

FISCHER-TROPSCH DIESEL FUEL PREPARATION AND TESTING

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ABSTRACT

Synthetic diesel fuel which is sulfur and aromatic free has been produced using the Syntroleum Process. The main difference between the Syntroleum Process and traditional Fischer-Tropsch (FT) processes is the use of a nitrogen diluted syngas stream to the FT reactors. This Syngas stream is produced in an air-blown autothermal reformer using natural gas. In the FT reactors, a cobalt based catalyst is used to convert the syngas to paraffinic oils and waxes. These products are then separated, saturated, and cracked to produce the desired products.

The emissions from two diesel fuels, this FT diesel and a conventional low sulfur diesel were measured according to the Code of Federal Regulations (CFR) Title 40 specifications in a Cummins 5.9 liter heavy duty diesel engine and a 1.9 liter light duty diesel engine. The FT diesel showed substantially reduced emissions compared to the other diesel fuels.

INTRODUCTION

The Syntroleum process is a modification of the Fischer-Tropsch (FT) process originated¹ by Franz Fischer and Hans Tropsch in 1923 to convert coal to fuels and lubricants. This process was practiced in Germany¹, and Japan² during the Second World War, and has been practiced in South Africa since it was forced to be essentially energy self-sufficient during its apartheid era. Obviously, the drivers for these uses of the Fischer-Tropsch process were not open market economics. The first commercial development of the FT process involved fixed bed reactors using cobalt based catalysts³. Nine commercial FT plants were completed in Germany between 1935 and 1939. However during this same period research continued targeted at developing higher process efficiency and cost savings with three phase reactor systems⁴⁻⁶.

The earliest work on three phase, liquid circulating reactor systems was conducted by Dufschmidt⁷ for I. G. Farbenindustrie beginning in 1934. Initially this work involved circulating a liquid through a fixed bed of catalyst⁸⁻¹⁰, however, a system with an expanded bed was developed and patented¹¹. This work was largely interrupted by the war. However, it served as the basis for FT slurry reactor development after the war². This early work taught novel features included in many current slurry type FT reactors, including external circulation loops, and inclusion of pumps and separators into those circulation loops⁷⁻¹¹.

The primary steps in the process are generation of synthesis gas (CO and H₂) from a hydrocarbon feed, conversion of the synthesis gas to hydrocarbons, and then refining of the desired products. The initial commercial plants all used coal as the hydrocarbon source, and cobalt catalysts in the FT reactors. The main fuel produced from the process was diesel, because of the excellent cetane number obtained from the highly paraffinic products.

Broader application of Fischer-Tropsch technology has awaited substantial improvement in process economics. In addition, the continued discovery of vast quantities of natural gas around the globe has reduced the emphasis on generating synthetic fuels from coal and "bottom-of-the-barrel" hydrocarbon sources, and emphasized the importance of gas-to-liquid (GTL) processes. It is likely that there are economically viable applications for a number of different hydrocarbon to synthetic fuels processes.

The Syntroleum Process (Figure 1) is designed to reduce costs in critical, capital intensive areas while providing excellent product yields. The critical cost reduction areas are syngas generation, Fischer-Tropsch reactor design, and process integration. In conventional FT processes, the syngas generation step can require 50% to 60% of the total capital investment for the plant. An air-blown process can reduce this to the 25% range because of a combination of the elimination of the air separation unit, use of a small autothermal reformer (ATR), and using a gas turbine to provide the air compression for the air fed to the ATR.

Syngas generation from natural gas has traditionally been done using either steam methane reforming (SMR) or partial oxidation (POX). Both of these require substantially pure oxygen streams from an oxygen plant, which adds significantly to the size and capital cost of the plant. The Syntroleum Process utilizes a proprietary catalytic ATR to convert natural gas to syngas using air as the oxygen source. The reactions occurring in the ATR are shown below.



Small amounts of steam are added to the system to suppress the formation of carbon. Because the system is in heat balance, no heat transfer system is required, and the reactor is much more compact than is possible with SMR or POX. The H₂ to CO ratio of the resulting syngas is close to the approximately 2:1 ratio in the hydrocarbon products from the FT process (4).



The Fischer-Tropsch products are highly paraffinic, but also contain low levels of primary olefins and alcohols. If desired, these can be saturated to produce an essentially totally paraffinic material. Generally, economics are most favored by production of the long chain hydrocarbons which are cracked to the desired products rather than maximizing the amount of product in the fuel range produced directly by the FT process. This is because the latter approach tends to produce undesirably high levels of low value C₁ to C₅ hydrocarbons. Cracking to fuel range products is done using typical refining methods. However, the conditions needed to convert this synthetic crude into products are milder than those required for traditional natural crudes, which generally contain substantial amounts of unsaturated and heterocyclic species.

Because syngas produced in this air-blown process is diluted with nitrogen relative to an oxygen-blown system, there is some increase in the size of the downstream equipment associated with gas processing. However, economic evaluations show that elimination of the entire oxygen plant can be a significantly greater savings than the costs associated with nitrogen in the synthesis gas. An air-blown system allows the use of a turbine for the air compressor thereby enhancing thermal integration as well as allowing an inexpensive method for producing electric power for resale and/or driving other processes. Furthermore, the dilute light hydrocarbon stream that typically would be flared can be used as fuel for the turbine. The air-blown system offers greater flexibility in achieving higher carbon efficiencies and energy integration over a broad range of natural gas compositions. The economic incentives for the air blown system are evident at all plant throughputs and are greatest when evaluating small to mid size plants (< 50,000 bpd).

Cost savings in Fischer Tropsch reactor design are accomplished with a moving bed system, where catalyst microspheres are suspended by the gas in circulating liquid. This system provides more effective multiphase mixing thereby enhancing catalyst productivity and selectivity while minimizing the required heat transfer area. This gives a reactor that is more efficient than tube and shell reactors that have previously been commercialized⁶. Our economic evaluations strongly indicate that the Syntroleum moving bed system with our proprietary cobalt based FT catalyst provides significant

cost savings over the three phase bubble columns previously described in the technical literature^{12, 13}. The improved economic performance of the moving bed system is due to the integration of catalyst performance with reactor design. The catalyst possesses high activity, attrition resistance, excellent hydrodynamic properties and is readily separated from the hydrocarbon products. Additionally, reaction kinetics have been tailored to give the preferred selectivity in the nitrogen-diluted environment.

PILOT PLANT DESIGN AND PERFORMANCE

The ATR and moving bed FTR combination for the Syntroleum process were demonstrated using a pilot plant constructed at ARCO's Cherry Point, Washington refinery. The individual process units were modular in design, constructed in Tulsa, OK, and shipped to the site in Washington state, where they were erected. The objectives of the Cherry Point pilot plant are to confirm the commercial design basis, identify optimum operating conditions for different natural gas feed compositions, and to generate the data necessary to validate Syntroleum process models. The unit was sized to reflect the hydrodynamics and multi-phase flow processes anticipated in commercial operations. Instrumentation was installed to monitor all critical axial and radial variables associated with phase holdups, interphase transport and recirculation rates. Process conditions were varied over a broad range to determine optimal conditions for the production of fuels and/or specialty products. The pilot plant was initially designed with a nameplate capacity of 70 barrels of FT product per day. Higher catalyst productivities and selectivities have been achieved due to better than expected catalyst performance in the turbulent mixing regime associated with commercial sized moving bed reactors. The first portion of the plant started operation in April 1999, and has achieved in excess of 6000 hours of ATR operation and 4500 hours of FT operation. We have successfully demonstrated ATR operation without significant carbon formation, and the FT unit has met or exceeded all design criteria associated with multiphase mass and heats transfer as well as with hydrodynamic and phase partitioning and separation parameters.

The autothermal reformer was designed to generate sufficient syngas to support 70 barrel per day FT product yields as well as allow for production above that nameplate capacity. The ranges of operating parameters being studied involve natural gas formulations containing significant quantities of C₂⁺ hydrocarbons and CO₂. After determining critical residence times and reaction rates, the unit has given excellent performance in terms of carbon conversion efficiency to CO and operating stability.

The catalyst used in the pilot plant is a powder composed of cobalt on alumina-based microspheres. This material was produced in a full commercial- sized batch in commercial manufacturing equipment. Catalyst development involved starting with preparations of gram quantities at the laboratory scale, moving to pound quantity preparation procedures in order to define commercial manufacturing procedures. The final catalyst used in the pilot plant is from a 25,000 lb lot produced using low cost commercial manufacturing equipment.

In order for the catalyst to function effectively in the process, it must first be activated (reduced), because it is cobalt metal that is the actual catalytic species, while cobalt oxide is the form produced during manufacturing. Conditions and procedures were developed and followed at commercial scale, and resulted in catalyst in service in the reactor that met or exceeded the performance requirements in terms of activity and selectivity.

As previously mentioned, catalyst attrition and catalyst-product separation are some of the critical issues to be determined in the unit. After over 4500 hours of operation under widely varying conditions, there is no evidence of significant attrition within the unit. The attrition resistance of the catalyst has been monitored using particle size analysis, the settling characteristics of the particles, and the filter/separator performance. In addition, catalyst life and activity maintenance have met or exceeded expectations.

FUELS PREPARATION AND ENGINE TESTING

Syntroleum has produced a number of fuel range materials by refining Fischer-Tropsch wax, including synthetic analogs of gasoline, JP-5, JP-8, and diesel fuel. Synthetic diesel

is currently receiving considerable attention because diesel engine emissions are under regulatory scrutiny. Syntroleum S-2 fuel is a sulfur free, aromatics free fuel with an exceptionally high cetane index. Table 1 shows S-2's properties compared to typical properties of low emissions EPA D-2 Diesel.

Unmodified Heavy Duty Diesel Engines. Numerous studies have evaluated engine emissions from conventional, unmodified diesel engines using a variety of FT fuels. Engine tests with three S-2-like fuels consistently show decreases of hydrocarbons, carbon monoxide, nitrous oxides and particulate matter emissions¹⁴. We have confirmed these results in work at Southwest Research Institute comparing Syntroleum S-2 with EPA #2 using an unmodified heavy duty 5.9L Cummins engine on a test stand (Table 2) and an unmodified heavy-light duty diesel vehicle with the same engine on a chassis dynamometer (Table 3)¹⁵. None of these tests included engine timing modifications which could have taken advantage of the significantly higher cetane of Syntroleum S-2. In both tests, the Syntroleum S-2 significantly reduced emissions from the 5.9L Cummins engine. The 40% to 45% reduction in particulate emissions using the Syntroleum S-2 is especially notable.

Although our testing did not examine emission reductions from aromatic-containing FT fuels, previous engine tests¹⁶ have shown that those fuels do not achieve the same level of improvement achieved from the more hydrogen saturated FT fuels in this study.

Table 1
Properties of US EPA Diesel and Syntroleum S-2

Property	Test Method	Units	US EPA D-2 Diesel	Syntroleum S-2 Fuel
Specific Gravity	ASTM D-1298	g/cc	0.846	0.771
API, Max	ASTM D-1298	deg	35.9	52
Flash Point	ASTM D-93	deg F	157	148
Cloud Point	ASTM D-2500	deg F	32	<0
Color	ASTM D-1500	Inspection	-	<0.5
Sulfur	ASTM D-2622	wt. %	<0.05	nd
Aromatics	ASTM D-1319	vol %	30	nd
Olefins	ASTM D-1319	vol %	1	nd
Saturates	ASTM D-1319	vol %	69	>99
Cetane Number, min	ASTM D-613	-	45	>74

Table 2
Emissions from a 5.9 liter Cummins B engine on a test stand
Average results from 2 runs

Test (g/bhp-hr)	HC	CO	NOx	Particulates
EPA # 2 Diesel	0.10	1.30	4.00	0.10
Syntroleum S-2	0.10	0.80	3.20	0.06
% reduction for S-2	0	38	20	40

Table 3
Emissions from a Heavy light-duty truck (2000 Dodge Ram 2500) with a 5.9 liter
Cummins B engine on a chassis dynamometer using the US06 test protocol
Average results from 2 runs

Test (g/bhp-hr)	HC	CO	NOx	Particulates
EPA # 2 Diesel	0.19	0.70	5.24	0.11
Syntroleum S-2	0.16	0.50	4.50	0.06
% reduction for S-2	16	29	14	45

Light Duty Diesel Engines. Emissions evaluation of Syntroleum S-2 and EPA #2 were conducted on a 1.9L Volkswagen diesel engine in a 1999 Golf GL TDI (Table 4). This is a current production model, U.S. market passenger car, and is equipped with a catalytic converter. The hydrocarbon, CO, and NOx emissions from both fuels were equivalent within the experimental error of the test. However, the particulate emissions were dramatically lower from the Syntroleum S-2 fuel.

Table 4
Emissions from a light-duty passenger car (1999 Volkswagen Golf) with a 1.9 liter
engine on a chassis dynamometer using the US06 test protocol
Average results from 2 runs

Test (g/bhp-hr)	Particulates
EPA # 2 Diesel	0.42
Syntroleum S-2	0.05
% reduction for S-2	88

CONCLUSIONS

Syntroleum and ARCO have successfully demonstrated a GTL conversion process that utilizes an air blown autothermal reformer and moving bed Fischer-Tropsch reactor. The process is robust, and is ready for scale-up to commercial scale fuels production plants. Economic evaluations of such commercial plants show that production of synthetic fuels is now economically competitive with conventional fuels.

Synthetic S-2 fuel produced substantially lower emissions than EPA diesel under all of the conditions tested. This S-2 fuel has substantial advantages compared to other alternative fuels because, in addition to being environmentally acceptable, it is backward compatible with current vehicles, and is compatible with the existing fuels delivery infrastructure. Syntroleum S-2 also exceeds engine manufacturers desires for ultra-low sulfur fuel which is needed to allow use of NOx absorption catalyst in future vehicle designs.

The need for backward compatibility with little or no modification to the engine is important because owners of current vehicles will not generally volunteer to make their vehicles obsolete because the actions of non-market forces. Furthermore, since it will take considerable time from the introduction of any new engines until they represent a majority of the vehicles on the road, substantial advantage in achieving environmental goals may be made using the existing inventory of vehicles.

The need for compatibility with the existing extensive fuels delivery infrastructure is important for several reasons. It allows consumers to maintain current behavior

patterns while still adopting new technology. In addition, it allows the many fuels distributors to become partners instead of competitors in technology introduction. This eliminates the need to for the new engine and new fuels suppliers to invest billions of dollars in a delivery system (service stations, etc.) and allows existing fuels marketers to pursue their own marketing strategies. The synthetic GTL fuels facilitate this approach because they are compositionally compatible with the existing tanks and pumps in service stations and fueling facilities, and may require little more than clean out of the tanks.

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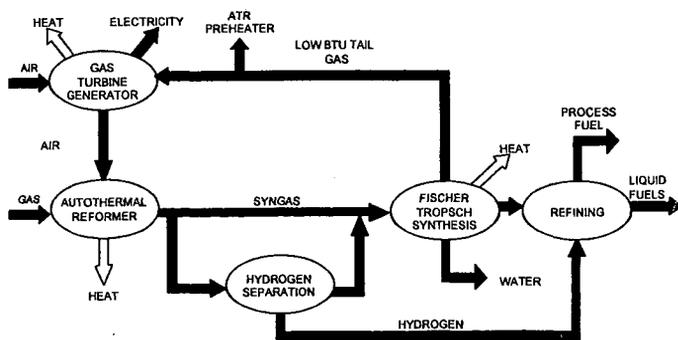


Figure 1. Process schematic for fuels production via the Syntroleum Process.