

A Comparison of the Properties and Cold Flow Performance of 'Summer' and 'Winter' GTL Diesel

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ABSTRACT

Gas to Liquids (GTL) diesel has been produced commercially for several years. GTL diesel is known for its excellent properties, including zero aromatics, near zero sulphur and a high cetane number. Most of the GTL diesel produced by commercial plants is utilised as a blend component, especially in blends up to 20%. In these applications, the cold flow properties are potentially less critical, as the cold flow properties of the blend will mostly be determined by the petroleum-derived component. In certain markets, however, it is possible that GTL diesel can be used as a neat diesel, therefore requiring good cold flow properties.

An advantage of GTL technology is that the cold flow properties of GTL diesel can be tailored to meet the climatic requirements of a specific geographical area. In the current study, GTL diesel samples with cold flow properties ranging from 'summer type' to 'winter type' and varying intermediate cold flow qualities were evaluated. In line with expectations, it was shown that increasing the degree of isomerisation will improve the cold flow properties of the GTL diesel, whilst the other bulk properties such as density, cetane and viscosity of the fuels are not significantly altered. It is also shown that the excellent cold flow properties of these 'winter type' GTL fuels translate into excellent operability performance.

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INTRODUCTION

The demand for alternative fuels is increasing constantly, driven by the requirement to become less reliant on conventional liquid fuels and increasingly stringent environmental requirements. Although significant efforts have been made to find alternatives, the overall market share of these alternative fuels is relatively small. In recent years, the interest in biofuels has increased, but their contribution to the overall commercial product spread is still minimal, amidst growing questions regarding the sustainable production of biofuels from an environmental and legislative point of view. Paraffinic fuels (including Fischer-Tropsch diesel and Hydrotreated Vegetable Oil (HVO) have gained significant momentum over the past few years. These products generally have excellent intrinsic properties (zero sulphur, ultra-low aromatics and high cetane number) and are frequently used as blend components (typically below 20 volume% in a blend). [1, 2, 3, 4]

Since TL diesel is mainly used as a blend component in warmer climates, extremely good cold flow properties are not required. In some countries, however, it would be possible to sell GTL diesel as a neat fuel. In this article it will be shown that GTL diesel, produced via Fischer-Tropsch (FT) technology, can be tailored to different climatic conditions, thereby enabling GTL diesel to be sold as a neat or blended fuel with excellent cold flow properties.

Overview of Fischer-Tropsch (FT) Technology

With the continuous increase in natural gas production, interest in Fischer-Tropsch technology has grown over the last few years. [1, 2, 3, 4] In broad terms, FT technology entails three basic steps namely; synthesis gas (syngas) production, FT synthesis, and product upgrading. The syngas production process depends on the feedstock used, but typically includes a gasification step (if coal or biomass is used as feedstock) or a methane reforming step when natural gas is used as feedstock. [5,6,7]

Fischer-Tropsch synthesis technology can be differentiated by distinguishing between either low temperature or high temperature process conditions, respectively known as the High Temperature Fischer-Tropsch (HTFT) or the Low Temperature Fischer-Tropsch (LTFT) pathways. [7,8] Typically, the HTFT process yields LPG, gasoline, diesel, kerosene and chemicals (such as olefins and oxygenates), whereas the LTFT process can be tailored to produce LPG, naphtha, diesel, kerosene and base oils. In addition, both incarnations of the technology offer the production of various chemical feedstocks. The type of FT synthesis employed will also depend on the feedstock as well as the desired product slate. One of the commercial processes using FT technology to produce liquid fuel is the Gas to Liquids (GTL) process.

The GTL Process

In the commercial GTL process, FT technology is used to convert natural gas into liquid hydrocarbon products. The Sasol Slurry Phase Distillate (Sasol SPD™) process, otherwise known as the Sasol GTL process, is an example of a fully commercialised GTL process using LTFT technology. This process consists of three main processing steps. The first step, or the reforming step, converts natural gas to syngas consisting of carbon monoxide and hydrogen. The second step of this process involves the conversion of the syngas to FT synthetic crude (syncrude) typically using a cobalt catalyst. Although different reaction conditions will yield unique product slates, all syncrudes consist of highly paraffinic, wax molecules. In the third step, known as the product workup step, the syncrude is upgraded into middle distillate fuels using hydroconversion processes, including hydrocracking, hydrotreatment and/or hydro-isomerisation. Typical products which may be expected from this process include; LPG, naphtha, diesel, kerosene and base oils, although product slates may differ depending on the reactor configuration, catalyst, operating conditions and economic drivers. [5,9] GTL diesel is known for its unique properties including ultra-low sulphur and aromatic levels, high paraffin content, high cetane number as well as containing little to zero metallic components. [10, 11, 12]

The bulk properties of the diesel, produced via the GTL process, depend largely on the branching structure and carbon number distribution of the paraffins. [1,5] GTL diesel consists almost exclusively of paraffins varying in carbon chain length and degree of isomerisation. GTL diesel has a high cetane number (greater than 70), low density, and a high hydrogen to carbon ratio. The cold flow properties of GTL diesel depend on the degree of hydroprocessing and can be tailored for a specific market or customer. [9]

Cold Flow Properties of Sasol Gas to Liquids (GTL) Diesel

Since 2006, Sasol's commercial GTL experience was further extended to the ORYX GTL plant in Qatar. [11,13] The plant produces about 34 000 bbl/d GTL product (1 936 640 cubic metres per annum) and is situated on the north eastern seaboard of Qatar, near Ras Laffan.

In Figure 1, an overview of the commercial ORYX GTL plant in Qatar is shown.

The ORYX GTL plant mainly produces GTL diesel, GTL naphtha, and liquefied petroleum gas (LPG). [7,14] GTL diesel produced at this facility is destined for markets with warmer climates, which are considered to be mild relative to the requirements of other geographic areas, such as the arctic regions, for example. The GTL diesel produced here would typically have a maximum cloud point of 2 °C to 5 °C. [15,16] Sasol may, in future, expand its GTL technology into markets where the cold flow properties may be critical. The cold flow requirements in some of the North American markets and certain European countries are significantly more severe than what has been required historically by markets supplied with Sasol diesel. This resulted in the need to produce a GTL diesel suitable for use in areas having extremely cold winters. For improved cold flow properties,

shorter chain branched paraffins (iso-paraffins) are preferred to long chain normal paraffins (n-paraffins) since iso-paraffins are less likely to form wax crystals. The amount of short chain molecules present in the diesel are, however, limited by the flash point. A second option is to use cold flow additives. Cold Filter Plugging Point (CFPP) improver additives are typically used to improve the cold flow operability of diesel fuels. However, when a diesel fuel is used as a blend stock, it is frequently desirable to leave these fuels unadditised. Should an unadditised diesel be required, it is possible to isomerise the diesel fraction to improve the cold flow properties. Another option is to cut the diesel lighter, but this results in a loss in yield. It is also possible to blend a diesel with a kerosene in order to improve the cold temperature operability properties. Although many of these options are viable, there are also disadvantages such as product yield loss and cost implications. [26,27] The GTL diesel from the ORYX GTL facility is a full boiling range GTL diesel. The properties of typical ORYX GTL diesels are shown in Appendix A.

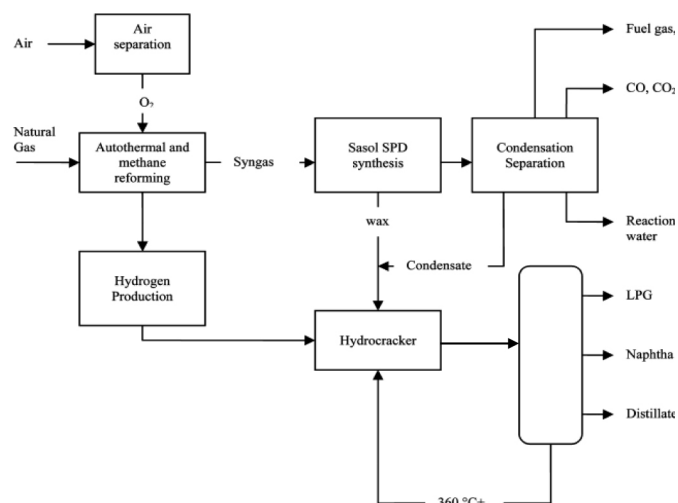


Figure 1. Overview of the ORYX GTL plant in Ras Laffan, Qatar [7]

Most countries specify Cold Filter Plugging Point (CFPP, or similar tests) as an indication of diesel cold temperature operability. The CFPP of a diesel can often be improved significantly by the use of a CFPP improver additive. There are, however, circumstances (e.g. specific refiner/off-taker requirements) where the cloud point (CP) is preferred as an indicator of cold temperature performance. Generally, the CP is an inherent property and is more difficult to improve using additives than the CFPP. CP is mostly considered to be a conservative indicator of diesel cold temperature operability performance. The cloud point is also an indicator of the wax settling propensity of a fuel during extended storage at low temperatures.

ORYX GTL and several other commercial GTL plants are not equipped with a diesel isomerisation unit. However, it is relatively easy to integrate an isomerisation unit into a GTL flow scheme, in order to improve the cold flow properties of the distillate (diesel) fraction. The severity of the isomerisation unit's operating conditions will determine the degree of isomerisation of the fuel, which will in turn decrease the cetane number and improve the cold flow properties of the fuel. [1] It is therefore possible to produce GTL diesel with

varying cold flow properties ranging from 'summer type' GTL diesel to extreme 'winter type' GTL diesel as well as various 'midgrade' GTL diesels.

Seasonal Requirements - Low Temperature Operability

Diesel fuels containing long chain linear n-paraffins are expected to precipitate paraffin wax upon prolonged exposure to cold temperatures. [17] If the diesel fuel is cooled further, the crystals will start to agglomerate and more precipitation of the wax crystals can be expected. [18] Low temperature vehicle operability could present operational problems when paraffins present in the fuel crystallise at cold temperatures. [19,20] The formation of wax crystals could result in blockage of the fuel filters preventing the fuel from the tank reaching the engine. [18,21, 22, 23] This phenomenon could result in a number of vehicle operability issues including power loss and erratic running or stalling during running, and in extreme cases, failure to start. [21] An extended storage period in ambient temperatures below cloud point may cause wax settling in above ground fuel retail storage tanks (may take weeks) and in vehicle storage tanks (may take place even over a weekend in a parked vehicle). Additionally, the cold flow properties of diesel could have an impact on the fuel logistics chain. The formation of wax in a pipeline and other diesel transportation modes can cause blockages preventing the flow and delivery of the fuel. [24,25] It is widely accepted that low temperature vehicle operability is dependent on both the vehicle technology as well as the fuel type. [20,22] It is therefore important to ensure that the diesel fuel is suitable for use in its intended market.

The current study evaluated the range of cold flow properties that can be achieved by the GTL technology. Additionally, the impact of varying degrees of isomerisation on the bulk properties of the diesel fuel, with emphasis on the density, viscosity, and cetane, were evaluated. Finally, the cold flow operabilities of selected GTL diesels were evaluated, using a CEC M-11-T-91 cold temperature operability rig.

Experimental

Materials

Fourteen GTL diesel samples with significantly different cold flow properties were evaluated in the current study. None of the fuels, evaluated in the current study, contained any cold flow improvers. The chemical and physical properties of the GTL diesels are presented in [Appendices A and B](#), in comparison to the technical requirements of ASTM D975, the standard specification for automotive diesel in the US. The properties of the petroleum-derived diesel, used in the operability testing, are shown in [Appendix C](#). The sample matrix included several commercial and experimental (non-commercial) GTL diesel samples. These were:

- i. A commercial ORYX GTL diesel fuel- representative of a 'summer grade' GTL diesel.
- ii. A selection of GTL diesel samples with varying cold flow properties.
- iii. A highly isomerised GTL diesel - representative of an extreme 'winter grade' GTL diesel.

Experimental Methods

The properties of the diesel fuels, evaluated in this study, were determined in accordance with the appropriate ASTM International and CEN methods as shown in [Appendix A](#) and [B](#). In the section below, the cold flow test methods, as employed in the current study, are discussed. There are various laboratory testing techniques which may be used to define or quantify the cold flow behaviour of a diesel fuel such as cloud point (CP), Cold Filter Plugging Point (CFPP), pour point (PP), Low Temperature Flow Test (LTFT), Freezing Point (FP), Wax Appearance Point (WAP), and Simulated Filter Plugging Point (SFPP). GTL diesels in this study were evaluated for CP, LTFT, CFPP and PP with results shown in [Appendix A](#).

All these cold flow test methods provide an insight into the cold temperature behaviour of diesel fuels. However, none of these techniques can fully predict how a vehicle will operate under cold temperature conditions. The vehicle hardware and the climatic conditions (e.g. fast cool-down or slow annealing) all play a role. The ultimate is therefore to carry out the testing of a vehicle under cold temperature conditions. However, this is expensive and requires a large climatic chamber. An alternative is to use a cold flow bench rig test to study operability. In the current study, the CEC M-11-T-91 protocol was followed, using a Ford Escort fuel injection system. Although this engine technology is not common in the market anymore, it represents an older technology mechanical distributor injector pump design. This diesel injection technology is representative of a moderately severe technology in terms of sensitivity towards cold temperatures.

Cloud Point

When a diesel fuel is cooled, it reaches a temperature where the wax paraffins start to precipitate out of the diesel fuel. If the diesel fuel is cooled further, these wax crystals may agglomerate and result in a milky appearance. The temperature where this is first observed is referred to as the cloud point (CP). [18] The referee method for determining the CP of a diesel is ASTM D2500, which defines the CP as: "The temperature of a liquid specimen when the smallest observable cluster of hydrocarbon crystals first occurs upon cooling under prescribed conditions" [28] The CP of the diesel is a function of the total n-paraffin content, average length of the n-paraffins and their size distribution. [29] The petroleum industry widely accepts the CP of a fuel as a conservative indicator of vehicle operability at low temperatures. It is generally accepted that a fuel will be operable at temperatures at or above its CP. [29,30] The cloud points evaluated in this study were determined by the following methods; ASTM D5773, ASTM D7689 and ASTM D7683. Different methods employ different techniques to determine the CP of a fuel and it may therefore be possible that results may also differ. Additionally, many of the methods have a relative bias to the referee CP method (ASTM D2500), which also has to be taken into account. Care should be taken when analysing samples at very low temperatures since the capability of the instrumentation used for analysis does not always correspond to the precision data reported for the method, as shown in [APPENDIX D](#). Based on the experimental data generated in this study, the ASTM D7689 method was successfully applied to analyse the samples in this study.



Low Temperature Flow Test

In countries with extremely low winter temperatures, such as Canada, the low temperature operability of a fuel is defined by CP, Wax Appearance Point (WAP), or the Low Temperature Flow Test. [31] It is recognized that actual vehicle performance in extreme winter conditions will be determined by the engine, fuel system technology and fuel properties. However, it is widely accepted that, although CP is a good cold temperature failure predictor, LTFT is considered to be an even better indicator of real life vehicle operability. [19,22] The LTFT mesh size (17 μm) and slow cooling rate (1 $^{\circ}\text{C}/\text{h}$) is considered to be more representative of vehicle operability at extremely low temperatures in the North American markets. [32,33] The extended periods of gradual exposure to progressively colder temperatures, during the LTFT test, simulates the process of wax formation in the fuel tank of a vehicle and is therefore considered to be more representative of real life cold vehicle operability. It is generally accepted that the fuel will perform adequately at temperatures at or above the LTFT minimum pass temperature. [32] In this work, LTFT measurements were conducted in accordance to ASTM D4539.

Cold Filter Plugging Point

The CFPP of a fuel is regarded as the temperature at which the wax crystals formed in the fuel will block filters, as defined by the standard CFPP test method used in this study; ASTM D6371. [34] The CFPP is less conservative than the CP and is considered to provide suitable protection for vehicles that do not operate in severe winter conditions, such as southern Europe. [35,36] Canada specifies fuel low temperature operability by either Cloud Point or LTFT - a laboratory test to predict/ensure vehicle operability of the primarily heavy-duty truck vehicle fleet in this country. Other countries, with similar extreme winter conditions (e.g. Scandinavia, Russia), specify and/or use a different laboratory test - the CFPP to predict vehicle operability and ensure adequate low temperature fuel performance in their light-duty passenger car and heavy-duty truck vehicle fleets. In this paper the authors have selected to use the LTFT to quantify GTL diesel low temperature performance [37]

Pour Point

The pour point of the fuel is considered an extreme cold flow measurement and indicates the point when the diesel fuel loses its fluid-like qualities. [35] At temperatures below the PP, most of the fuel has solidified and therefore cannot flow under its own weight. Since PP is generally considered to be the least conservative indication of a fuel's cold flow properties it generally does not form part of standard diesel fuel specification in either Europe or North America. [36,38] However, in North America many of the pipelines used for transportation of diesel fuel require both a maximum cloud point and pour point, rather than a CFPP or LTFT minimum pass temperature. [39, 40, 41] As in the case of cloud point, the pour points were determined by various methods employing different techniques namely; ASTM D5949, ASTM D6749 and ASTM D7346. Although ASTM D93 is still frequently used, it is not considered to be suitable for use at extremely low temperatures. Secondly, the error range for this method is large. ASTM D7346 has replaced ASTM D93 due to better precision and accuracy. The reader is referred to

APPENDIX D for a summary of the test methods and their precision statements. The preferred method for pour point analysis is ASTM D7346, based on the analytical data generated in this study.

Cold Temperature Operability

Testing of the cold flow operability of the diesel fuels was conducted according to the CEC M-11-T-91 test protocol. The test rig consists of a 1980's Ford Escort fuel injection system. The fuel filter is located before the fuel pump, making the cold flow performance of the fuel critical in preventing blocking of the filter. The testing was conducted as follows:

The rig is cooled down over a period of 18 hours. Testing, per each discrete temperature, is conducted over 24 minutes. The performance of the fuel is rated in terms of demerit points, as per the CEC M-11-T-91 protocol. Following the test, the rig is heated to 55 $^{\circ}\text{C}$ in order to remove any residual wax molecules.

Testing Range

Before any testing can be carried out on the operability rig, the cloud point of the fuel is determined. The temperature of the operability rig is then set to 5 $^{\circ}\text{C}$ above the cloud point, and the temperature is maintained for 2 hours. The fuel is then cooled linearly over a period of 12 hours. The temperature is maintained for 4 hours before testing commences.

At the set temperature, the following actions are conducted:

- Idling for 30 seconds
- Accelerate to 60 km/h within approximately 35 seconds
- Drive at 60 km/h for 3 minutes
- Accelerate to 110 km/h and drive for 30 minutes

The results are interpreted as follows:

- The demerit scale ranges from 0 (no issues) to 100 (vehicle stalls in the first minute) - 40 is considered as the pass/fail limit
- A demerit of 0 to 20: surge / misfire (max 10) and pedal adjustment (max 10)
- A demerit value of 20 to 40: speed loss
- A value of 60 to 100: driving stall

DISCUSSION

The data in [Appendix A](#) provides an indication of the range of cloud points that can be produced using GTL technology. The physical and chemical properties of diesel fuel, considered to be most affected by an increase in the extent of isomerisation, are discussed below.

Cold Flow Properties

The range of cold flow properties that can be achieved with GTL technology is shown in [Figure 2a](#) and [b](#). From the data presented it is evident that generally the cold flow properties of the GTL diesels evaluated in this study improved with an increase in the number of iso-paraffins present. Although there is some scatter in the data, it is