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Keywords
Fischer-Tropsch; Alternative motor fuels; Emission measurements
THE ENERGY BALANCE AND GHG AVOIDED EMISSIONS IN THE PRODUCTION / USE OF ETHANOL FROM SUGAR CANE IN BRAZIL: THE SITUATION TODAY AND THE EXPECTED EVOLUTION IN THE NEXT DECADE
"Emissions from Road Vehicles Fuelled by Fischer Tropsch Based Diesel and Gasoline"

Ulrik Larsen, Peter Lundorf, Anders Ivarsson, Jesper Schramm
Technical Univ. of Denmark

Björn Rehnlund
Atrax Energi AB, Sweden

Magnus Blinge
The Swedish Transport Institute

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Background
There is a growing demand for new alternative motor fuels to replace conventional fossil fuels and to improve tailpipe emissions. This paper deals with aspects concerning tailpipe emissions from vehicles fuelled by Fischer-Tropsch (FT) fuels.

The Fischer-Tropsch technique is a way to make synthetic fuels and many other products such as waxes, alcohols and gases. The technique was discovered by two German coal researchers, Hans Tropsch and Franz Fischer in 1923, but was first implemented on a larger scale during World War 2. The technique proved to be useful fueling the German war machine during the oil embargo. It was implemented again during the oil embargo of the South African Apartheid regime and as a consequence the method has been further developed to this date, mainly by Sasol Oil. Many international oil companies today have adopted the technique and are working to improve the process. Among those are Shell, BP, Statoil, Chevron and Texaco, but the principal producers of FT fuels today are Shell and the two South African oil companies PetroSA and Sasol Oil. The process is, at this point in time, mostly used to produce diesel fuel and to some limited extend also gasoline.

FT fuels can be alternative motor fuels of brilliant quality and can be produced from as different feedstocks as coal, natural gas, biomass and even municipal waste. The technology is as such a GTL (Gas to Liquids), CTL (Coal to Liquids) or BTL (Biomass to Liquids) technology – depending on the feedstock. Though the process was originally used as a substitution for traditional oil refining, the process could also use oil as feedstock in order to make cleaner fuels.

In order to get an overview of the emission performance of FT fuels an investigation has been carried out. During the study the goal has been to find any available data on emission 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 there have not been made studies in this area or at least that they haven’t been made publicly available.

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

Emissions performance tests were made 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 at least partly made via the FT process. The tests were made in order to evaluate eventual emissions advantages of the three fuels. Due to the rather unknown composition of the FT gasoline, and the lack of availability of another FT gasoline, the Swedish Aspen fuel was brought into the project. Aspen 4T is pure alkylate gasoline and was expected to be a fuel similar to neat gasoline produced by the FT process (if such a fuel even exists).

The goal of the project is to examine the emission performance of FT gasoline including pollutants such as hydrocarbons (HC), carbon monoxide (CO), carbon dioxide (CO₂), nitrogen oxides (NOₓ) and particulate matter (PM). An analysis of the soluble organic fraction (SOF) of the PM regarding the carcinogenic poly aromatic hydrocarbons (PAH) is also included.

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 (from late 2005) were 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.

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 including another literature review of FT diesel made by the US National Renewable Energy Laboratory (NREL).

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 FT diesel and regular diesel studies and tests with different driving cycles are amongst the results.

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 [26]. The hydrocarbons are chained and are usually a blend of cyclic-, iso-, 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-paraffins 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 PetroSA that has a high aromatic content of 10%.

Besides the appearance of PAHs in the exhaust gas, aromatics influence the combustion process of the engine and therefore the emission of other pollutants.
Emissions from Vehicles Applying Fischer Tropsch Diesel.

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 HC, CO, CO\textsubscript{2}, NOx, PM and PAH.

Due to the variation of the individual vehicle/ engine configuration and testing conditions, comparisons can in practice only be made of emissions from the same running conditions i.e. the same engine, after treatment device, reference fuel, measuring setup etc. Despite this, some overall figures across engine type, year, exhaust after treatment devices, reference fuel etc., 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 have been apparent: Influence of fuel composition, cold vs. hot-start performance, driving pattern, after treatment devices, blending properties and adaptation of engine technology to FT diesel.

Figure 1 – 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 2 – 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.

Overall Figures.

Figures 1 and 2 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 1, which to some extend shows the variety of test setups, there is evidence that FT diesel produces cleaner emission in almost any case. The reduction of pollutants is evident in almost any of the test setups. Figures 1 and 2 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.

As seen in Table 1, 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 even FT fuel adapted engines.

![Table 1: Vehicles and Engines]
Driving patterns, vehicle/engine type and other info was not always available in the literature. As seen in the table, there are not many tests having 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 2 and 3

### Table 2 – Table of relative emission reduction for HD engines and vehicles.

<table>
<thead>
<tr>
<th></th>
<th>HC</th>
<th>CO</th>
<th>CO2</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average %</td>
<td>34.4</td>
<td>43.1</td>
<td>3.9</td>
<td>-1.1</td>
<td>32.0</td>
</tr>
<tr>
<td>StDev.</td>
<td>33.0</td>
<td>39.8</td>
<td>2.2</td>
<td>12.7</td>
<td>27.2</td>
</tr>
</tbody>
</table>

### Table 3 – Table of relative emission reduction for LD engines and vehicles.

<table>
<thead>
<tr>
<th></th>
<th>HC</th>
<th>CO</th>
<th>CO2</th>
<th>NOx</th>
<th>PM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average %</td>
<td>43.1</td>
<td>34.8</td>
<td>3.2</td>
<td>13.0</td>
<td>26.7</td>
</tr>
<tr>
<td>StDev.</td>
<td>31.5</td>
<td>29.7</td>
<td>2.3</td>
<td>9.8</td>
<td>19.4</td>
</tr>
</tbody>
</table>

The tables show that the HC, CO and PM emissions are significantly reduced. NOx emission is reduced to some degree for HD engines and CO2 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 CO2 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 CO2 emission in most cases. There are examples of up to 10% lower brake specific fuel consumption though. [21]

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.

**PAH**

Some PAH’s (polycyclic aromatic hydrocarbons) are categorized as being carcinogenic and are as such unwanted substances in the environment. PAH’s are a part of a larger group of molecules called aromatic hydrocarbons or just aromatics. The conventional diesel fuel in the review contains up to 34% aromatics and up to 5% PAH’s. 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.

Reference [29] contains studies that show a reduction of 35% and 50% reduction of PAH’s using FT diesels compared to conventional diesels, even though some of the conventional diesels are very clean fuels (low on sulfur and aromatics). In [3] this is supported without giving percentages. In [6] results of 17% PAH 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 45% was found in the [8] study. This gives an average PAH emission reduction of 35% compared to an average quality of conventional diesels.

**Trends.**

The reviewed literature suggests several trends for engine and tailpipe emission and the use of FT diesel, for example interesting non-linear blending properties, relations between fuel composition and emission and improved cold start emissions.
Emission Measurements from Fischer Tropsch Gasoline.

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. The alkylate gasoline was expected to be a fuel similar to gasoline produced by the FT process.

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 (CO₂), nitrogen oxides (NOx) and particulate matter (PM). An analysis of the soluble organic fraction (SOF) of the PM regarding carcinogenic polycyclic aromatic hydrocarbons (PAH) was also included.

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 some other fuel of unknown composition. 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.

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.)

Experimental

The testing 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 can be seen in table 5

<table>
<thead>
<tr>
<th></th>
<th>Aspen 4T</th>
<th>Regular Swedish Mk2 Gasoline unleaded</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane no. RON</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>Octane no. MON</td>
<td>90</td>
<td>85</td>
</tr>
<tr>
<td>Steam Pressure</td>
<td>55-65</td>
<td>70-95</td>
</tr>
<tr>
<td>Sulfur ppm</td>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>Aromatics vol%</td>
<td>0.1</td>
<td>30-35</td>
</tr>
<tr>
<td>Benzene vol%</td>
<td>0.01</td>
<td>1</td>
</tr>
<tr>
<td>Cracked components vol%</td>
<td>0</td>
<td>5-13</td>
</tr>
</tbody>
</table>

Table 4– Table of comparison, Aspen and regular gasoline (25). Note that it was a Danish gasoline fuel that was the reference fuel.
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.

### 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,\(^1\), it has a kerb weight of 1184kg, a 1600cc displacement, 4 cylinders with 4 valves each, a max output of 84.3 kW, a CO2 emission of 168 g/km, a compression ratio of 12:1 and a direct fuel injection system.

### Results

An overall average of gaseous emission factors running FTP75 and NEDC tests is shown in figure 3. 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 CO2 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 3 – Average gaseous emissions using different fuels.

Figure 4 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 for Aspen but not FT.

Figure 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\textsubscript{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\textsubscript{2} emission gives reason to believe that the brake specific fuel consumption of the car is decreased accordingly. CO\textsubscript{2} is increased with neat FT gasoline.
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.

PAH Analysis

Quite significant trends can be seen on figure 6. Compared to the regular Danish unleaded gasoline, 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.

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 is showing relatively low PAH emission for Aspen, high for R/FT and even higher for FT.

Conclusions

The literature review has shown that application of FT based diesel fuels generally reduces emissions of CO, HC, PM and PAH significantly, meaning more than 25%, depending on which component that is considered (results are shown in Table 2-3). NOx is reduced about 10% and CO2 is reduced with a few percent.
exception was that PAH emissions increased with the application of FT fuel.

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