

# The Properties and Injector Nozzle Fouling Performance of Neat GTL and GTL/EN590 Diesel Blends in Various Diesel Engines

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## ABSTRACT

The combination of high crude oil prices, energy security concerns and environmental drivers have resulted in an increased focus on alternative fuels. Gas to liquids (GTL) diesel is considered to be a promising alternative diesel fuel, given that it can be used directly as a diesel fuel or be blended with petroleum-derived diesel or biodiesel. GTL diesel fuels are predominantly paraffinic and possess several excellent inherent properties including virtually zero sulphur, very low aromatics (<1%) and very high cetane values (typically >75).

Currently GTL diesel is mostly sold into the European market as a blend stock for the extending and upgrading of petroleum-derived diesel fuels. Given GTL diesel's inherent paraffinic nature, the density of this product is below the European minimum 820 kg/m<sup>3</sup> EN590 specification (at 15 °C). Typically up to 20% (vol) GTL diesel can be blended into crude oil derived diesel in order to meet the minimum European density specification, although neat applications of GTL diesel have also received some attention in literature. This study presents some findings pertaining to injector fouling for neat and 20% (vol) GTL diesel blends on a variety of diesel engines. There is however, very little information in the open literature on the physical and injector fouling performance properties of higher binary blends of petroleum-derived and GTL diesel. Several markets do not have a minimum density specification (e.g. the USA, Canada, Uzbekistan), while several countries have winter density specifications lower than 820 kg/m<sup>3</sup>, including countries like China, potentially enabling GTL diesel to be used at higher blending ratios and in its neat form.

In the current study, neat low temperature Fischer Tropsch (LTFT) GTL diesel and EN590 diesel fuels, together with blends containing 10, 20, 30, 50, and 80 volume percent GTL, were analysed for their physical and chemical properties. The injector fouling performances of these blends were assessed in the CEC F-23-01 XUD9 and Sasol common rail tests. Many of the physical properties of these blends were influenced positively by the addition of GTL diesel to the EN590 fuel. Overall, it was concluded that at low percentages, blends of GTL diesel with EN590 resulted in similar injector fouling performance in the CEC F-23-01 XUD9 and Sasol common rail tests. At higher GTL diesel contents, a significant injector fouling performance improvement was found.

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## INTRODUCTION

There is currently a strong worldwide drive towards alternative liquid fuels for transportation, mainly driven by emissions reduction, energy security concerns, volatility in the oil price and the search for renewable fuels to complement the dwindling world oil supplies. Diesel plays an important role in the heavy duty transport sector, but in several countries, diesel is now also a dominant or significant player in the passenger car segment. Although most of the diesel fuel in the market is still obtained by processing crude oil, several alternative sources of diesel have also been gaining

momentum. Fatty Acid Methyl Esters (also known as FAME) have been legislated and used in several countries. Another promising alternative diesel is Gas to Liquids diesel (GTL diesel), produced by the Fischer Tropsch process. In this process, natural gas is converted into synthesis gas and ultimately into fuel products, including diesel. Although the current commercial GTL diesel production is limited to a few plants including the Shell plant in Bintulu, Malaysia, the PetroSA plant in Mossel Bay, South Africa, the ORYX GTL plant in Qatar (jointly owned by Qatar Petroleum and Sasol) and the Shell Pearl plant in Qatar, it is foreseen that GTL diesel may become a more prominent player in the

international market, driven by an increased projected future demand for diesel.

Up to now, the properties and performance of neat GTL diesel in vehicles has been well described [1,6]. The current study is therefore aimed at contributing to the existing data by establishing the properties and injector fouling performance of GTL diesel and EN590 blends across the full spectrum of binary blends. A thorough analysis of the full specification properties and fuel stability of the blends is presented as well as a detailed study on injector deposit formation (fouling). This focuses on neat GTL diesel as well as the same range of binary blends with EN590 diesel without any zinc addition in both older and newer generation diesel engines. As the effect of fuel solvency is more relevant to metal contamination such as zinc, it has not been covered here. A further study is currently underway to focus on solvency and zinc related deposits. The current study therefore aims to:

i. Investigate the stability performance of neat GTL diesel and EN590 diesel and blends thereof using various standard ASTM tests.

ii. Study the effects of neat GTL diesel and blends on injector fouling to quantify and link the risks or benefits of the observed stability behaviour to real life engine applications.

## LITERATURE REVIEW

GTL diesel has several beneficial properties compared to conventional petroleum-derived diesel [1,2,3,4,5,6], including virtually zero sulphur, negligible quantities of aromatics and heteroatomic species such as sulphur and nitrogen. The combustion of neat GTL diesel offers a significant reduction in several emissions including soot, PM, carbon monoxide and hydrocarbon emissions, and blending of GTL diesel with petroleum-derived diesel fuels also result in significant emissions benefits compared to the neat petroleum-derived diesel fuel alone [2,3,6]. Typically these fuels also have excellent compression ignition properties [7,8]. GTL fuels can be blended with conventional petroleum-derived diesel fuels, and due to the excellent properties, may significantly upgrade the properties of these petroleum-derived diesel fuels [7].

Similar to other severely hydrotreated fuels, there are however certain properties that are different to petroleum-derived fuels such as lower density and lower inherent lubricity, which is due to the absence of heteroatomic species. The addition of a suitable lubricity additive or biodiesel is effective in optimising lubricity and providing sufficient wear and anti-seizure protection [6,18].

The lower density of GTL diesel limits the application of GTL distillates in their neat form as final products in certain markets, although it is possible to use neat GTL diesel in certain niche applications as well as in markets where no minimum density for diesel is specified. The CEN Workshop agreement also enables the use of paraffinic diesel in higher blends [31]. Consequently, it is anticipated that GTL diesel

could be best utilised when blended with highly aromatic distillates such as conventional petroleum-derived diesels, thereby producing a final diesel with a higher cetane number and lower sulphur and aromatics contents. Due to the low density of GTL diesel (typically around 770 kg/m<sup>3</sup>), only up to 20% GTL diesel has usually been blended into petroleum-derived diesel, and only this blend ratio has been widely studied in literature. [6]

The stability of diesel fuels is of importance, as this ensures problem free use of the fuel in the market, including during the storage phase (e.g. in depots, filling stations) and the use phase. Stability is typically divided into thermal stability and storage stability, where thermal stability is defined as the exposure of the fuel to temperatures above storage temperature for short periods of time and storage stability is defined as the stability of the fuel when exposed to near ambient temperatures for longer periods of time [16]. Although GTL diesel is typically highly paraffinic, which potentially indicates good stability; there are some factors that may result in a decreased stability, including the potential presence of olefins and the presence of trace compounds [16]. Typically, hydrotreatment would result in the removal of olefins and any oxygenated species present, however, hydrotreatment requires hydrogen which adds to the cost of production of these fuels. GTL diesel also does not contain any aromatics, which is thought to increase the stability in petroleum-derived diesel fuels. O'Rear suggested the use of sulphur-free antioxidants to improve the stability of unhydrotreated GTL diesel fuels [16].

Experience has however indicated that commercial neat Fischer-Tropsch (FT) middle distillate fuels are very stable under thermal exposure, with FT fuels outperforming petroleum-derived fuels in many studies [17]. Several methods for the evaluation of diesel fuel stability have been discussed in literature. These methods include for example ASTM 6468 [9], where the fuel is exposed to a temperature of 150 °C for a period of 90 or 180 minutes. After the exposure period, the fuel is filtered through a filter paper. The filter paper is then dried and the reflectance of the filter paper is measured spectrophotometrically. O'Rear used a reflectance of higher than 65% as an indication of a stable fuel [17].

Although it is more typically applied to jet fuel stability, ASTM D3241 JFTOT [10] has also been used to assess the stability of diesel fuels. The method relies on the detection of a deposit on a heated tube and classifying the stability of the fuel according to the deposit intensity and colour. During the test, the fuel is typically exposed to a pressure of approximately 500 psi, and the analysis time is around 2.5 hours. Although the technique was developed for jet fuel, several authors have also applied this to diesel fuels [13,14]. A tube rating of 1 or less may be considered to be a stable fuel. Cherillo [13] used temperatures of 300, 320 and 330°C for analysis.

Diesel stability is of significance when applied in a diesel engine with the phenomenon of injector deposits. Particularly in modern common rail engines the fuel is stressed more than ever before by exposure to extremely high temperatures [24] and pressures [25] in the fuel injection system. This provides the conditions for any unstable compounds in the fuel to form precursors for deposit formation. This phenomenon has been widely studied [26, 27]. Not much is known however, on how the abovementioned stability methods translate into injector fouling performance. Both deposits on the outside of the injector nozzle and a build-up of deposits inside the injector nozzle holes may influence injector fouling performance [20,22,23,24].

A recent patent application WO 2011/140572 [15] describes the beneficial effect of neat GTL diesel and blends thereof in reducing deposits in diesel engines fitted with high pressure fuel injection systems. In these modern injection systems, the formation of even a small quantity of deposit may result in significant engine performance problems, given the extremely small sizes of the injector nozzle holes. The fuel is also under significantly higher stress due to increased injector rail pressures (up to 2000 bar is now common) and increased temperatures in the injection systems of modern diesel engines, resulting in the fuel being continuously stressed to more than 1000 bar and up to 100 °C.

Fuels like biodiesel may also cause an increase in these deposits, resulting in a requirement to carefully consider the stability of these fuels before use [21]. The stability of the fuel and the design of the injector holes are especially critical in ensuring good operation of the fuel injection equipment [20,23,24]. Unfortunately the reactions resulting in or contributing to the formation of these products are still speculative although some potential mechanisms have been proposed. [20,25,26] Much of the literature is focused on a metal deposit formation mechanism caused by traces of zinc or copper in the fuel [22,23,24]. Deposits of a carbonaceous type are also known to form by a different mechanism and noticed specifically with the use of less stable fuels such as bio-diesel [21,26]. Formation of either deposit type could result in engine power loss and deterioration in emissions performance.

ASTM D6468 [9] is commonly used for the evaluation of the high temperature stability of distillate fuels. Contradictory ASTM 6468 stability results on FT diesel/petroleum-derived diesel blends have been reported in literature, raising a concern regarding the stability of FT fuels when blended with petroleum-derived fuels. Work carried out by Bacha et al [16] and Bacha and O'Rear [17] revealed that the blending of FT diesel fuels with highly aromatic stocks such as unhydrotreated light cycle oil (LCO) result in products with reduced stability, as measured by ASTM D6468, and increased formation of filterable insoluble materials. They did however also show that hydrotreatment of LCO before blending with FT diesel could substantially improve the stability of the FT/LCO blend. In their paper they do however indicate that FT blend components are typically very stable

against peroxide formation, leading to excellent stability. It was only possible to indicate this relationship in general terms and an exact explanation was not possible. Indications were that the highly paraffinic nature of the FT diesel reduced the ability to keep oxidised species in solution due to the low solvency of these fuels [17]. They stated that the formation of insoluble degraded products in the fuel could be attributed to three factors: the concentration of the species that are readily oxidisable, the ability of the blend to keep these oxidised species in solution and the conditions of the oxidation (e.g. temperature and pressure). In their work, they showed that the addition of FT diesel increased the stability of a low aromatic diesel. The addition of FT diesel to light cycle oil (LCO), however, resulted in an unexpected antagonistic behaviour [17], where some of the blends were less stable than the FT diesel and the LCO respectively. Light cycle oil is known for its low oxidation stability [18]. Similar effects were found for blends of low sulphur diesel and LCO, however, the effect was more extreme for the FT/ LCO blends.

Antagonism is normally defined as a phenomenon where two or more agents in combination have an overall negative effect not obtainable by any of the agents independently. Thus, when two fuels that are stable individually become less stable when combined the two fuels are said to have "antagonistic properties". In the work by Bacha and O'Rear [18], very mild antagonistic behaviour was observed in all the blends and slightly intensifying in blends containing 30 to 90 volume % of the highly paraffinic distillate fuel blend in LCO. Jones et al. [19] also reported reduced thermal stability in blends of hydrotreated fuel with a straight-run fuel. However, further work by Bacha et al did not show antagonistic behaviour when FT distillates were blended with low aromatics diesel (LAD). These observations indicate that the molecular composition of a fuel is a very significant factor that contributes to antagonism.

## TEST FUELS

Most previous studies have focused on GTL diesel blends in the 20% range as this typically still complies with the EN590 density specification. This study looks at a complete range of binary blends. The fuel matrix shown in Table 1 was used for all the experimental work, including laboratory stability measurements and engine testing. The reference fuel was a conventional petroleum-derived diesel fuel which conformed to current European EN590 specifications for 10ppm sulphur diesel and contained a lubricity improver additive and potentially a cold flow additive.

The GTL diesel fuel was a highly paraffinic diesel fuel with no aromatics or sulphur and had a high cetane number. The fuel was sourced from ORYX GTL in Qatar. Details of the production process and properties of GTL diesel fuels have been described in a number of previous publications [4,5].

**Table 1. Matrix of test fuel blends**

| Fuel Name | % GTL | % EN590 | Additives                             |
|-----------|-------|---------|---------------------------------------|
| EN590     | 0     | 100     | LIA* and cold flow improver (unknown) |
| G10E90    | 10    | 90      | 225ppm LIA in GTL**                   |
| G20E80    | 20    | 80      | 225ppm LIA in GTL**                   |
| G30E70    | 30    | 70      | 225ppm LIA in GTL**                   |
| G50E50    | 50    | 50      | 225ppm LIA in GTL**                   |
| G80E20    | 80    | 20      | 225ppm LIA in GTL**                   |
| GTL       | 100   | 0       | 225ppm LIA in GTL**                   |

\* Lubricity Improver Additive

\*\* Commercial ester based Lubricity Improver Additive

## EXPERIMENTAL

### Full Specification Testing

To evaluate the effect of blending of GTL diesel with EN590 diesel, full specification analyses for the neat and blended fuels were performed according to ASTM test methods.

### Laboratory Stability Evaluations

The following chemical stability methodologies were used to assess the stability of the neat and blended fuels:

#### ***ASTM D4625 - The long term storage stability (LTSS) measurement procedure***

ASTM D4625 is the most widely accepted test method for assessing the storage stability of middle distillate petroleum fuels. The fuel is stored at 43°C for selected periods, up to 24 weeks. One week of storage under these conditions is generally accepted as equivalent to one month of storage at 17°C (65°F). Typically a sample is filtered to determine the total insolubles on a weekly basis. After filtering the aged sample, the filtrate is analyzed for various properties such as total acid number (ASTM D664) [11], contaminants (IP440) and oxidation stability (ASTM D2274)

#### ***ASTM D6468 - The thermal oxidative stability (TOS) test method***

This experimental procedure measures thermal oxidative stability of a fuel at 150°C. Filtered middle distillate fuel (50ml) is aged for 90 or 180 minutes at 150°C in open glass tubes under air exposure. The fuels in this study were aged for 180 minutes. After aging and cooling, the fuel samples are filtered and the average amount of filterable insolubles is estimated by measuring the light reflectance of the filter pads. An unused filter pad and a commercial black standard are used to define the 100 and 0 % extremes of the reflectance rating range. The reflectance measurement works well with petroleum diesel fuel as the particles formed during the aging

are typically brown or black. Hence, increased amounts of particles result in decreased reflectance values.

#### ***The ASTM D3241- JFTOT method***

Jet Fuel Thermal Oxidation Testing (JFTOT) is commonly used for the evaluation of the stability of aviation turbine fuels (ASTM D3241) [10]. However, it has been used in the past to determine the stability of diesel, including literature references [13,14].

The JFTOT measurements were conducted on an Alcor Mark III JFTOT instrument. All evaluations were carried out under standard ASTM 3241 JFTOT conditions with the exception of the temperature, which was varied in order to determine the specific break point of the fuel. In the current study, the break point temperatures of the test fuels were evaluated and compared in order to evaluate the effect of blending of GTL diesel and EN590 on the fuel stability. The pressure differential (zero for all samples) and the tube ratings were also used as indications of the fuel stability.

### Engine Test Methods

Engine test work focused specifically on injector nozzle fouling in diesel engines typically found in the market. When deposits form and obstruct the flow in the diesel injector nozzle the effect is referred to as injector fouling. There are basically two main methods used in industry to assess the injector fouling tendency of fuels in older and new generation diesel engines.

#### ***(CEC) F-23-01 XUD 9 injector fouling test method***

This test is a well established and trusted industry standard method for quantifying the effect of injector fouling in an engine representative of older indirect injection diesel technology. The objective of the (CEC) F-23-01 [29] test procedure is to provide a means of discriminating between fuels of different injector nozzle fouling propensity using a diesel engine with indirect injection.

The test method is strictly regulated by the CEC and there are a number of third party service providers who perform this test. These providers regularly test and continuously reference their results against other service providers. A suitably approved service provider was selected to carry out the XUD9 testing for this study. While the test does represent old technology, it is still considered to be a reliable indicator of the injector fouling propensity of a given fuel. The method is well established and sensitive to small differences which was particularly desirable in this case when trying to distinguish between different blend ratios.

#### ***Sasol common rail injector fouling test method***

Since the widespread introduction of common rail direct injection diesel engine technology to the market there has been a concerted international effort to develop a test method for assessing injector fouling of common rail diesel engines. The Bosch method [30] was one of the first to be widely used