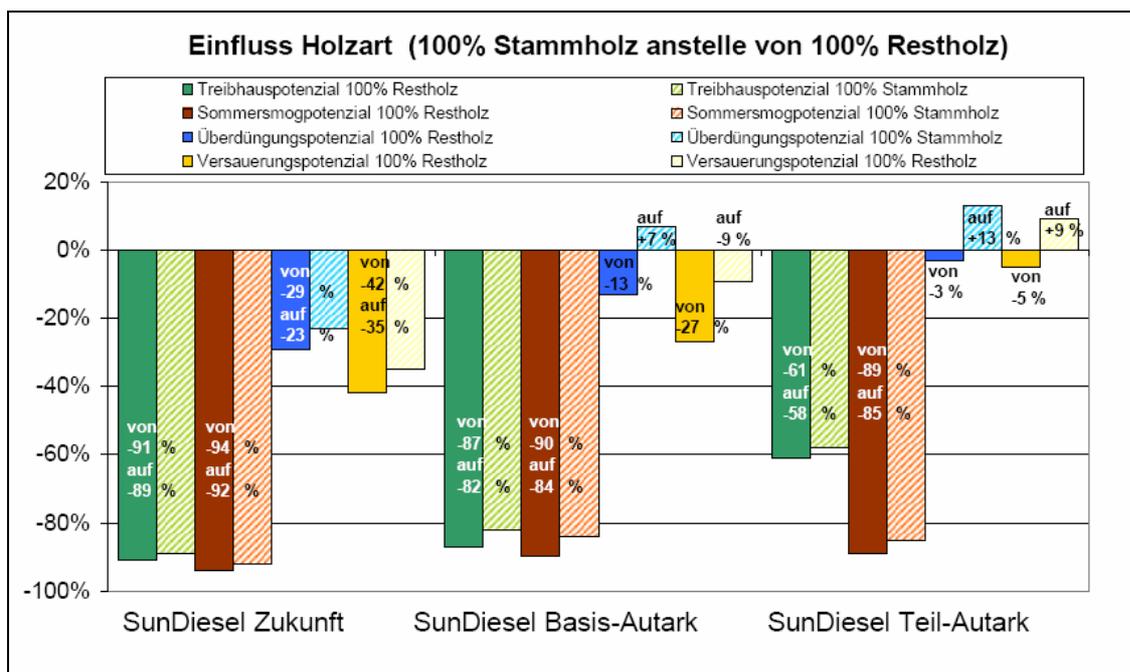
Figure 57: Influence of type of wood (100% trunk wood instead of 100% residues) - Change of impact potentials

The study shows that SunDiesel possesses a big potential to emit much less **greenhouse gases** compared to conventional diesel and to contribute positively to climate protection. Furthermore SunDiesel promises a reduced **summer smog potential** nearly independent of varying boundary condition. For the environmental impacts **acidification and eutrophication** this study evaluated the transport- and wood supply conditions, which still leads to smaller impacts of SunDiesel compared to conventional diesel.

Thus, SunDiesel according to the Choren-procedure can contribute to the reduction of the environmental impact in the evaluated categories, in particular in the areas climate change and summer smog.

10.3 Conclusions

- *Gas to Liquids Life Cycle Assessment. Synthesis Report. Prepared for: ConocoPhillips, Sasol Chevron, Shell International Gas. Prepared by: Five Winds International. August 2004.*

The three LCA studies examine two comparable technologies. The scope and objectives of each study is similar, as are the main findings. Although different data sources have been used and the boundary conditions of the assessments vary, the overall findings indicate that the conclusions can be generalized.

While conventional refinery systems have undergone decades of continuous improvement, it is prudent to note that the GTL system is relatively new. Improvements and innovations to the GTL system can be expected in the future and thus the comparison between the technologies in this report is conservative.

The overall conclusions from summarizing the three LCA studies can be categorized into environmental performance, market compatibility and societal relevance:

Production and use of GTL fuel can contribute less greenhouse gas to the atmosphere than production and use of conventional diesel fuel. The study commissioned by ConocoPhillips indicated the reduction in greenhouse gas emissions is significant if the GTL fuel is produced from associated gas2 that is otherwise flared in amounts of 10% or greater. More conservatively, and in cases where the feedstock is from other sources, the greenhouse gas contribution of GTL fuels is comparable to conventional diesel technology. In the expanded GTL technology system, available natural gas is used for space heating and electricity generation, whereas conventional refining technology uses more carbon intensive light fuel oil and residual fuels respectively, to meet these needs. While the GHG emissions from production and upstream processes of the GTL system are higher compared to the refinery-based system, the advantages in the use phase, at a minimum, compensate for the disadvantages in those phases.

Fuelling vehicles with GTL fuel consumes fewer petroleum resources per distance travelled than with conventional diesel. In addition, the study commissioned by ConocoPhillips indicated that, given forecasts of the rate of development of stranded gas projects, GTL fuel production will continue after crude oil reserves are depleted based on today's assessment of the life span of crude oil reserves. This is because GTL technology exploits remote gas reserves and not crude oil. Extrapolating from this point, using remote gas to create GTL fuel will extend the lifetime of crude oil reserves accordingly.

However, producing GTL fuel currently requires more energy and resources per unit mass produced than conventional diesel production. For both production of GTL fuel and across the full life cycle, GTL requires fewer petroleum resources than conventional diesel production.

Natural gas is the cleanest fossil fuel. There is potential for remote natural gas to provide energy to the global market for many decades. With respect to environmental impacts, remote natural gas can provide this energy in a manner comparable or better than petroleum reserves.

As for air quality in urban centers, GTL fuels are virtually free of sulphur and aromatics. Per distance traveled, GTL fuels contribute fewer emissions and negative impacts on urban air quality than conventional diesel.

According to the studies, GTL technology creates fewer air pollutants (SO2, NOx, VOCs and particulate emissions) and therefore contributes less to acidification of the air and formation of smog. Although the results of each of the studies are somewhat different, it appears that there are fewer environmental and health impacts from GTL fuel than from conventional diesel. While the emissions from GTL are lower, there is no direct link between the amount of emissions and actual acidification, because actual acidification depends so heavily on factors specific to the environment where the emissions are received (such as climate, soils, geology, etc.).

The Shell and ConocoPhillips studies indicated that the GTL system generates less solid waste (up to 40% less according to the Shell study) and less hazardous waste than conventional refining technologies.

GTL fuel can be used either directly or blended with conventional diesel and burned in conventional diesel-powered vehicles. Tanks, pumps and other fuelling infrastructure can be filled with GTL fuel without significant retrofitting or capital investment. While there is potential to optimize vehicle engines to run even more efficiently on GTL fuel, such re-design is not essential. Technological advances in design of advanced engines can be a longer-term goal consistent with the growth of GTL markets.

From a market compatibility aspect, the GTL technology combines a reliable feedstock with a potential long-term supply. GTL fuel can be used neat or blended with conventional diesel in conventional diesel powered vehicles and existing infrastructure. Another aspect is that the GTL technology is complementary to the refinery-based system.

As for societal relevance, consumers and commercial fleet operators can benefit from the advantages of the GTL system without investment or changes to their existing infrastructure and assets. GTL fuels may even offer performance advantages in some cases. Higher distance traveled per unit mass or increased performance may be possible. The overall environmental profile of the GTL system is well balanced and offers advantages. Being at an earlier stage of its development, the technology has room for improvements. It may contribute to meeting current environmental concerns around fuel and energy systems, including air quality improvements in urban areas and reducing the specific GHG intensity of fuel systems. No single environmental attribute was identified to be a major environmental disadvantage.

- *GM Well-to-wheel analysis of energy use and greenhouse gas emissions of advanced fuel/vehicle systems – a European study. L-B-Systemtechnich GmbH for GM, ExxonMobil, Shell, BP and TotalFinaElf. 27 September 2002.*

Biomass-derived fuel supply pathways analysed in the study show in general the highest complexity depending on cultivation method, fertilizer use, soil and climate conditions. They lead to drastically reduced greenhouse gas emissions especially in combination with fuel cell powertrains. FTD doesn't show any real benefit over conventional diesel according to this study.

Greater usage of energy well to wheel for FTD fuel compared to conventional diesel, but only marginally greater exbodied greenhouse gas emissions.

The general conclusion of the study is that renewably produced hydrogen combined with fuel cell powertrains has a capacity of significantly lowering greenhouse gas emissions.

- *Well-to-Wheels analysis of future automotive fuels and powertrains in the European context. WELL-to-WHEELS Report. Version 1b, January 2004*

A Well-to-Wheels analysis is the essential basis to assess the impact of future fuel and powertrain options. Both fuel production pathway and powertrain efficiency are key to GHG emissions and energy use. A shift to renewable/low fossil carbon routes may offer a significant GHG reduction potential but generally requires more energy. The specific pathway is critical. No single fuel pathway offers a short-term route to high volumes of "low carbon" fuel. Contributions from a number of technologies/routes will be needed. A wider variety of fuels may be expected in the market. Blends with conventional fuels and niche applications should be considered if they can produce significant GHG reductions at reasonable cost. Transport applications may not maximize the GHG reduction potential of renewable energies.

GTL (Gas-to-Liquids) processes enable high quality diesel fuel to be produced from natural gas. However, the well-to-wheel GHG emissions are somewhat higher than for conventional diesel fuel. Only limited GTL volumes can be expected to be available by 2010 and beyond.

Where a GTL plant sited near a remote gas field the high-energy requirement for the conversion process is partly compensated by the lower transportation energy although CNG obtained with liquefied gas from the same remote location is still more advantageous in well-to-wheel energy and GHG terms. The GTL pathway is notably more energy-intensive than conventional diesel fuel. In GHG terms the difference is smaller because of the beneficial effect of using natural gas rather than crude oil as primary energy source. Pathways involving natural gas import and GTL plants near markets result in higher energy consumption and GHG emissions.

The higher efficiency of the synthesis process gives DME a slight advantage on the FT diesel fuel. In the DME process, the sole product is DME that translates into high yield of fuel for Diesel engines compared to FT diesel fuel.

The wood pathways produce hardly any GHG because the main conversion process is fuelled by the wood itself. Optimum use of renewable energy sources such as biomass and wind requires consideration of the overall energy demand including stationary applications. New BTL (Biomass-to-Liquids) processes are being developed to produce synthetic fuels with lower overall GHG emissions, though still high-energy use. BTL processes have the potential to save substantially more GHG emissions than current bio-fuel options at comparable cost and merit further study.

- *Life-cycle Emissions Analysis of Alternative Fuels for Heavy Vehicles; CSIRO, Australia, 2000.*

FTD has an advantage in that it contains virtually no sulfur or aromatics that would lead to expected lower particle exhaust emissions and that oxidation catalysts and particulate traps will operate at maximum efficiency. 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 carbon dioxide stream that would provide an option for the collection and sequestration of carbon dioxide. The FT diesel exhaust is regarded as an air

toxic just as conventional diesel exhaust. Because of the extra processing energy FTD produces more exbodied greenhouse gases than conventional diesel.

This report quotes that Louis (2001) found that for passenger cars exbodies greenhouse gas emissions associated with FTD were less than those of petrol but greater than those of conventional diesel. FTD produces slightly lower tailpipe emissions but upstream emissions of greenhouse gases during production of FTD are much greater than those emitted during production of conventional diesel.

To sum up, while the environmental impacts are considered to be about the same as for conventional diesel, FTD has a benefit over lower air pollutant emissions and the FTD plant does not produce undesirable co-products like a refinery does

10.4 Results

Resource consumption:

- Fuelling vehicles with GTL fuel consumes fewer petroleum resources per distance traveled than with conventional diesel.
- The GTL technology extends the availability of crude oil reserves.
- GTL fuel production is based on a resource that will continue to be available for up to two decades after crude oil reserves are depleted, according to current data.
- Overall energy use of the GTL system is higher.

Figure 58 Example table from GM study:

Energy consumption well-to-wheel

MJ/km (energy requirements)

Category	Value
FT Diesel Residual Wood	~4.3
FT Diesel Remote NG	~3.3
Diesel	~2.2

(Horizontal axis: 0, 1, 2, 3, 4, 5)
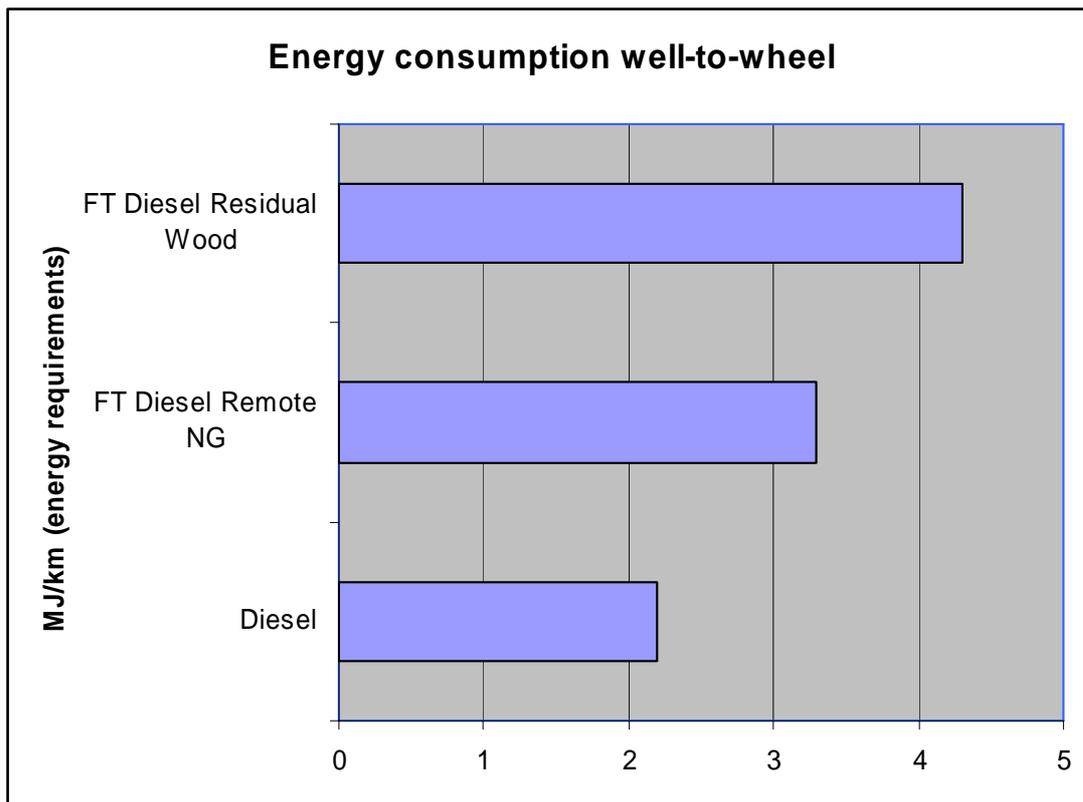
GHG performance:

- Production and use of GTL fuel has the potential of contributing less greenhouse gas
to the atmosphere than production and use of conventional diesel. Currently, the GTL
system is at least neutral in its total GHG impact compared to the refinery system.
- Because of the extra processing energy FTD produces more exbodied greenhouse gases than
conventional diesel. While the GHG emissions from production and upstream processes of the
GTL system are higher compared to the refinery-based system, the advantages in the fuel
consumption or use phase, at a minimum, compensate for those differences.

Figure 59 Example table from GM study:
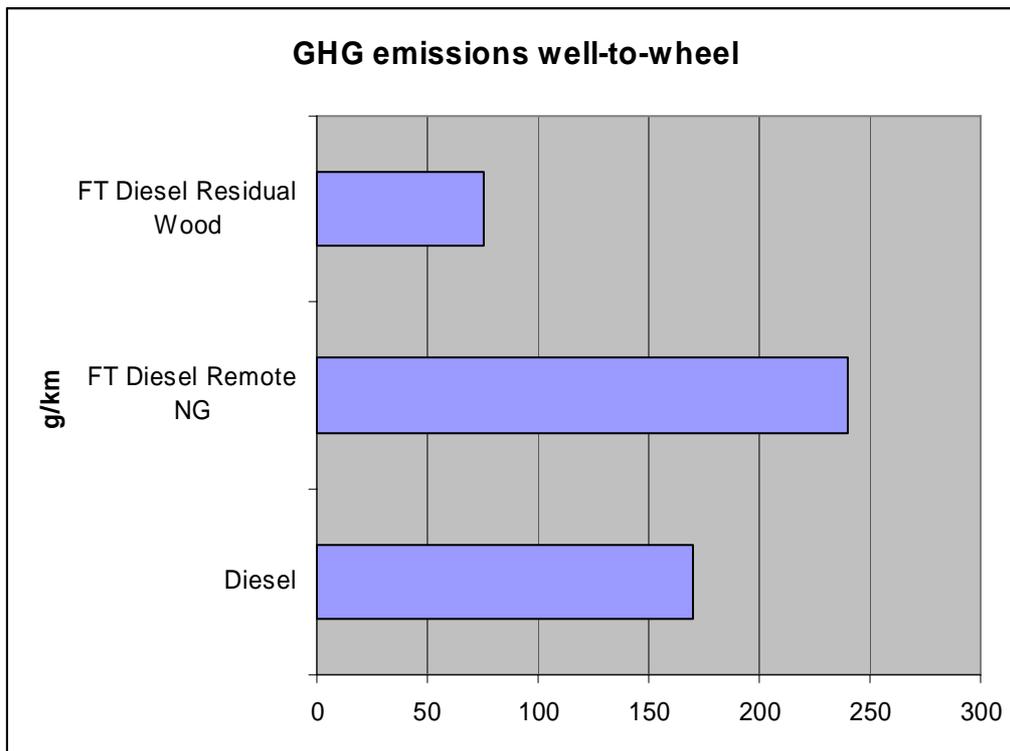
Air pollutants:

- One kilogram of GTL fuel takes a vehicle further than one kilogram of petroleum based diesel. The combustion of less fuel for the same distance traveled can reduce negative impacts on urban air quality.
- With significantly lower emissions of acidifying gases, GTL technology potentially causes less air acidification than the refinery technology.

Waste:

- GTL fuel production generates less solid waste and less hazardous waste.

To sum up, FTD produces slightly lower tailpipe emissions but upstream emissions of greenhouse gases during production of FTD are much greater than those emitted during production of conventional diesel. While the environmental impacts are considered to be about the same as for conventional diesel, FTD has a benefit over lower air pollutant emissions and the FTD plant does not produce undesirable co-products like a refinery does.

Table 21 Summary of full life cycle emissions per km from FT diesel and low sulphur diesel in heavy vehicles (Csiro, 2000)

Exbodied emissions per km	FTD	LS diesel
Greenhouse (kg CO2)	0.9926	0.9250
NMHC total (g HC)	0,94	1.509
NMHC urban (g HC)	0.524	1.192
NOx total (g NOx)	10.305	11.250
NOx urban (g NOx)	8.896	10.638
CO total (g CO)	2.333	2.723
CO urban (g CO)	2.010	2.612
PM10 total (mg PM10)	266.1	438.4
PM10 urban (mg PM10)	246.6	423.1
Energy embodied (MJ LHV)	17.10	12.7

11. Scenario studies

Clearly, it is theoretically possible to replace all fossil fuels with biomass-based fuels. The sun is very generous in providing the earth with energy. We also have enough land where biomass can grow. The problem is primarily economical. The biomass-based energy cannot compete with the fossil energy as long as the external costs on society is not internalised. It is also a logistic problem. The available land suitable for bio energy production is not situated close to the users. The enormous amounts of biomass needed to substitute all fossil fuels used in the world will probably have large impacts on other parts of the economy besides the energy and transport sectors, such as the prices on food, paper and wood industry and on suitable land. There is also a substantial need for investments in production plants and infrastructure for the new energy system. It is not possible within the resources of this project to do a thoroughly analysis of these issues.

In order to do a first attempt to make the consequences visible of what a biomass based Fischer-Tropsch production process will have on the logistic- and transportation systems for a selected number of representative countries, four scenarios is shown below.

- Finland, with forest residues as feedstock for biomass based F-T Fuel
- Polen, with energy forest as feedstock for biomass based F-T Fuel
- Denmark, with energy forest as feedstock for biomass based F-T Fuel
- USA, with Natural Gas as feedstock for fossil F-T Fuel

The scenarios are based of the following principle steps:
1. Assessment of realistic size and efficiency of the plants
2. Biomass potential in respective country
3. Energy efficiency and realistic usable land area in respective country
4. Transport distance
5. Amount of fuel that can be substituted
6. Results in terms of number of vehicles and transport work

11.1 Assessment of realistic size and efficiency of the plants

In this scenario have a syngas reactor with fluidised bed and an IGT reactor been used.

The capacity for the plant at 80 ton dry mass/hour and an energy content of 1,5 GJ/ton dry mass gives an outcome of 167 MWh F-T fuel and 15 MWh electricity. This implies an efficiency of 50 %, where 46 % is F-T fuel and 4 % is electricity.

Biomass 367 MWh

FT-plant

F-T Fuel 169 MWh

El 15 MWh
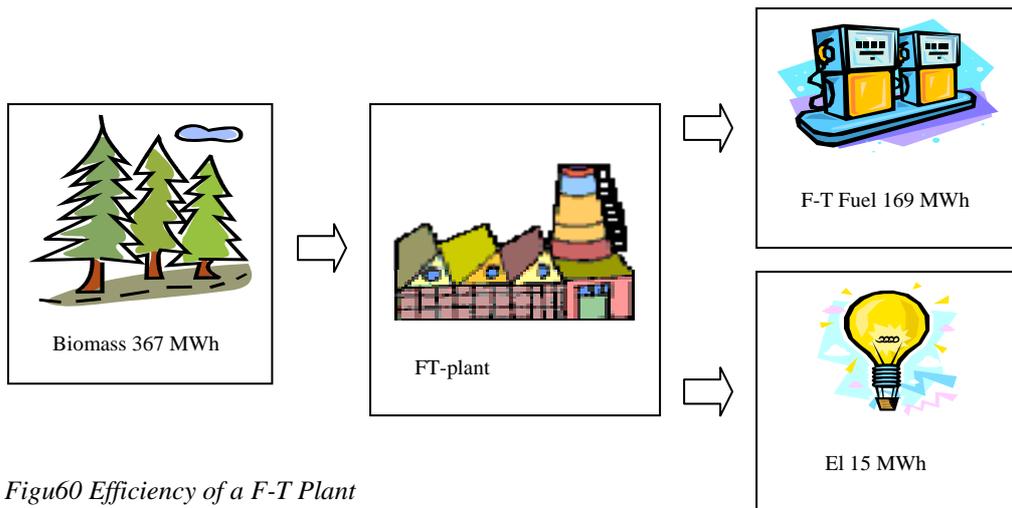
Figu60 Efficiency of a F-T Plant

The optimal size of the plant is calculated from an economy of scale perspective. The total costs decreases until the costs for transporting the biomass up weights the benefits from enlarging the plant size. The graph shows that a plant needs to be of a size over 1 GWh to economically feasible (Modh, 2006). It can be noted that the presently largest plants that is constructed is 400 MW. To be able to reach a size over 1 GW several parallel reactors is needed. Thus, in this scenario is a 1,2 GW plant used as being over 1 GW and a multiple of 400 MW (3 times 400 MW).
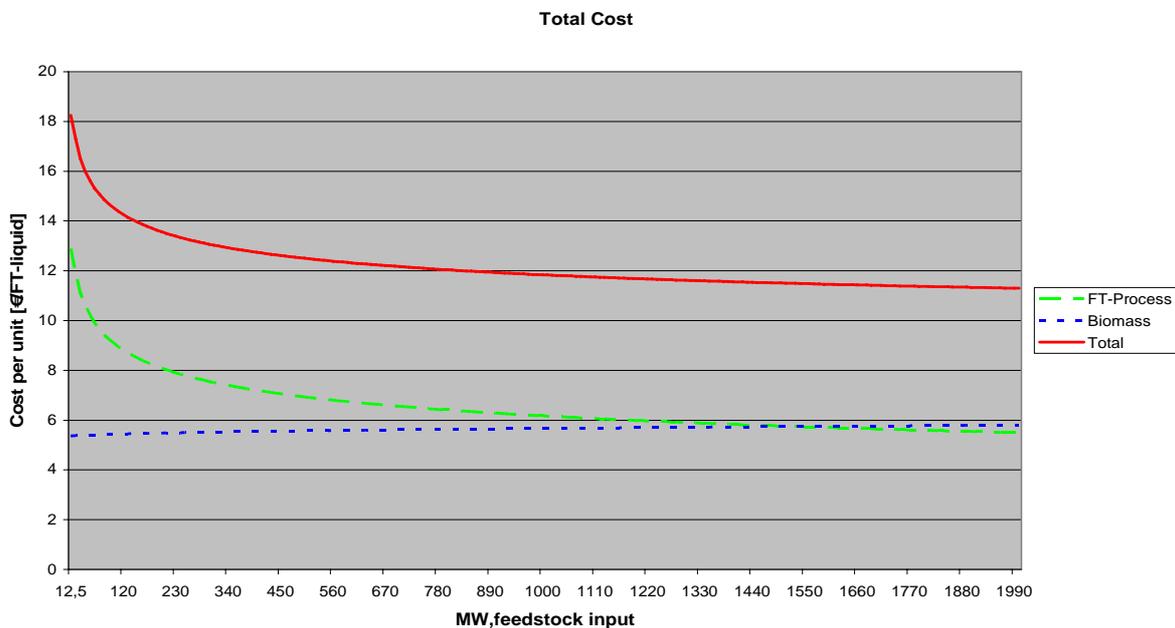

Figure 61 Optimal size of biomass F-T plant due to economy of scale (Modh, 2006)

11.1.1 Scenario Finland

The Finnish scenario is based on forest residues. The amounts and location of available forest residues is charted by Ranta (2005). This study has been used to design the scenario.

With a supply- and demand analysis are the regions identified that have the largest potential to produce forest residues (figure 54). Further, the report shows a chart of the areas that are most suitable for placing the production plants. The result showed 19 places with the supply of at least 300 GWh/year and a maximum transport length of 100 km.

Figure 62
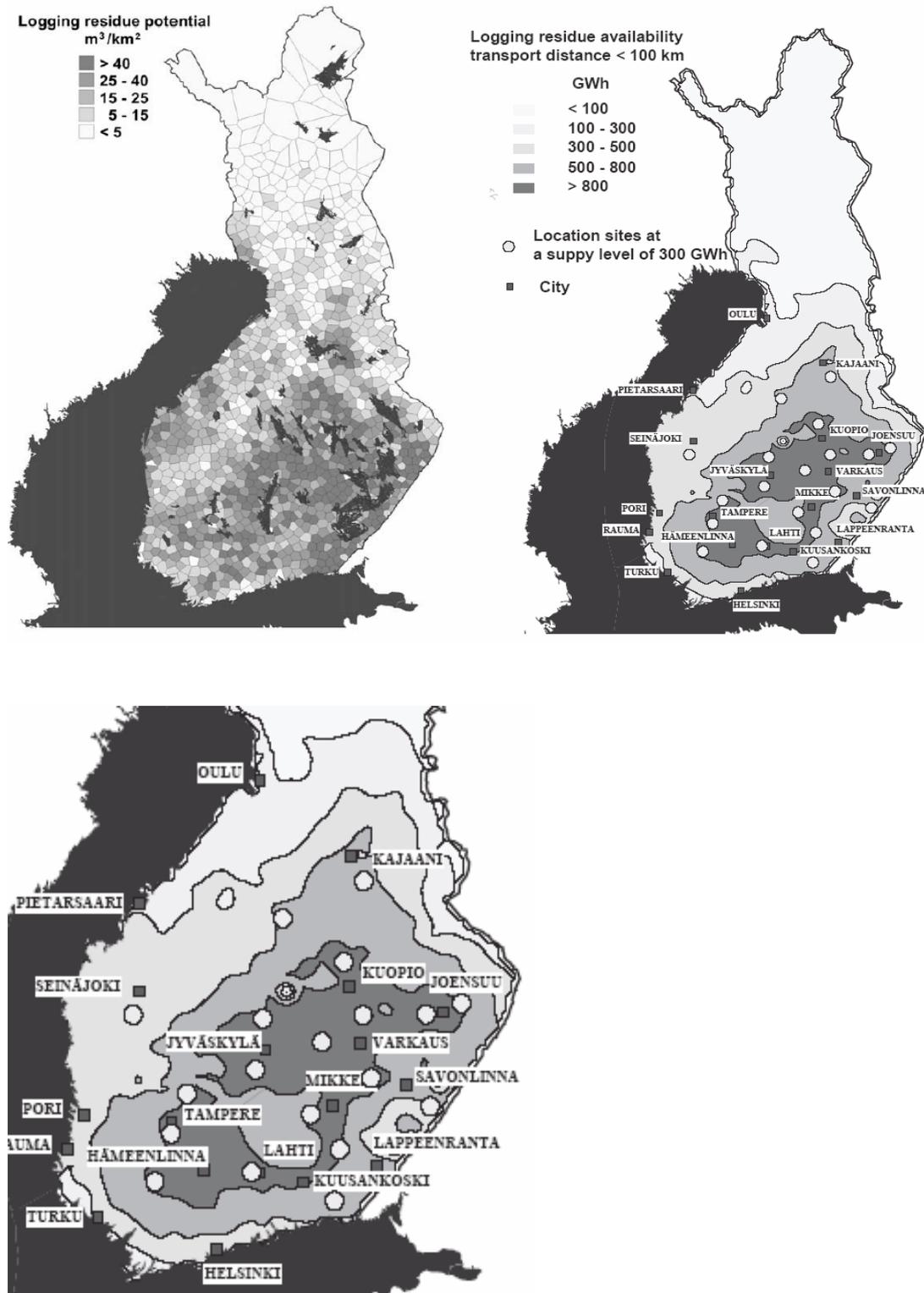
*Table 22   Results of the Finnish scenario*

F-T prod GWh	F-T prod m³	Ton	Truck/day	Area km2	Plants	% of cons. Fuel
4258	118421	1661538	166	27692	1	10%
8517	236842	3323077	333	55385	2	20%

The results of the Finnish scenario shows that if 20% of the Finnish fuel consumption shall be substituted by F-T fuels must 2 plants of the size of 1,2 GW each be built. However, there is not enough biomass from forest residues available in Finland today to cover that demand. According to Ranta (2005) the present production is about 1500 GWh/year and the demand for the 2 plants in the scenario would demand 9600 GWh/year. Thus, heavily increased forestry, or outtake of whole logs from the forest would be needed to cover the demand.

The trucks used in this scenario have a max weight of 60 ton. These large trucks are presently only allowed in Sweden and Finland. Every plant will need about 160 trucks per day or 1 truckload every 9 minute.

To assess the feasibility of the transport needed for these plants has a comparison been made with the transport need of biomass to the paper mills in the Nordic countries. A medium sized paper mill in Sweden receives approximately 1 60-ton truck every 30 minute. A Large sized mill receives one truck every 15 minute.

The largest paper mill in Sweden, receives wood corresponding to 1 truck every 10 minute. However, the larger mills do normally have a harbor and receives presently about 1/3 of the material by rail or ship. Thus, if a plant of this size would be situated in the middle of a forest, 1 truck every 9 minutes would imply a 50% increase in truck transport activities around a plant compared to the present situation for the largest Nordic paper mills.

11.1.2 Scenario Poland

The Polish scenario is based on cultivated energy forest, e.g., Salix. Available farming land has been shown in (Fischer et al., 2005). The plant size of 1,6 GW is chosen in this scenario. The main reason is that the energy output per ha is much greater when energy forest is cultivated compared to forest residues and the transport distances will be much shorter. The other reason is to have a scenario where the needed transport activities are assessed for an even larger plant. This might be of interest if the economic benefits of building larger plants are greater than the theoretical transportation costs. To see the transport activities around a plant if 1,2 GW plants was assumed instead, please see the next section "Scenario Denmark".

Another important difference between this scenario and the Finnish one is that smaller trucks (max 40 ton) are used.

Poland is a country with huge areas of available farming land for energy forest. More than 2200 kha is regarded as "very suitable" (Fischer et al., 2005) and more than twice as much is regarded as "suitable" (Viewls, 2004). This corresponds to about 7 % of Poland's total area.
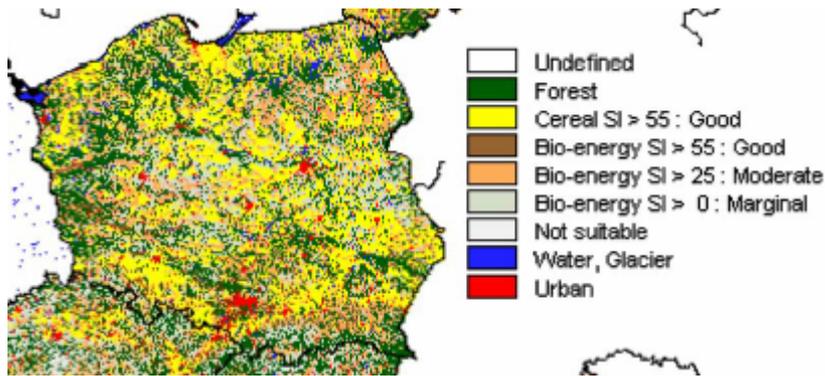
Figure 63 Suitable land for energy forest in Poland (Fischer et al., 2005)

Table 23   Results of the Polish scenario

F-T prod GWh	F-T prod m³	Ton	Truck/day	Area km2	of available	Plants	% of cons. Fuel
5678	157894	2363077	450	2541	6%	1	6%
11356	315789	4726154	899	5082	11%	2	13%
17034	473683	7089231	1349	7623	17%	3	19%

The results show that for a large country like Poland, must 3 large plants with the size of 1,6 GW (or four 1,2 GW) is build to exchange 19% of the fuel consumption. The transport need is also greater due to the fact that the plant size is assumed to be larger, but mostly because the maximum weight for trucks in Europe is 40 ton compared to 60 ton in Finland. Each plant must be therefore be served by 450 trucks per day or one truck every 3 minutes. This means five times as many trucks as serving the largest paper mills in the Nordic countries today. The consequences for the infrastructure and the logistic system are obvious. The production is supposed to be running 24 hours a day and will be very vulnerable to shortages. It will require large storage and internal logistic facilities.

The results stresses that plants of this size must be located where there are possibilities to have a harbour and/or a large railway terminal. This reduces the location possibilities and will naturally affect other activities that today are located at the coastline. Most of the cost line in Poland is probably already built or occupied for recreation, tourism, protected area or other activities. To find appropriate locations for plants of this size and with this transport activities will not be an easy task in many European countries.

11.1.3 Scenario Denmark

For Denmark has a similar scenario as for Poland been analysed. The main difference is that the plant size is set to 1,2 GW. The feedstock is based on cultivated energy forest, e.g., Salix. Available farming land in Denmark is much more limited. Viewls (2005) calculate the available farming land for energy forest to only 50 kha. This means that there is not enough available farming land in Denmark today to supply 1 plant. Denmark will have to import biomass or shift from food production to energy production.

Table 24   *Results of the Danish scenario*

F-T prod GWh	F-T prod m³	Ton	Truck/day	Area km2	of available	Plants	% of cons. Fuel
4258	118421	1772308	337	1906	381%	1	10%
8517	236842	3544615	675	3811	762%	2	19%

For the rest does the scenario for Denmark show similar results as for Poland. Large plants must be built and if each of them should be served solely by trucks, there will be an arrival every 4 minute. Thus, the plants must be located with access to a harbour.

11.1.4 Scenario USA

For the USA case there is a different approach. The feedstock in this scenario is natural gas. USA has own supplies of natural gas, but the consumption today is larger than the production and import from Canada is necessary.

A calculation of the gasoline consumption in the USA and the amount of gas that would be needed to substitute 20 % of the consumption is shown below:

U.S. gasoline consumption is 320 500 000 gallons /day or 117 000 000 000 gallons /year (532 000 000 000 l/year). This corresponds to about 4 800 TWh/Year.
With the energy efficiency of approximately 50%, about twice as much natural gas would be needed per year, i.e., 8 000 TWh or about 800 billion m³.

The production in the US was 542 billion m³ in 2004 (BP, 2005). The proven reserves today in the US is estimated to 5,3 trillion m³ (BP, 2005). Totally in the world was 2691 billion m³ produced (BP, 2005). The demand for natural gas in the world would in this scenario increase by 30 %.

The present production in Colombia, Venezuela and Trinidad Tobago is about 70 billion m³ and the proven reserves in these countries are 5,77 trillion m³ whereof Venezuela stands for 4,22 trillion m³ (BP, 2005).

This calculation shows that even with a 20 % substitution there will be enormous capacity shortage in the region. Note that the calculation for the U.S. case only dealt with the gasoline consumption and not the diesel consumption. For a substantial substitution of petroleum based gasoline and diesel to F-T from natural gas must the US rely on Liquefied Natural Gas from remote sources. The effects on the prize on natural gas will most likely be substantial.

11.2 Discussion

It is clear from these scenarios that a biomass based F-T production scenario will heavily affect the transport and logistic systems. It is clear that it is possible, but many obstacles must be considered. It will not only be investment costs for the plants, but also for infrastructure around the plants. The consequence of will be a significant amount of heavy traffic around the plants, and as there will be several very large plants needed to meet the demand for fuel in the future, it might also affect the land use in costal areas. To secure the flow of raw material for a

plant of this size a system of storage facilities for large amounts of biomass must be developed.

The examples shown above are limited to the replacement of about 20 % of the fuel market. This corresponds to the amount that is feasible to achieve for European domestic production according to Viewls (2005). The production will primarily be in the CEEC countries. (Former East European Countries) What if 100 % shall be replaced? Then the plants must be located at harbours due to that import of biomass must be made. For Denmark 10 locations around the coast must be found. For Polen the corresponding figure is 15.

To substitute 15 % of the EU 15 countries fuel consumption would an area of 310 000 km² be cultivated with Salix. This corresponds to an area of the size of Poland. It would also require 122 FT-plants of 1,6 GW. If we widen the perspective and think about the rest of Europe we can only imagine the problems of finding enough space at the coastline to support the European total fuel consumption. It will not only be a logistic problem, but also a land use problem. Coastlines are attractive land and by that also expensive. If, for example, a new road is suggested in Germany, the authorities and constructors count on that it will take about 30 years to be finalised. The reason is not that the Germans are slow builders, but that they have a democratic process for what the land shall be used for. If there will be plans for building new plants at attractive land it is likely that the people living there will object.

Theoretically, it is possible supply the worlds need for energy with biomass. The sun is very generous with energy, but a full-scale biomass based energy system will imply dramatic changes in the supply chain. Planning the production, the localisation of plants, building the infrastructure, this will take time and requires long-term investments. If this shall be done in a smooth way must the planning start before the technology is fully developed. Otherwise the shift to a fossil free economy will be even further delayed.

The supplies of Natural gas in the world are large and the possibility of replacing petroleum based gasoline with GTL large. The technology is well known and the environmental analyses of the production and use of this fuel is comparable or better than the traditional. However, the use of gasoline in the world is of a magnitude that a large-scale substitution is questionable. One option that has been discussed, and that is very promising, is to use remote gas that is presently flared. The problem is that it is not enough in a global perspective. The demand for gas is increasing and there is no way for the US to meet an increased demand from supplying the vehicle fleet with F-T fuels from domestic reserves. With the political situation in the Middle East and in Venezuela, it doesn't seem likely that this solution will ease the US problems with reducing their oil dependences.

There are, however, enough reserves of coal in the world to meet the demand for large-scale introduction of F-T fuels. It can also be produced at a competitive prize. It is not likely that the production prize of biomass based F-T will ever be competitive with coal or natural gas based F-T unless there will be some kind of global regulation introduced on emissions of fossil CO_2. The fact that the oil prize has reached high levels recently has intensified the debate on that we are seeing the beginning of the end of the petroleum economy and that the oil prize will continue to increase significantly. However, looking to the fact that coal can be converted to fluent fuels to a cost below the present oil prize levels and the fact that there are coal reserves in the world that will last for hundreds of years it is more likely that the prize on fluent fuels will stabilise somewhere at the present level. A large-scale production of CTL would, however, more than double the emissions of fossil CO_2 per litre fuel used compared to

traditional fuel (JRC, 2004). This stresses the argument that we need regulations and globally agreed measures to reduce the emissions of fossil CO2. It is very unlikely that we will see a large scale introduction of biomass based F-T before that.

Beside the issue on how the logistic system will be designed, there are other issues that would be interesting to investigate but that is not in the scope of this report. What will happen to the market prize on biomass in the future? There are several assessments on future production costs. If an increase in demand in this magnitude will be realised will several other industrial sectors be affected. Wood and paper industry, energy for heating and electricity, plastics, etc. How will investments in these sectors be affected?

European domestic production will be able to replace about 20 % of the fossil fuel (Viewles, 2005). The rest, 80 % must be imported. An interesting issue is, from where? How will this affect the world economy and the political situation in the world? The cheapest production of biomass will naturally be in regions that are warm and have sufficient supplies of water and, probably, cheap labour. This will probably be done in developing countries. Is this good or bad? Poor countries will have a possibility to grow their economy and be less dependent on foreign aid. Shall the production plants be situated close to the consumers (industrial regions) or close to the producers (developing countries)? How can we ensure that the production of biomass will be done in a sustainable way? How will this "mega-large-scale" production affect wild life and biodiversity in the regions? How can the replacements of minerals and neutrions to the soil be ensured?

It is clear that replacing petroleum-based fuels with F-T fuels is combined with enormous practical difficulties both with fossil and renewable feedstock. Unless we will se a major breakthrough in the development of solar power or similar renewable, flowing and easy distributed energy that can run the transport sector, we will have a practically unsolvable problem with the increasing demand on mobility and fluent fuels in the industrial as well as the developing countries. A reduction of the total energy use in the transportation sector will be unavoidable and a prerequisite for reaching a sustainable transport sector. This means to reduce the energy consumption per vehicle as well as reducing the travel- and transport demand.

11.3. Conclusions

- Production and use of GTL fuel has the potential of contributing about the same or slightly less greenhouse gas to the atmosphere than production and use of conventional diesel. Production of CTL emits more than twice as much greenhouse gases compared to traditional fuels.

- Production and use of biomass based F-T reduces the emissions of greenhouse gases by 60-90 %. Reduction of smog inducing matters is about 90% and the reduction emissions affecting acidification and eutrification is about 5-40 %

- It is clear from these scenarios that a biomass based F-T production scenario will heavily affect the transport and logistic systems. It is clear that it is possible, but many

obstacles must be considered. It will not only be investment costs for the plants, but also for infrastructure around the plants.

- To substitute 15 % of the EU 15 countries fuel consumption would an area of 310 000 km² be cultivated with Salix. This corresponds to an area of the size of Poland. It would also require 122 FT-plants of 1,6 GW. We can only imagine the problems of finding enough space at the coastline to support 100 % of the European total fuel consumption.

- Theoretically, it is possible supply the worlds need for energy with biomass. However, planning the production, the localisation of plants, building the infrastructure, this will take time and requires heavy long-term investments. To avoid further delays in shifting to a fossil free economy must the planning start before the technology is fully developed.

- The demand for Natural gas is increasing and there is no way for the US to meet an increased demand from supplying the vehicle fleet with F-T fuels from domestic reserves. With the political situation in the Middle East and in Venezuela, it doesn't seem likely that this solution will ease the US problems with reducing their oil dependences.

- It is not likely that the production prize of biomass based F-T will ever be competitive with coal or natural gas based F-T unless there will be some kind of global regulation introduced on emissions of fossil CO_2.

It is clear that replacing petroleum-based fuels with F-T fuels is combined with enormous practical difficulties with both fossil and renewable feedstock. A reduction of the total energy use in the transportation sector will be unavoidable and a prerequisite for reaching a sustainable transport sector. This means to reduce the energy consumption per vehicle kilometre as well as reducing the travel- and transport demand.

12. SWOT analysis

Based on the literature review and the investigations regarding emission measurements, the authors of this report (Björn Rehnlund - Atrax Energi AB, Magnus Blinge - TFK, Jesper Schramm and Ulrik Larsen - DTU) have performed a so-called SWOT analysis.

The purpose of this SWOT analysis was to identify Strengths, Weaknesses, Opportunities and Threats of the Fischer-Tropsch technology and of the distribution and use of FT-Fuels.

The most important SWOT items that were identified are listed below. It would have been possible to list some of the items under more than one of the headings. In these cases the most appropriate heading according to the view of the authors has been chosen. This holds of course for the whole SWOT analysis – it is the view of the authors. Some readers of this report might miss some items and some others might believe that some of the items listed are superfluous or are not adequate. This is also a result of the fact that the SWOT analysis is carried out not only based on the literature review and the emission measurements, but it is also based on the authors' further knowledge and experiences, and on personal opinions regarding the Fischer-Tropsch technology. However, we have tried to be as objective as possible and to only list items that clearly are motivated in the other parts/chapters of the report. Furthermore, our choices are mainly based on the literature review and the emission measurements.

12.1 Strengths

- Reduced airborne emissions such as HC, CO, NOx, PM, SOF, VOF and PAHs compared with the use of conventional crude oil based fuels such as diesel oil and gasoline. Furthermore, compared to crude oil based products, FT-Fuels contain very low levels of sulphur and aromatic compounds.

- Flexibility concerning feedstock (natural gas, coal, oil, biomass, garbage, etc).

- Well established and operational technology concerning:

    - Production (natural gas and coal),

    - Infrastructure (distribution in existing systems for conventional fuels),

    - Engine technology (diesel engines or gasoline engines).

- FT diesel (paraffin) and FT gasoline (alkylate) can be used in neat form in existing engines, and they can also be blended in conventional fossil fuels (diesel oil and gasoline).

- It is possible to use domestic feedstock (natural gas, coal, biomass, etc.), and because of that the need of imports from other countries/regions can be reduced – Supply

security and stable raw material price.

- Domestic production will result in increased job opportunities.

- The relative stable price of coal, natural gas and biomass compared to the increasing and fluctuating price of crude oil and crude oil products.

12.2 Weaknesses

- When setting up a FT- plant today, it has to be of a rather big scale to be economically feasible. This has the following implications:
    - A large space/area to build the plant is needed, which may restrict the possibility to find proper locations to erect a plant.
    - High investment cost, which may restrict the number of investors.
    - When in the future biomass is used as feedstock, rather long transportation distances may occur when collecting the biomass. This may result in higher costs and increased environmental impact from feedstock transport.
    - Increased/long distribution distances of the final product.

- When using coal as feedstock, there will be a rather large amount of ash and slag that has to be taken care of/stored, and that might result in an unacceptable impact on the environment (for example by leak water).

- When using coal, the mining of the coal might result in unacceptable environmental impact.

- When using coal and gas there is almost no reduction of the emissions of carbon dioxide compared to the production and use of the conventional fuels diesel oil and gasoline.

- Reduced crude oil prices (new wells) can rather fast reduce the economical feasibility of FT-Fuels.

12.3 Opportunities

- The synthesis gas that is used for the FT-process can also be used for the production of other synthesis gas based fuels such as methanol and DME, which gives a high flexibility concerning the choice of the final product when the synthesis gas is available.

- New feedstocks can be developed and used - Almost all carbon containing material that can be gasified can be used.

- Increasing crude oil prices can make way for production of other raw materials for the FT-Process. It may lead to new ways of using agricultural land, offering new

possibilities for farmers, for example in Eastern Europe.

- The possibility to use garbage for the production of the synthesis gas can contribute to the solution of the garbage problem (storage and handling).

- If the FT-Fuels are produced from biomass and if the energy for the process is largely produced with biomass as feedstock, FT-Fuels can contribute to a reduction of carbon dioxide emissions from the transport sector, which helps reducing the impact on the climate of this sector.

12.4 Threats

- The need to build rather large FT-Plants to obtain economical feasibility might results in logistic problems (long distance for transportation of raw material and final product).

- The production of biomass will fluctuate over the years (and/or seasons) and that may give rise to the need of huge raw material storage, which might be problematic to handle. For example the need of land area will restrict the number of possible plant/storage sites and it may be difficult to avoid attacks and deterioration of the biomass by insects, bacteria and fungus.

- A large increase of the use of biomass (which in the long term will be necessary if we want to replace today's fossil fuels with renewable FT-Fuels) will increase the competition in the biomass sector, which probably will result in increased and unstable biomass prices.

- Increased biomass prices may put the FT-Fuels in a less favourable position compared to crude oil– Not at least if the crude oil prices will decrease and then stay on a stable level.

- The biomass gasification technology is not yet ready for a market introduction and further research and development has to be carried out. Therefore it is not yet possible to conclude if and under which circumstances (environmental impact, costs, etc.) competitive FT-Fuels can be produced from biomass.

- If using agricultural land for production/farming of biomass that will be used for gasification and production of FT-Fuels, there might be a risk of competition with food production.

- Biomass will not be available as feedstock in all countries. When the supply of natural gas and coal is consumed, this will put these countries back in a "lack of feedstock supply situation" similar to the situation where we have built our fuel supply almost totally on crude oil based products.

- Large scale farming of for example grass or energy wood suitable for gasification and production of FT-Fuels may result in monocultures that may have a severe impact on

the environment.

- Biomass might be more efficiently (regarding energy and economy) used in other applications than in vehicle fuel production, for example by direct combustion for the production of electricity and heat.

13. Conclusions

Based on the information found in the literature that was reviewed, the scenario studies and the emission measurements, a number of conclusions can be drawn. For example:

- FT-Fuels such as FT- Diesel (FTD) and FT-gasoline (FTG) produced through Coal-To-Liquid (CTL), Gas-To-Liquid (GTL) and Biomass-To-Liquid (BTL) technologies can contribute to decrease the dependency on crude oil.

- FTD and FTG are attractive for use in neat form as well as for the use as blending components in low quality diesel and gasoline, to upgrade these fuels to meet the ever more stringent regulations.

- Natural gas is the cleanest fossil fuel. There is potential for remote natural gas to provide energy to the global market for many decades. With respect to environmental impacts, remote natural gas can provide this energy in a manner that is comparable or better than the petroleum reserves can do.

- Producing GTL fuel currently requires more energy and resources per unit of mass produced than conventional diesel production. However, for both the production of GTL gasoline and GTL diesel, the GTL production chain requires less petroleum resources than conventional diesel production.

- Production and use of GTL fuels has the potential of emitting about the same or slightly less greenhouse gas to the atmosphere than the production and use of conventional diesel.

- Production and use of CTL emits more than twice as much greenhouse gases than traditional fuels.

- Production and use of BTL reduces the emissions of greenhouse gases by 60 – 90 % compared to fossil diesel and gasoline.

- The technology to gasify biomass is not yet ready for a full-scale market introduction. Further research and development are needed in this area.

- The FT process is still a relatively expensive technology and requires large-scale production plants or further development in order to be economically viable. However, production from humid biomass might reduce the need for steam reforming and consequently the plant size could be reduced.

- The options of making FTD and/or FTG from remotely located and/or low quality (flare gas) resources of natural gas are at this point less capital intensive than other methods of exploitation. Since a large part of the known gas reserves are remotely located this is a very probable option.

- According to information from Sasol it is possible to produce FT-fuels with coal as feedstock to a market competitive price as soon as the crude oil price is higher than 30

to 40 USD per barrel.

- It is not likely that the production price of biomass based FT-fuels will ever be competitive with coal or natural gas based FT-fuels, unless there will be some kind of global regulation introduced on the emissions of fossil carbon dioxide.

- Use of biomass as feedstock for production of FT-Fuels will most likely increase the competition for biomass and also the price of biomass, which might reduce the competitiveness of FT-Fuels compared to crude oil products (diesel oil and gasoline).

- The production and use of FT-fuels reduces smog-inducing matter with about 90 % and the emissions affecting acidification and eutrofication are about 5 – 40 % reduced.

- No engine modifications are required to use FTDs and FTGs in diesel and gasoline engines, and the existing fuel distribution system can also be used as it is.

- Compared to conventional diesel, various kinds of regulated an non-regulated pollutant emissions are reduced with the vehicle use of Fischer-Tropsch fuels: HC, CO, NOx, PM, SOF, VOF and PAHs.

- FT-fuels enable the use of more efficient exhaust after treatment devices, which further contribute to reducing the emissions of regulated as well as non-regulated pollutants.

- FTD has good cold starting properties and cold start versus hot starts tests show larger emission reductions for cold starts.

- More aggressive and more urban-like driving cycles lead to larger reductions with FTD, relative to conventional fossil diesel.

- When using FT-fuels there is no statistically significant change in vehicle fuel consumption found yet, compared to the use of conventional fossil fuels.

- The transport and logistic system will be strongly affected by a biomass based FT-fuels production. It is possible, but there are many obstacles that must be considered, and also the costs for the infrastructure around the plants have to be taken into account.

- To substitute 15 % of the EU 15 countries transportation fuel consumption would for example require an area of 310 000 km^2 cultivated with Salix. This corresponds to an area of the size of Poland. It would furthermore also require 122 FT-plants of 1.6 GW each.

- Aspen's alkalyte gasoline 4T produces cleaner emission than the other contenders. The pollutants CO, NOx, CO_2, PM and PAH are reduced.

- Regarding gaseous emissions, the Aspen fuel reduces NO_x emissions by more than 20% compared to regular gasoline. This observation and the fact that CO_2 emissions

are reduced by ca. 9% indicate that the combustion of Aspen could be a bit different than the combustion of regular and FT gasoline.

Acronyms and Abbreviations

ATR	Auto Thermal Reforming
BFB	Bubbling Fluidised Bed
BLGCC	Black Liquor Gasification Combined Cycle
BTL	Biomass To Liquid
CAT	Catalyst
CCRT	Catalysed Continiously Regenerating Technology
CD	Conventional Diesel
CH_4	Methane
Cl	Chlorine
CPO	Heterogeneous Catalytic Partial Oxidation
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CSHVR	City Suburban Heavy Vehicle Route
CTL	Coal To Liquid
DDC	Detroit Diesel Coorporation
DME	Di Methyl Ether
DPF	Diesel Particle Filter
EGR	Exhaust Gas Recirkulation
EPA	Environmental Protection Agency
ESC	New Staedy-state cicle for truck bus engines
ETC	Euro Transient Cycle
FAME	Fatty Acid Methyl Esther
FT	Fischer-Tropsch
FTCOD	Fischer-Tropsch Conversion of Olefins to Distillate
FTD	Fischer-Tropsch Diesel
FTG	Fischer-Tropsch Gasoline
FTP	Federal Test Procedure
GTL	Gas To Liquid
H_2	Hydrogen (gas)
HC	Hydrocarbons
HD	Heavy Duty
HFETR	Highway Fuel Economy Test
HPLC	High Performance Liquid Chromatography
HTFT	High Temperature Fischer Tropsch
HTW	The High Temperature Winkler
IGCC	Integrated Gasified Combined Cycle
KRW	The Kellog Rust Westinghouse
LCA	Life Cycle Analysis
LD	Light Duty
LPG	Liquid Petroleum Gas
LTFT	Low Temperature Fischer Tropsch

MPG	The Lurgi Multi-purpose gasifier
N_2	Nitrogen (gas)
NEDC	New Euro Driving Cycle
Nm^3	Normal Cubic meter
NO_x	Nitrogen Oxides
NYCB	New York City Bus
PAH	Polycyclic Aromatic Hydrocarbons
PM	Particulate matters
POX	
ppm	Parts per million
RDF	Refused Derived Fuels
S	Sulphur
SAE	The society of Automotive Engineers
SOF	Soluble Organic Fraction
StDev	Standard Deviation
US06	Extra urban driving cycle addition to FTP cycles
VOF	Volatile Organic Fraction

References

1. Ekbom Tomas, Presentation ISAF XV, Sandiego, September 2005
2. G.Bub and M Baerns. Chemical Enginering Scientiost, 35, 1980
3. R.Euel and C Bartholomew, J Catl, 85, 1984
4. R.L.Dictor, phD Thesis, University of California (Berkely), 1984
5. E.Erichm phD thesis, University of Karlsruhe, 1990.
6. A.P. Steynberg and M.e: Dry Fischer-Tropsch Technology, Studies in surface science and catalyst, 152, 2004.
7. A-G Collot, Matching gasifiers to Coals. IEA Clean Coal Centre, October 2002
8. http://www:cleantechindia.com.eicnew(News/news-coalgasifif.htm
9. C.Higman and M van der Burgt, Gasífication, Elsivier Science, USA. 2003
10. Trace sulphur Component Analysis Models 4025/4026/4027/4028/4029
11. Calo Hameling, phD thesis Outlook for advanced biofuels
12. http://ww.dtu.dk
13. Värnamoverket, En demonstrationsanläggning, Sydkraft, 2000.
14. Technical and commercial Feasibility Study of Black liqur gasification with methanol/DFEM production as motor fuel for automotive uses – BLGMF, ALTENER contract 4.1030/z/01-087/2001 Nykomb, STFI, Chemrec, Ecotraffic, Methanex, OKQ8, Volvo.
15. van Ree, Oudhuis A, Faaij and Curvers A, 1995 Modeling of a biomass integrated gasifier/combined cycle (BIG/CC) system with the flowsheet simulation programme ASPEN+, Netherlands Energy Research Foundation ECN, Petten the Netherlands
16. Faaij a, Meuleman B and van Ree R, 1998, Long term perspectives of biomass integrated gasification with combined cycle technology, Netherlands agency for energy and the environment NOVEM, Utrecht the Neteherlands.
17. Ogden JM, Steinburger MM and Kreutz TG, 1999, A comparison of hydrogen, methanol amd gasoline as fuels for fuel cell vehicles. Implications for vehicle design and infrastructure development. Journal of power sources 79(2).
18. Vosloo A, 2000, Colloquinumat Utrecht University by Vosloo, Sasol FT expert.
19. Larson ED and Jin H, 1999, Biomass conversion to Fioscher-Tropsch liquids, preliminary energy balances. In: Overend R and Chornet E, Proceedings of Fourth Biomas Conference of the Americas, Elsivier Science, Kidlinton UK
20. Schultz H, 1999, Short history and present trends of Fischer-Tropsch synthesis, Aspplied Catalysis A: General 186
21. Sic ST and Krischna R, 1999 Fundamentals and selection of advanced Fischer-Tropsch reactors, Applied Catalysist A General 186.
22. Syntroleum Corporation, "S-2 Synthetic Diesel Fuel Driving Clean-Fuel Innovation", http://www.syntroleum.com/media/syntroleum_s2.pdf, 2002.
23. Teresa L. Alleman and Robert L. McCormick at NREL, 'Fischer-Tropsch Diesel Fuels – Properties and Exhaust Emissions: A Literature Review', SAE 2003-01-0763, 2003.
24. Teresa L. Alleman, Robert L. McCormick and Keith Vertin at NREL, "Assessment of Criteria Pollutant Emissions from Liquid Fuels Derived from Natural Gas", NREL/TP-540-31873, www.eere.energy.gov/vehiclesandfuels/epact/pdfs/ftd_docket/epact_assessment.pdf, 2002.
25. Brian P. Frank, Greg Rideout, Sougato Chatterjee, Dana Lowell and others, "A Study of the Effects of Fuel Type and Emission Control Systems on Regulated Gaseous Emissions from HD Diesel Engines", SAE 2004-01-1085, 2004.

26. Ian Myburgh, Mark Schnell, Koji Oyama, Hideaki Sugano, Hisashi Yokota, Shigeki Tahara, "The Emission Performance of a GTL Diesel Fuel - a Japanese Market Study", SAE 2003-01-1946, 2003.

27. Paul W. Schaberg, Ian Myburgh, Jacobus J. Botha, "Comparative Emissions Performance of Sasol F-T Diesel in Current and Older Technology HD Engines", SAE 2000-01-1912, 2000.

28. Presentation by Mike May, "Development and Demonstration of Fischer-Tropsch Fueled Heavy-Duty Vehicles with Control Technologies for Reduced Diesel Exhaust Emissions", http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer_2003/session3/2003_deer_may.pdf, 2003.

29. Syntroleum, "Petition for rulemaking pursuant to 10 C.F.R. Part 492", www.eere.energy.gov/vehiclesandfuels/epact/pdfs/ftd_docket/syntroleum_petition.pdf , 2000.

30. R. Carbone, A. Jørgensen, N. Ranchet, D.J. Rickeard, C.J. Rowntree, R.J. Stradling, P.J. Zemroch, "Fuel effects on the characteristics of particle emissions from advanced engines and vehicles", www.concawe.org/Content/Default.asp?PageID=31, 2005.

31. Bengt Aldén, Andreas Eklund, Thomas Larson, "Flottförsök med Eco-Par®", www.framtidsbranslen.se/bilder/slutrapport.pdf, 2002.

32. P.W. Schaberg, P.M. Morgan, I.S. Myburgh, P.N.J. Roets, J.J. Botha, "An Overview of the Production Properties and Exhaust emissions Performance of Sasol Slurry Phase Distillate Diesel Fuel", http://www.sasolchevron.com/dwn/ovrview2.pdf, Year?

33. Nigel N. Clark, Christopher M. Atkinson, Gregory J. Thompson, Ralph D. Nine, "Transient Comparisons of Alternative Compression Ignition Fuels", SAE 1999-01-1117, 1999.

34. M.B. Sirman, E.C. Owens, K.A. Whitney, "Emissions Comparison of Alternative Fuels in an Advanced Automotive Diesel Engine", SAE 2000-01-2048, 2000.

35. US. DOE approved by Steven Chalk, "Progress Report for Fuels for Advanced CIDI Engines and Fuel Cells", http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/13.pdf, 2000.

36. Presentation by Rudolf R. Maly, "Effect of GTL Diesel Fuels on Emissions and Engine Performance", http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer_2004/session2/2004_deer_maly.pdf, 2004.

37. Presentation by Ralph A. Cherrillo, Mary Ann Dahlstrom, Richard H. Clark, "Rigorous HDD Emissions Capabilities of Shell GTL Fuel", http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer_2005/poster1/2005_deer_cherillo.pdf, 2005.

38. Henry NG, Steve Ciatti, Scott Miers, Munidhar Biruduganti, "Comparing the performance of SunDiesel™ and Conventional Diesel in a LD Vehicle and Engines", http://www.eere.energy.gov/vehiclesandfuels/pdfs/deer_2005/session7/2005_deer_ng.pdf, 2005.

39. Leslie Eudy, Robb Barnitt, Teresa L. Alleman, "Yosemite Waters Vehicle Evaluation Report", http://www.eere.energy.gov/afdc/pdfs/38195.pdf, 2005.

40. Paul Schaberg, Johan Botha, Mark Schnell, H. Hermann, N. Pelz and Rudolf Maly, "Emissions Performance of GTL Diesel Fuel and Blends with Optimized Engine Calibrations", SAE 2005-01-2187, 2001.

41. Henry Ng, Munidhar Biruduganti and Kevin Stork, "Comparing the Performance of Sundiesel™ and Conventional Diesel in a Light-Duty Vehicle and Heavy-Duty Engine", SAE 2005-0-3776, 2005.

42. Scott A. Miers, Henry Ng, S. A. Ciatti and Kevin Stork, "Emissions, Performance, and In-Cylinder Combustion Analysis in a Light-Duty Diesel Engine Operating on a Fischer-Tropsch, Biomass-to-Liquid Fuel", SAE 2005-01-3670, 2005.
43. Simon C. Clarke, Foster Wheeler Energy , "MANAGING THE MOLECULE - REFINING IN THE NEXT MILLENNIUM", http://www.fwc.com/publications/tech_papers/oil_gas/sclarke.cfm, (25/2 2006)
44. Website of Aspen Petroleum, www.aspen.se, (latest May 2006).
45. Website of Carfolio http://www.carfolio.com/specifications/models/car/?car=113938&Volkswagen, (March 2006).
46. "Policy Guidelines for Reducing Vehicle Emissions in Asia", http://www.adb.org/documents/guidelines/Vehicle_Emissions/cf_ch04.pdf, (May 2006).
47. http://www.dieselnet.com, (April 2006)
48. http://a257.g.akamaitech.net/7/257/2422/12feb20041500/edocket.access.gpo.gov/cfr_2004/julqtr/40cfr86.544-90.htm, (May 2006)