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Engine Combustion, Performance and Emission characteristics of Gas to Liquid (GTL) Fuels and its blends with Diesel and Bio-diesel

Abstract:

Crude oil price hikes, energy security concerns and environmental drivers have turned the focus on alternative fuels. Gas to liquid (GTL) diesel is regarded as a promising alternative diesel fuel, considering the adeptness to use directly as a diesel fuel or in blends with petroleum-derived diesel or bio-diesel. GTL fuel derived from Fischer-Tropsch synthesis is of distinctly different characteristics than fossil diesel fuel due to its paraffinic nature, virtually zero sulfur, low aromatic contents and very high cetane number. GTL fuel is referred to as a “clean fuel” for its inherent ability to reduce engine exhaust emission even with blends of diesel and Bio-diesel.

This paper illustrates feasibility of GTL fuel in context of comparative fuel properties with conventional diesel and bio-diesels. This review also describes the technical attributes of GTL and its blends with diesel and bio-diesel focusing their impact on engine performance and emission characteristics on the basis of the previous research works. It can introduce an efficacious guideline to devise several blends of alternative fuels, further development of engine performance and to constrain exhaust emission to cope with the relentless efforts to manufacture efficient and environment friendly powertrains.

Keywords: Gas to liquids (GTL), fuel properties, Combustion, Engine performance, Exhaust emission

1. Introduction

Since the evolution of civilization the motive of fuel was only to move the engines. The gradual advancement of civilization associated with growth of transport sector has influenced the excessive usage of fossil fuels initiating a confrontation of dual exigency between abrupt depletion of fossil fuel as well as environmental degradation [1-6]. The single motive of fuel usage has now been diversified to other issues like improved engine performance with exhaust emission constraint in future emission legislations. The projections up to 2020 demonstrate the increased demand of fossil fuels up to three times that will boost the pollution levels in terms of airborne pathogens (i.e. infections, particles and chemicals), greenhouse effect in context of local, territorial and global spectrum.

According to the viewpoint of curbing global warming and strict emission legislation, the introduction of powertrains with low exhaust emission has been desired. Diesel engines have been expected to be a promising candidate because of higher thermal efficiency and CO₂ reduction over gasoline engines [7]. The diesel-fueled engine has recently been besieged with concerns over its contributions to the atmospheric emissions inventory due to less emission reduction specially failing to decrease NO_x and PM emission simultaneously [8, 9].

In these consequences a strong worldwide drive towards alternative liquid fuels for transportation, mainly driven by emissions reduction, energy security concerns, volatility in the fuel price and the search for renewable fuels to compliment the dwindling world fuel supplies. Moreover, goals of improving air quality and diversifying energy resources have intensified research into identifying suitable alternative fuels for internal combustion engines [7, 10-12]. Gas to Liquid fuels synthesized from natural gas by means of Fischer -Tropsch process [13-15], can play a promising role as a clean alternative fuel [16]. GTL fuels have several distinguished beneficial properties as an alternative clean diesel fuel compared to

conventional fossil diesel including virtually zero sulfur, negligible amounts of aromatics and hetero atomic species like sulfur and nitrogen . Higher Cetane number and the absence of PAH content, which are the principal properties of GTL fuels, have potential to reduce Particulate Matter (PM) emissions [9, 17-24]. This distinguishing characteristic has a potential to reduce NO_x emissions [8, 17, 20, 24-28] by increasing the EGR (Exhaust Gas Recirculation) ratio without significant smoke penalty [9, 23, 25, 26, 29] up to a certain level. Significant reduction in desulfurization process frequency associated with tremendous development of after-treatment catalyst results improved fuel efficiency. Higher cetane number leads towards improved combustion that yields lower CO emission [9, 17, 18, 20-22, 25, 26, 30] and HC emission [18-21, 23, 25, 26, 30, 31]. For the above mentioned reasons, GTL fuels have been expected to have a potential to achieve low emissions without any major engine modifications [29, 32-35] and insignificant loss in efficiency [8, 9, 17-20]. GTL fuels can be blended with conventional petroleum-derived diesel fuels [36-40] and Bio-diesels [41-45] and due to the excellent properties, may significantly upgrade the properties of these fuel blends.

Large GTL plants have been commissioned such as 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 and some other are in the design phase with a tremendous need in process instrumentation including process analyzer systems. 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 [10].

Nomenclature

MMBtu -Million Btu (British thermal unit)	Bbl -barrel
ASTM- American Society for testing and Materials	CN- cetane number
LTFT- Low Temperature Fischer Tropsch	TC-turbocharged
HTFT-High temperature Fischer-Tropsch	CR-compression ratio
EGR-Exhaust Gas Recirculation	L-liter
REGR-Reformed Exhaust Gas Recirculation	S- Stroke
ROHR-rate of heat release	DI-Direct injection
ROPR-Rate of pressure rise	NA-Natural Aspirated
ULSD- Ultra low sulfur diesel	RS-rated speed
BSOY-soybean biodiesel	RP-rated power↑ increasing
GHG-Greenhouse gas	↓ decreasing
JBD- Jatropha biodiesel	++ Addition
G+BD20- blend of 80% GTL and 20% Biodiesel (blend of waste cooking oil: soybean oil by ratio of 7:3) by volume	SOI-Start of Injection
G+BD40- blend of 60% GTL and 40% Biodiesel (blend of waste cooking oil: soybean oil by ratio of 7:3) by volume	+ SOI- retarded start of injection
	-SOI – advanced start of injection
	ECU-Engine control unit
	FT- Fischer Tropsch
	GTL- Gas-to-Liquids

2. Gas to Liquids

Gas to liquids technology can be regarded as a process chain to convert natural gas in to synthetic oil, which is upgraded in to synthetic fuels associated with other hydrocarbon-based products. The concept of gas to liquids originated a long time ago. Table 1 illustrates a timeline of GTL development.

Table 1

Comprehensive Timeline of Gas-to-liquids: from Alchemy to Industry [46].

2.1 Gas to liquid fuels-Key drivers

The present decade is more prospective than last 50 years for investment in GTL projects. The influence of some factors that implies several drivers from various perspectives, classified as strategic, market, environmental and economic drivers,

2.1.1 Strategic and Market driver's scenario

An increase in the gas reserve (specially associated gas) is regarded as “stranded gas” due to rapid increase in exploratory endeavors just after OPEC embargo in 1970s. The liberalization of world energy market (specially the natural gas and electricity market), accompanied by fluctuations in gas prices pressurizing the stability of long time contracts and hindering the financing of huge gas pipeline as well as LNG project.

Fig. 1. Worldwide Stranded Gas fields scenario [51]

GTL inherits the potential to transform a noticeable percentage of this stranded gas reserves (depicted in Fig. 1) in to several hundred billion barrels of liquid fuels which is sufficient to meet the worldwide demand for upcoming 25 years. Commercialized GTL plants can represent a new context of the international energy market based on natural gas providing wide range of flexibility in contracts along with least interdependence between buyers and sellers.

2.1.2 Environmental driver scenario

Implication of restrictions on the flaring and venting of natural gas concerned to the petroleum production and the strictest rules and regulations regarding exhaust emission in transport sectors are prime factors that influence the urge for the development of GTL technology. Each year about 15.5 trillion cubic feet (tcf) of stranded gas become flared or vented as a result of disposition of gas produced along with crude oil known as AD (associated-dissolved) gas which gets flared or vented in to atmosphere releasing greenhouse gases like methane and carbon monoxide. Emergence of GTL plants can utilize the AD gas as a feed stock that contains negative cost of opportunity.

Fig. 2. Comparative analysis between GTL diesel and Fossil Diesel in context of emission

[51]

GTL synthetic products derived from natural gas is regarded as clean fuel because of lower emission than diesel (as seen in Fig.2.) that exhibits the flexibility to use as a direct fuel or in blends with lower characteristics fossil fuels to upgrade the fuel property to comply with the updated emission regulations. Several studies [47-50] illustrated, higher greenhouse gas (GHG) emission within the range of 7.4%~27.3% compared to conventional diesel fuel supply chain. A joint research commissioned by Conoco-Shell-Chevron had demonstrated significant diminution of approximately 10% or higher in GHG emission when GTL produced from AD gas which can be referred as flared gas. According to Hao et al [49] when GTL technology efficiency increases to 75% the GHG emission level of GTL fuel supply may comply with conventional diesel fuel supply chain.

2.1.3 Economic Drivers strategies on GTL Economics

The economic eligibility of inauguration of GTL plants basically depends upon lower Gas price, higher fossil fuel price, in-depth analysis of capital cost (CAPEX) and operating cost (OPEX) and revenues of GTL product. As seen from Fig.3 and Fig.4 the diminution of gas price in last five years with fluctuated price hikes in crude oils has turned the situation favorable for GTL fuels. The utilization of large amount of flared gas and the supply of natural gas with lowered price as feedstock increases the economic viability of GTL [51].

Fig. 3. Annual Gas Pricing from 1997 to 2012 [52].

Fig. 4. Crude oil Cost per Barrel in last Decade [53].

In the 1980's capital costs of a GTL plant of 30000 bbl/day capacity was approximate \$70000 bbl/day. Further development decreased the cost with in the ranges \$30000 ~\$20000 bbl/day which was almost double of the then refineries but can reduce GTL fuel cost from \$16 to \$11 /bbl when feed gas price at \$0.5/MMBtu. At around \$11K for each barrel per day GTL plants can commercially compete with new crude refineries of costing \$15K for each barrel per day [54]. The capital cost reduction depends on the efficiency of the GTL plants process technology, plant's capacity, manufacturing of LUB/wax etc. Fig.5 describes the CAPEX breakdown of GTL products.

Fig. 5 . Typical GTL products CAPEX analysis [55].

Fig.6. illustrates the depreciation of Total cost of GTL plants from early 70's to present condition.

Fig. 6. Capital cost reduction of GTL in decades [51].

According to the analysis of Al-Shachi [51] using \$0.5/MMBtu gas pricing an approximate production of \$4.5/bbl can be achieved. Assuming feed stock costs as same as operating costs and half of capital repayment the total overhead cost can be calculated from Table 2.

2.2 Gas to liquid Industry-current trends

As premium-grade hydrocarbon feed-stocks prices increase, synthetic fuels as well as novel petrochemical technologies have gained a momentum in the energy industry. Natural gas has the potential to be a verdant alternative hydrocarbon source to crude oil. Therefore, the method of converting natural gas to marketable liquid hydrocarbons (GTL) gets increasing interest worldwide. OPEC predicts an increase in primary energy demand of 51% in the period of 2010–2035. Currently petroleum derived fuels contribute 87% of commercial energy supply and will provide 82% of the world demand by 2035. As seen from Fig.7, the demand for an additional 23 Mb/d by 2035, middle distillates and gasoline-naphtha shares are respectively 57% and 40%. These demands append a progressive modification in the fabrication of the future fuel demand slate. Middle distillates will definitely show the largest volume increase associated with an elevation in share of the overall slate from the present 36% to 41% within 2035.

Fig.7. Projection of Global Product demand by OPEC

Now-a-days a number of GTL plants have emerged which can be categorized according to the Table 3.

Table 2

Approximate Cost analysis of Gas to Liquid Fuels [51]

Table 3

Features of different categories of GTL plants [53, 54]

Large scale GTL plants are governed by Fischer-Tropsch technologies mainly retained by two GTL giants like Sasol and Shell. Sasol commissioned first ever commercial GTL plant at Mossel Bay in 1992 now governed by PetroSA known as PetroSA GTL plant. Shell inaugurated the Bintulu GTL plant at Malaysia in 1992 operated by the unique shell middle distillate synthesis (SMDS). The Six of world's mega GTL plants are presented Table 4.

Table 4

Six Mega GTL Plants all around the World [56]

The joint venture of Qatar petroleum and Shell ,Pearl GTL plant in Qatar is known as the largest GTL facility commissioned in 2011. Sasol has been planning to establish GTL plants in Canada, Uzbekistan and USA .CompactGTL a UK-based company specialized in modular GTL technology has been planning to build offshore or onshore GTL projects in Latin

America, Russia, Africa as well as Asia Pacific zones with a target to produce 200–5000 barrels/day syncrude [57]. Oxford Catalyst Group introduces “Velocys” technology of 1000 barrels/day modular design (US\$14/barrel operating costs) for offshore facilities that can yield GTL diesel and naphtha at a cost of US\$67.5/barrel [58]. Small GTL plants invented by Alchem with a capacity of 1,000 – 5,000 bbl/day are designed with a viewpoint to utilize the remote gas reserves. Besides offshore GTL plants; subdivided in fixed and portable category of capacity ranging 2,000 – 10,000 bbl/day are also introduced by Statoil and Syntroleum. Fig. 8 shows the production projection of the GTL projects since 2005 up to 2030.

Fig. 8. Production projection of the GTL projects since 2005 up to 2030 [59].

GTL plants can be maneuvered by adjusting the operating conditions of Fischer-Tropsch reactors to manipulate the production process that yields wide range of products like petrochemical naphtha, lubricants, waxes and some special chemical compounds. In modern GTL plants the production ranges are like diesel fuels (C_{14} - C_{20}), kerosene/jet fuel (C_{10} - C_{13}), naphtha (C_5 - C_{10}), lubricants ($>C_{50}$) and a little LPG (C_3 - C_4).

Fig. 9. Analytical comparison of conventional barrel with GTL-FT barrel [60]

Traditional catalytic cracking crude oil refineries production depends on the qualitative property of the crude oil and the features of the fuel-oil transformation units. On the contrary F-T GTL plants are exclusively assembled to produce merely higher-value (compared to crude petroleum) middle and light distillates (as depicted in Fig. 9).

2.3 Summary

Based on the brief analysis regarding energy market, environmental impact and economical features, the following conclusions are available:

- A number of market studies have forecasted that GTL fuel production using the current stranded gas reserve can meet the worldwide energy demand for 25 years.
- Several studies showed that GTL fuel production using vented or flared gas as feedstock has a positive impact to reduce environment pollution.
- Inauguration of several large scale GTL plants by GTL giants like Shell, Sasol and improvements of efficiency in production technology through relentless research will definitely reduce the capital cost and make GTL fuel more viable in future.
- Current industrial survey demonstrated that beside the GTL giants, small companies like Oxford catalyst group, Exxonmobil, CompactGTL, Statoil and Syntroleum have emerged to contribute in R&D of GTL fuel production techniques and fuel quality. Considering all of these endeavors GTL researchers have predicted the current production of GTL fuels will be doubled within 2030.

3. Gas to Liquids-Basic process and Alchemy

GTL process chain consists of three basic fundamental stages [58, 61-63].

1. Formation of Synthesis Gas(Syngas)
2. Catalytic Synthesis(Conversion of Syngas)
3. Post Processing (Cracking)

3.1 Formation of Syngas

Syngas is a mixture of carbon monoxide and hydrogen, is a significant intermediate for different synthesizing chemical elements and environmentally clean transportation fuels, like ammonia, methanol, dimethyl ether (DME), acetic acid and methyl-tertiary -butyl ether (MTBE) and also for production of synthetic liquid fuels by F-T synthesis [64].

Fig. 10. Improved Economics and Reduced Investment Risks for Integrated large-scale Gas/FT-GTL Projects [58].

Syngas can be formed from any carbonaceous elements such as: natural gas, petroleum coke coal or biomass as seen in Fig. 10. Naphtha, residual oil and even from organic wastes [65]. At present Natural Gas is the largest source of syngas and its usage is rapidly increasing because of its better environment performance and lowest cost than other sources [66]. Initially the carbon and hydrogen are differentiated from methane molecule, coal and biomass, later those are reconfigured in several processes available for syngas production depending on the feed stock, such as partial oxidation, steam reforming, auto thermal reforming (ATR), gasification and a combination [58, 67-71] of those which result in different Hydrocarbon-carbon monoxide ratio [72]. The production of syngas can be capital intensive. About 70% of total capital and operating cost is devoted to Syngas production [73].

3.2 Catalytic Synthesis

Most of the current commercial syngas conversion processes are on the basis of Fischer-Tropsch catalytic synthesis. The products depend on the types of reactors, choice of catalysts, and overall on the operating conditions. The gaseous mixture of CO and H₂ (Syngas) is

processed in various Fischer-Tropsch reactors and yields long-chain, waxy hydrocarbon and considerable quantity of water as by-product. The reactor used in catalytic synthesis are specified by different design targeting the technology to produce wide ranges of paraffinic long-chain molecules hydrocarbon (Synthetic crude) [74].

3.2.1 Fischer-Tropsch Synthesis

The Concept of Fischer –Tropsch Technology originated at the beginning of the 20th Century when French Scientists Sabatier & Sanders [75, 76] prescribed a first of its kind process to produce methane from syngas ($\text{CO} + \text{H}_2$) using Cobalt, Iron and Nickel catalyst. In 1923 renowned Scientist professor Franz Fischer, director of “Kaiser-Wilhelm Institute of Coal research” in Mulheim an der Ruhr along with Head of Department, Dr. Hans Tropsch discovered a synthesis to produce longer chain hydrocarbons which can be refined to yield gasoline, kerosene or diesel known as Fischer-Tropsch (F-T) Method [77]. The Fischer-Tropsch technique produces longer-chain molecules of hydrocarbon from polymerization of syngas ($\text{CO} + \text{H}_2$) [62, 63, 78-81]. By products are carbon dioxide emission and production of steam or water. Fig.11 illustrates the overall schematic of Fischer-Tropsch technology. The syncrude composition from Fischer–Tropsch synthesis is basically governed by catalyst types, the operating regime, other supplementary factors like catalyst promoters, reactor designs and Syngas composition (various ratios of $\text{H}_2:\text{CO}$). Although theoretically variations of syncrude composition can be infinite but industrially only two types are practiced:

- I. High Temperature Fischer-Tropsch (HTFT) Syncrude
- II. Low Temperature Fischer-Tropsch (LTFT) Syncrude

Figure 11: Overall process Schematic Fischer-Tropsch [51].

3.2.2 Catalysts of F-T process

A desirable FT catalyst should possess high hydrogenation activity in order to catalyze the hydrogenation of carbon monoxide in to higher hydrocarbons. Several transition metals are used as catalysts in F-T synthesis such as Iron, Cobalt, Ruthenium, Nickel, Rhodium etc. Selection of catalysts in GTL process depends basically on the operating mode (LTFT or HTFT) and the targeted feedstock (biomass, natural gas or coal) [82]. Commercially Fe-based and Co-based catalysts are widely used which are depicted in Table 5 and Table 7.

Table 5

Comparative Features Commercial Catalyst [83-85]

Co –based catalysts are preferred for FT synthesis with natural gas derived syngas, where the syngas has a higher H₂: CO ratio and is relatively lower in sulfur content. Iron catalysts are preferred for lower quality feedstock such as coal [86]. Based on greater intrinsic activity and adaptability with operating conditions Ruthenium based catalysts are regarded as the most dynamic catalyst for FT synthesis [87]. Due to its higher expense and lower availability than other catalysts commercial large GTL plants cannot afford to use it as prime catalyst. Ruthenium based compounds are used as promoters with Fe/Co-based catalysts instead of a unique catalyst. Ni-based catalysts demonstrate greater level of methane selectivity due to higher hydrogenation activity. Recent researches revealed new commercially used catalysts

like Co-Al₂O₃ and Co-SiO₂. In addition to the active metal, the catalysts typically contain a number of promoters, including potassium and copper, as well as high surface area binders/supports such as silica and/or alumina. The commercial catalysts have the problem of vulnerability to deactivation. GTL giants like Sasol and Shell demonstrated similar problems in case of lifecycle of the Fe-based and Co-based catalysts respectively. Recent researches have revealed that lifecycle of FT catalysts are affected by physical characteristics (accumulation of wax between the catalyst pellets, catalyst corrosion, partial pressure drop through the reactors etc.) and occurrence of fouling [87]. Further research should be conducted in this field to increase the activation level and efficiency of the current commercial catalysts.

3.2.3 Features of Fischer-Tropsch classification and Reactors

Fischer-Tropsch process can be sub divided into two major categories [24] implicated as: Low temperature Fischer-Tropsch (LTFT) process and High temperature Fischer-Tropsch (HTFT) process which are used in several F-T reactors. These processes and different F-T reactors are summarized respectively in Table 6, Table 7 and Table 8.

Table 6

Comparative Features of LTFT and HTFT processes [28, 76, 82, 88-91]

For production of distillate blend stock, usually LTFT is preferred to HTFT. To cover the increasing demand for clean transportation fuels, it is of interest with LTFT systems to maximize transportation fuels production, which is possible by making on-specification gasoline rather than marketable naphtha as a secondary product [92]. Fig.12 shows the major reactors used in F-T technology in current industries. Modern micro-structured reactors are

also gaining popularity with the three featured conventional reactors like fixed bed reactor, slurry phase reactor and fluidized bed reactor.

Table 7

Current prospects of commercial Fischer-Tropsch synthesis [86, 87]

Table 8

Comparative feature of industrial Fischer-Tropsch reactors [93-101].

Fig. 12. Modern micro-structured reactor (left) with three Main reactor families of FT technologies [102].

3.3 Post Processing (Cracking)

The Synthetic crude produced either from HTFT or LTFT process is processed by means of traditional refinery cracking operations in presence of zeolite catalysts and hydrogen to yield catalytically cracked shorter hydrocarbons. Finally distillation leads to production of variety of fuel products ranging from kerosene to diesel, naphtha and lube oils [103]. In most modern plants, Fischer-Tropsch GTL units are now designed and operated to obtain desired product distribution [58, 104].

3.4 Summary

Based on the brief analysis of GTL production process, the following concluding remarks can be stated here:

- Cost and efficiency of GTL process depends mainly on syngas production. Recent research updates have contributed variations in syngas production technologies. Thus, in commercial aspect GTL process is now less expensive and more efficient than ever before.
- Based on operating condition, catalyst selection and product range Fischer-Tropsch synthesis can be classified in two categories: Low temperature Fischer Tropsch synthesis and High temperature Fischer Tropsch synthesis. Prime GTL products like GTL diesel and wax are produced by LTFT synthesis. HTFT synthesis is used to produce aromatics and olefins.
- Several FT reactors of distinguished features are used commercially in GTL process chain. Besides, the three main reactors (fixed bed, slurry phase and fluidized bed) that are engaged in large-scale GTL plant, micro-structured reactors have also been applied for offshore or mobile operation.
- In GTL process, catalysts are regarded as the heart of synthesis. Selectivity of catalysts depends on the operating mode and the feedstock group of Fischer-Tropsch synthesis. GTL giants like Shell and Sasol prefer Co-based and Fe-based catalysts. Further research progress is required to boost the activity level and efficiency of the catalysts.

4. Gas to Liquid products

Gas to Liquid fuel is regarded as a colorless, odorless, non-toxic, biodegradable product as (depicted in Fig.13) that significantly reduces vehicle emissions while, providing improved combustion. GTL also inherits the capability of producing products that can be sold or blended into refinery stock as superior products with fewer pollutants for which there is growing

demand. GTL products basically contain Synthetic LPG, Synthetic Naphtha, Synthetic Kerosene and Synthetic Diesel. The percentages of these products (as seen in Fig. 14) depend on the variation of technology applied, characteristics of catalysts, optimum conditions of the reactions etc.

Syncrude obtained from Fischer-Tropsch synthesis can be refined in to required distillate fuel fractions such as kerosene, naphtha and heating oil by means of conventional refining procedures. Diesel or Jet fuel products are an outcome of refined or blended kerosene. Naphtha can be refined in to gasoline or used as feedstock of thermal cracking for olefins production. Properties of GTL products are demonstrated in Table 9.

Fig. 13. Percentages of GTL products [51, 55].

Fig. 14. GTL products

Table 9

Properties of GTL products [51].

Besides production of significant light and mid petroleum derivatives, FT synthesis can produce other precious commercial chemicals like by Paraffin Wax, Normal Paraffin, Mixed paraffin and Synthetic lubricants by manipulating the operating conditions to modify chain growth of hydrocarbons.

4.1 Summary

Based on the discussion above, the following conclusions are available:

- Prime GTL product range includes synthetic diesel, synthetic LPG, synthetic naphtha and synthetic kerosene.
- Altering reactor operating conditions and catalysts in GTL process, some valuable commercial chemical components like high quality paraffins and synthetic lubricants are produced.
- Emergence of large scale GTL plants in recent years indicates the increasing demand of GTL products in market.

5. Fuel properties analysis in context of neat GTL and its blends

Feasibility of any alternative fuel with existing engine requires the in depth comparative analysis of fuel properties of concerned fuel. Table 10 contains the important physical and chemical properties of Gas –to-liquid fuels.

5.1 Kinematic viscosity

Viscosity effects on the fuel injection as well as spray atomization. Higher viscosity increases fuel pump power requirement, yields poor spray and atomization with increment in fuel consumption. ASTM D445 has widely been used to measure kinematic viscosity for engine fuels. In most of the previous works GTL showed lower kinematic viscosity values than Diesel which is advantageous on fuel spraying atomization [20, 105-107].

In blends with ULSD and EN590 diesel increasing trend of viscosity than neat GTL has been observed [10, 108] but Wu et al [25] reported unchanged viscosity till 50% volume ratio and abrupt increment in further GTL addition in blends. GTL- bio diesel blends showed higher viscosity compared to neat GTL due to higher viscosity of bio-diesel [41, 45].

5.2 Cetane number (CN)

Low CN causes ignition delay that leads towards startup problems, poor fuel economy, unstable engine operation, noise and exhaust smoke. As a result an optimum higher CN is desired for all CI engine fuels. GTL having high n-paraffin content exhibits much higher CN (>74) than other CI engine fuels which offers the benefits of better combustion performance. Less engine emissions were found in previous studies significantly at light and moderate loads. With an increase of 10 CN older technology engines exhibits 5% less NO_x where 2% less NO_x has been observed engines with newer technologies using GTL [109, 110].

With addition of GTL in blends of diesel (ULSD, EN 590 diesel and conventional) and biodiesel [41, 45] cetane number of blends shows increasing trends compared to diesel and biodiesel due to significantly higher CN of GTL fuels.

5.3 Density

A fuel of higher density indicates higher energy concentration that minimizes the chances of fuel leakage. Much higher density yields higher viscosity having significant influence in spray atomization efficiency resulting poor combustion with more emissions [111, 112]. Recent studies following ASTM D4052 identified lower density of GTL approximately 7.2% compared to Diesel due to higher hydrogen-carbon ratio of GTL [10, 25, 113].

Lower density had been demonstrated by GTL in blends with diesel [10, 25, 108, 114] and biodiesel [41, 45, 115] due to lower density of GTL.

5.4 Calorific Value/Heating value

Higher calorific value of any fuel is desired because it favors the heat release during combustion and improves engine performance. GTL demonstrates slightly higher HCV and LCV than Diesel. The heating value of GTL is 2.8% higher by weight, and the density is 5.7% lower than diesel, so the heating value is lower on a volumetric basis which leads to the less power for a fixed volume injection [49, 107, 116, 117].

As GTL inherits higher heating value than most of the Bio-diesel, conventional diesel and ULSD, blends with these fuels with GTL have demonstrated improvement in the heating value [10, 25, 41, 108].

5.5 Flash Point

Higher flash point ensures safety of fuel for handling, storage and prevention from unexpected ignition during combustion. Flash point contains inverse relation with the volatility of fuel. According to ASTM D93 several studies reported that GTL has around 20 °C higher flash point than Diesel [25, 118, 119].

5.6 Cloud Point (CP), Pour Point (PP) and Cold Filter Plugging Point (CFPP)

The characteristics of any fuel in low temperature zones are significant to investigate engine performance in cold atmosphere. Partial or complete solidification of fuel may incur blockage of the fuel system such as fuel lines, filters etc. It results interruption in fuel supply associated with inadequate lubrication resulting problems in driving or even damage of engine. CP, PP and CFPP are used to explain the cold flow characteristics of any fuel.

CP and PP are measured applying ASTM D2500, EN ISO 23015 and D97 procedures. GTL has slightly higher CP and PP than conventional diesel fuel. Blending with biodiesel and diesel showed improvement of the CP and PP [21, 41, 45].

CFPP defines the temperature at which fuel flow freely through a fuel filter, approximately halfway between the CP and the PP. Usually at low temperature fuel may become denser which degrades the flow property resulting poor performance of fuel system (fuel line, pumps, and injectors). CFPP is measured using ASTM D6371. GTL shows marginally higher CFPP than Diesel fuel and biodiesel. So blends with diesel and biodiesel demonstrates improved CFPP [21, 41, 45, 108].

5.7 Acid value

It indicates the proportion of free fatty acids (FFAs) present in a fuel. Higher portion of free fatty acid contents in a fuel exhibits higher acid value making the fuel severe corrosive. Higher acid value leads to corrosion in fuel supply system and degrades the longevity and performance of the engine. Acid value for GTL and Diesel is measured by ASTM D 974 and ASTM D3242 .GTL exhibits significantly lower values than Diesel and Bio-diesels making it more engine friendly [10, 32].Increasing percentage of GTL in consecutive blends of ULSD, EN 590 and Conventional Diesel linear decrement of acid number had been observed [10, 25, 108].

5.8 Iodine Number (IN)

Iodine number is used to determine the definitive amount of unsaturation in fatty acids in the form of double bonds, which reacts with iodine compounds. The higher the iodine number, the

more C=C bonds are present in the fuel. According to EN 14111 standards GTL has IN of 1.22 [120] which is comparatively lower than the biodiesels [112].

5.9 Lubricity

Lubricity reduces the damage caused by friction. Lubricity is a significant consideration for using low and ultra-low sulphur fuels. Lubricity can be adjusted with additives which are compatible with the fuel and with any additives already exists in the fuel. High frequency reciprocating rig (HFRR) ASTM D6079 and SLBOCLE ASTM D6078 are used to describe lubricity values. GTL and Diesel show same or slightly lower level of lubricity [10]. Addition of Biodiesel [45] and ULSD [108] in GTL blends significantly improves the lubricity of the blends.

5.10 Carbon residue

Higher carbon residue indicates poor combustion phenomenon. ASTM D524 and ASTM D4530 procedures are applied to determine the carbon residue mass percentage of GTL and Diesel. GTL shows lower carbon residue than Diesel [10, 107].

5.11 Aromatics

Aromatics improve seal-swell characteristics, but also enhance engine soot emissions. Particulate matter (PM) emissions increased with increasing aromatic molecular weight and concentration, which was attributed to an increase in soot precursors. ASTM D5186 measures aromatics content in fuel. GTL contained negligible aromatic compounds compared to diesel [7, 10, 105, 121]. Total aromatics as well as poly aromatics of the blended fuels decrease gradually when the GTL fraction increases in the blends [10, 25, 108].

5.12 Copper Strip Corrosion

It determines the corrosive nature of fuel when used with copper, brass or bronze parts.

One copper strip is heated up to 50°C in a fuel bath for 3 h followed by comparison with a standard strips to measure the degree of corrosion. Usually copper strip corrosion is measured by ASTM D130 standard. GTL and Diesel demonstrate the similar value under this standard [10].

5.13 Distillation properties

This property demonstrates the temperature range over which a fuel sample volatilize determined by ASTM D 975. As it is quite difficult to have precise measurements of the highest temperature obtained during distillation (known as end point) with good repeatability, 90%(T₉₀) or 95%(T₉₅) distillation point of fuel is commonly used. Engine manufacturer association (EMA) prefers T₉₅ because of its acceptable reproducibility and being nearest to fuel's end point than T₉₀. The T₉₀ of GTL is about 6.3% lower than that of diesel. The lowering distillation characteristic of GTL also improves atomization and dispersion of fuel spray, and also ensures ease of evaporation of fuel that accelerates the fuel mixing with air to constitute a more combustible air-fuel mixture. Lowering distillation characteristics reduces smoke and PM emission in spite of the high cetane number of GTL fuels [9, 25] .During operation at low loads and frequent idle periods lower end point is desirable to reduce smoke and combustion deposits.

GTL-Diesel (ULSD,EN590 and conventional) blends demonstrated lower Initial and intermediate boiling points but slightly higher end boiling point compared to neat GTL [10, 25, 108] whereas GTL-biodiesel blends showed throughout higher distillation temperature than neat GTL [41, 115].

5.14 Ash content

It indicates the extent of inorganic contaminants like catalyst residues, abrasive solids and the concentration of soluble metal elements present in a sample fuel. Higher concentrations of these materials leads to injector tip plugging, combustion deposits and injection system wear. Soluble metallic materials cause deposits while abrasive solids will cause fuel injection equipment wear and filter plugging. ASTM D482 is used to determine the mass percentage of ash in fuel. As per data from table 9 GTL shows significantly less ash than Diesel.

5.15 Sulfur Content

Presence of sulfur in fuel has hazardous effect on engine performance and environment. During combustion when sulfur reacts with water vapor to produce sulfuric acid and other corrosive compounds which deteriorate the longevity of valve guides and cylinder liners leading to premature engine failure. Moreover these corrosive compounds get mixed with atmospheric air cause acid rain which pollutes vast areas of arable land. ASTM D5453 and ASTM D2622 standards are used to determine sulfur contents as parts per million. Virtually GTL has zero sulfur but maximum 0.005 ppm has been observed in real scenarios which can decrease the emission of PM. On the contrary 0.0034 ppm for ULSD and maximum 11ppm sulfur has been found for ordinary diesel [7, 10, 107].

Higher ratio of GTL in blends exhibits lower sulfur contents. ULSD and EN 590 diesel inherently has lower sulfur content so 20% and 50% blends of GTL shows around 15% and 28% reduction in sulfur than neat low sulfur diesel [10, 25, 108].

5.16 Summary

Based on the analysis of the fuel properties stated above, the significant results are stated below:

- All of the previous research works have demonstrated low kinematic viscosity and density of GTL fuel. An established trend has been reported by all of the authors that presence of GTL in blends of diesel or biodiesels, lowers the density and viscosity of the blends compared to the respective diesel or Bio-diesels.
- Most of the literatures illustrated higher cetane number and higher calorific value of GTL than Diesel and bio-diesels. This result reflects also in the blends as GTL blended fuels showed linear relationship of cetane number and calorific value with the volume fraction of GTL contained in the blends.
- GTL has lower distillation characteristics than diesel and biodiesels. GTL-diesel blends showed lower initial and intermediate boiling points but marginal higher end boiling point than neat GTL. Higher distillation temperature was observed in all distillation range in case of GTL-biodiesel blends.
- All of the researchers reported lower carbon residue, ash and sulfur contents of GTL fuel. Blends of GTL-diesel showed significant improvement lowering these three properties compared to diesel.
- Overall, GTL diesel exhibits a number of beneficial properties compared to conventional fossil diesel including high cetane number, low density and viscosity virtually zero sulfur, negligible quantities of aromatics and hetero aromatic species like sulfur and nitrogen. Influenced by these properties, neat GTL demonstrates excellent ignition and combustion characteristics with significant emission benefits compared to neat petroleum-derived diesel fuel alone. Due to these excellent properties, blending of

GTL with conventional fuels like diesel and renewable fuels like Bio-diesel may significantly upgrade the properties of blends.

Table 10

Technical Attributes of GTL Properties [7, 10, 21, 23, 25, 27, 32, 106-108, 113, 115, 117, 118, 122-132].

6. Combustion phenomena of GTL

Combustion phenomena analysis of a fuel is of significant importance to predict engine performance and emission characteristics of powertrains driven by that fuel. It can be subcategorized in two phases: premixed and diffusion phase. Comparative analysis of the Combustion characteristics of GTL fuel with diesel have been discussed in section in context of fuel injection delay, injection duration, ignition delay, in-cylinder pressure and rate of pressure rise and rate of heat release.

6.1 Fuel injection delay

GTL has longer fuel injection delay than conventional diesel which demonstrates further increase with higher load at the same speed. The reason behind this is the elongated propagation of pressure wave of GTL due to higher compressibility results from the Lower density and bulk modulus of GTL compared to diesel. In case of pump-line-nozzle-typecast injection facility GTL fuel exhibits retarded injection timing compared to diesel which depicts later heat release rate (HRR) and maximum pressure peaks. Lower bulk modulus and lower density of GTL fuels enhance the compressibility that results abated advancement pressure wave in fuel injection system leading towards retarded injection timing [8, 21, 25].

6.2 Injection duration

Theoretically about 6% more GTL fuel (by volume) is required to be injected per cycle than diesel to obtain same output from engine which indicates around 6% prolonged injection. This can be explained regarding the lower volumetric energy content of GTL. In real scenario only 0.91% larger injection was found [26]. The explanation provided that the betterment of thermal efficiency obtained by GTL improvised the requirement of injected fuel per cycle for same outcome.

6.3 Ignition delay

GTL fuels exhibits shortened ignition delay owing to higher cetane number. Approximately 18.7% reduced ignition delay can be observed compared to diesel [26]. The basic alchemy of short ignition delay can be explained by higher paraffinic contents in GTL fuel that produce much more reactive radicals compared to diesel having cyclic compounds. GTL-biodiesel blends demonstrated longer ignition delay compared to neat GTL because of decreased cetane number in blends [45].

6.4 In cylinder pressure

GTL fuel demonstrates lower peak point of combustion pressure and also lower maximum rate of pressure rise (ROPR) compared with diesel. Due to higher cetane number, GTL possess shortened ignition lag associated with reduced premixed combustion stage that cause the lower pressure rise. The reduced ROPR facilitates improved combustion that ensures diminution in combustion noise and mechanical load [25, 114, 125]. Addition of Biodiesel in GTL blends caused higher peak cylinder pressure due to lowering the cetane number [45].

6.5 Rate of Heat release

Although GTL fuel demonstrates reduction in the rate of heat release (ROHR) and duration during premixed combustion phase, increment of ROHR and duration is observed in diffusion combustion scenario. In premixed combustion phase of GTL fuel less amount of fuel is injected due to short ignition delay that results less evaporation fuel prior to ignition. Thus, the decreased ROHR and duration is observed. In diffusion combustion phase of GTL the unused energy of premixed phase is utilized. The lower distillation temperature of GTL assists accelerated vaporization and mixing with air inside the cylinder which lead towards rapid diffusion combustion. GTL-biodiesel blends demonstrated marginally retarded but higher first peak of heat release rate in case of pilot injection [45, 115].

6.6 Effect of EGR and REGR

With the increase of EGR retarded combustion was observed with GTL. Introducing REGR (reformed EGR) in lieu of EGR repositioned the premixed combustion phase to a later stage and also increased the duration of energy release associated with this combustion phase [128]. At lower load increased REGR ratio shifted the peak pressure rise to expansion stroke, which increased the combustion duration compared to medium load. At medium load, 30% REGR demonstrated more efficient combustion with an abrupt raise of the maximum in-cylinder pressure and maximum rate of heat release [128].

6.7 Summary

It can be concluded that higher CN and paraffinic hydrocarbon characteristics GTL fuel demonstrates advanced commencement of combustion stage compared to conventional diesel fuel during pilot injection. Approaching at the second stage of combustion prevailed by “diffusion combustion” advanced heat release has also been observed. This trend has been justified by numerous previous studies which involved comparative analysis between GTL fuel

and petroleum diesel in context of commencement of combustion [9, 19-22, 27, 41, 107, 133], enhanced rate of pilot injection or minimizing main combustion at lower load scenarios associated with higher premixed phase.

7. Engine performance features of GTL and GTL Blended fuels

Featured parameters for in depth analysis regarding engine performance factors like Torque or power, Brake specific fuel consumption (BSFC) and Brake thermal Efficiency (BTE) are discussed in this section and findings of several studies are also demonstrated in Table 11.

7.1 Torque /power

GTL shows marginally lower torque and power compared to conventional diesel fuel. Several studies illustrated 2~5 percent decrease in maximum power output and 4~7 percent decrease in peak torque ranges in GTL than Diesel [44, 134]. The reasons may be because of fuel properties (lower density, LHV) of GTL and also unmodified ECU of the test engine. Application of GTL in a calibrated engine can overcome these discrepancies. GTL exhibits 2.8% higher LHV (mass) but 3% lower LHV (volume) than that of diesel. Moreover, in the unmodified engine volume of injected fuel/cycle is constant for same injection duration with common rail system. As a result, when fuel was switched from diesel to GTL, the LHV of injected fuel was reduced so as the power and torque. A calibrated engine can upgrade the maximum power and torque output [44, 134]. GTL Blends with diesel and bio-diesel did not demonstrate much variation than neat GTL.

7.2 Brake Thermal Efficiency (BTE)

Numerous studies showed slight decrease of efficiency of GTL fuel (38.7%) than Diesel (39.6%) [44]. Higher cetane number of GTL yields shorter ignition delay which induces lower decreasing rate of BTE for GTL fuel compared to diesel with retarding injection timing. The shortened premixed combustion stage of GTL fuel permits advanced injection timing which provides better engine efficiency constraining NO_x and combustion noise at low load levels [27]. GTL showed higher brake thermal efficiency than ULSD in medium load conditions than low-load operations due to less fuel consumption to overcome the mechanical losses at increasing load [128]. The influence of REGR on the BTE seemed to vary with the load. Increased REGR at lower load showed decreased BTE because of incomplete combustion but at higher load increased BTE was observed due to faster flame velocity of hydrogen associated with an increase in the expansion work [128]. The default combustion system in unmodified test engines may not be favorable for special properties of GTL like higher CN, low viscosity and density may lead to slight degradation of efficiency [44]. GTL blends with diesel and bio-diesel did not demonstrate much variation than neat GTL [41].

7.3 Brake Specific Fuel Consumption (BSFC)

As GTL fuel possesses higher LHV in gravimetric basis lower BSFC of GTL than conventional diesel and biodiesel has been illustrated in several studies [8, 25, 121]. Though GTL exhibited lower BSFC in mass than diesel fuel, higher volumetric BSFC (approximately 2.7%~3.8%) has been observed than diesel of for its lower volumetric heating value [44].

Lower BSFC of GTL blends had been found compared to conventional diesel and ULSD. Improvement of fuel economy was observed significantly in lower speed than in mid-higher speed [8, 21, 25, 108]. At lower load and speed conditions, BSFC of GTL-biodiesel (soybean oil and waste cooking oil volume ratio of 3:7) blends was appreciable but at higher load and

speed, BSFC increased due to the lowering LHV of the blends. LHV of G + BD20 and G + BD40 was 3.7% and 7.3% lower than that for GTL fuel respectively. As a result extra fuel was required at a given speed and load for compensation of different LHV values. Since Fuel conversion efficiency (FCE) has inverse relation with the BSFC and LHV, increased BSFC of bio-diesel blends with GTL had been compromised by decreasing LHV. As a result addition of Bio-diesel in GTL blends yield higher FCE as well as higher oxygen content that lead towards a complete combustion [41, 45].

7.4 Summary

Based on the engine performance tests in the previous studies, the following conclusions can be drawn:

- All of the authors have reported slight decrease or same engine torque, power output and brake thermal efficiency than diesel. In case of BSFC, GTL showed lower value compared to diesel and bio-diesel.
- The authors identified the reason for marginal decrease of torque and power of GTL fuel was the unmodified ECU of the test engine. They proclaimed that a GTL calibrated engine would definitely overcome the slight lack of power and torque compared to the diesel engine.
- Majority of the authors suggested the injection timing retarding and application of REGR to improve the BTE of GTL.
- GTL demonstrated lower BSFC than diesel and bio-diesel because of its higher LHV. In case of GTL blends with diesel and bio-diesel, the increment of BSFC was depended

on the volume fraction of diesel or bio-diesel on the blends. Higher volumetric content of diesel or biodiesel in blends resulted higher bsfc.

Table 11

Engine performance Feature of GTL and GTL Blended fuels

8. Engine Emission features of GTL and GTL Blended fuels

GTL fuels possess advantages as an alternative cleaner diesel fuel in context of lower emissions of CO, HC, NO_x, PM and smoke owing to its unique properties. GTL fuels have been expected to have a potential to achieve low emissions without any major engine modifications [29, 32, 34, 35, 135, 136]. Exhaust emission results of GTL and its blends are illustrated in Table 12.

8.1 CO emission

Formation of rich combustion mixture on account of lower air-fuel proportion can be regarded as the prime reason that induces CO emission. Flame quenching occurrence inside the over-lean region as well as the wall impingement quenching region also favors CO formation. Higher CO content in emission is an indicator of incomplete combustion. Presence of aromatic hydrocarbons which are more stable, are responsible for more CO formation due to the excess Total HC [137, 138].

GTL fuels exhibited lower CO emission compared to diesel and biodiesels irrespective of all loading conditions and injection timings [20, 44, 119, 129]. Some studies showed increased CO emission with retarding the injection timing; however, the increasing rate with GTL was lower than with diesel fuel [27, 29]. The mysteries of CO emission reduction of GTL lie within the fuel properties and combustion phenomena of GTL. Higher H/C ratio and very low aromatic content provides improved combustion that favors CO reduction. Higher CN of GTL induces shortening of ignition delay that prevents less over-lean zones. The lower distillation temperature of GTL induces rapid vaporization, which reduces the probability of flame quenching and ensures lower CO emission [26, 45].

GTL blends with Diesel showed higher reduction of CO with the increased GTL ratio in blend i.e. improving the blend properties dominated by GTL fuel [21, 25, 108, 114]. Significant decrease of CO emission approximately in the range of (16–52%) was observed for GTL-Biodiesel blends compared to diesel [42, 43, 45, 120]. With presence of bio-diesel in GTL blends the additional oxygen content and higher cetane number of GTL combination yields better combustion that actuates reduction in CO emission [139-141]. Lower ratio of Biodiesel (within the range of 20%~30%) in GTL-biodiesel blends showed less CO reduction than higher ratio of biodiesel in blends [45].

8.2 HC emission

In CI engine main reasons behind HC formation can be illustrated as fuel-trapping in the fissure volumes of the combustion chamber, low-temperature quenching associated with oxidation reactions, presence of local over-rich or over-lean air-fuel mixture, formation of liquid wall films due to excessive spray impingement and improper evaporation of the fuel [26, 137].

GTL fuel exhibits a lower HC emission in range of 31–60% compared to conventional diesel [44, 129]. With advanced injection timing lower trend of HC is still continued but in retarded injection timing slight increased HC was reported with in a range of 100~130 ppm which was still lower than of Diesel [27, 29]. Alike CO emission reduction HC emission reduction can be explained regarding the fuel properties and combustion phenomena of GTL. Higher CN of GTL fuel shortens the ignition delay which prevents formation of over-lean regions. Lower distillation temperature characteristic of GTL ensures proper pace of evaporation and mixing with air to constitute more effective combustible charge which results less unburned HC in exhaust emission [26, 44, 129].

GTL-diesel blends demonstrated significant reduction in CO emission with the increased ratio of GTL fuels in blends [8, 21, 25, 108]. In case of GTL-Biodiesel blends reduced HC emissions was observed compared to diesel and neat GTL fuel significantly at lower load conditions [20, 41, 43, 45, 120]. HC reduction in blends in spite of the diminution of CN was possible because of increased oxygen content with addition of biodiesel that leads towards proper combustion. Several Studies suggested to maintain lower ratio (within range of 20~30%) of Biodiesel in blends with GTL fuel to ensure the lower HC emission [41, 45].

8.3 NO_x emission

NO_x formation in CI engine can be described in context of zeldovich mechanism [142]. During combustion higher temperature disengage molecular bonds of nitrogen which takes part in series of reactions with oxygen resulting thermal NO_x. NO_x formation in the flame front and in the post flame gases, basically depends on oxygen contents, in-cylinder temperature and residence time [137].

GTL fuel exhibits lower NO_x emission than fossil diesel and biodiesels in all loading conditions and injection timing [20, 27, 29, 44, 119, 129]. NO_x emission of GTL fuel was about 22% and 33% less than diesel respectively with advanced and retarded SOI [20]. Higher CN induced shorter ignition delay, followed by lesser premixed charge results in the lower combustion temperature and pressure. It leads towards less NO_x formation in the cylinder on the basis of the temperature dependent thermal NO_x formation mechanism [44]. Significant lower Aromatic contents of GTL fuel favors local adiabatic flame temperature which assists in NO_x reduction [26, 129, 143].

GTL-diesel blends showed improved NO_x emission than Diesel but higher than neat GTL [8, 21, 25, 108, 114, 133]. GTL-biodiesel blends demonstrated higher NO_x compared to neat GTL

but lower than individual biodiesel like JBD,BSOY [41, 45, 115]. Higher bulk modulus of biodiesel advanced the injection timing in blends that yields earlier combustion followed by longer residence time and resulted in higher NO_x emissions [144-146]. Higher temperature of premixed combustion phase in GTL-biodiesel blends due to higher rate of heat release (ROHR). In addition, higher percentages of unsaturated fatty acids containing double bonds could be an additional reason for higher NO_x emission up to 12% in GTL-JBD blended fuels compared to diesel [45, 115, 147]. Exceptions against this trend has been observed where biodiesel showed improved NO_x emission and GTL –biodiesel blends showed higher NO_x compared to biodiesel [41].

8.4 Smoke /Soot emission

GTL demonstrated slightly higher soot emission at lower load but decreased at middle and higher load than that of Diesel. In variation of injection timing GTL showed lower soot emissions than diesel [27, 29]. At lower load decreasing of ignition lag with longer combustion duration of GTL than Diesel might increase the soot emission. GTL fuels featuring properties like zero sulfur and low aromatic content associated with higher H/C ratio may suppress the formation of particulate precursors. Rapid progress of diffusion combustion may also favor lowering smoke in the range between 22~73% than conventional diesel [26]. Several studies illustrated GTL-Biodiesel blends showed reduction of smoke opacity (indicator of soot emissions) as well as smoke emission compared to neat diesel and GTL fuel [41, 115]. Presence of bonded oxygen and absence of aromatics in biodiesel ensured local fuel rich mixture to fuel lean mixture associated with enhanced combustion efficiency that results in lower smoke emission in blends [148, 149].

8.5 Particulate Matter emission

PM is regarded as a complicated mixture of several fine particles and liquid droplets associated with soot, ash, soluble organic fraction originated from hydrocarbons and water. It varies in size, shape, number, surface area, solubility and sources [16, 150]. PM can be sourced from rich combustion zones having equivalence ratio greater than one. In the core region of fuel spray highest PM concentration is observed [137].

GTL fuel showed lower PM emission than Diesel and biodiesels [9, 24, 26, 44, 118, 134] even at all variations of injection timing [20, 119]. GTL-diesel blends showed significant reduction in PM compared to neat diesel [25, 108, 114]. GTL-biodiesel blends generally showed reduced PM emission compared to neat diesel [41-43, 45, 115]. GTL-Biodiesel blends containing 20%~50% of biodiesel demonstrated PM reduction ranges approximately 15%~36% compared to neat diesel and GTL fuel [45, 115]. The lower sulfur percentage associated with significantly lower aromatic content of GTL favors lowering PM emission [115, 131]. Higher oxygen content of Bio-diesel in GTL blends improved the combustion resulting low soluble organic fraction leading towards low PM emission [131]. Unlike GTL soot fractions of PM in biodiesel are usually compensated by a larger volatile organic fraction [17]. Accumulation of large amount of unburned compound had been observed in case of GTL-biodiesel blends than neat GTL and diesel in condensed phase surrounding the soot particles flowing through the exhaust pipe in the temperature range of 275°C -325°C [41]. The diminution in mean particle size was slightly higher in biodiesel than in GTL (and proportionally in the blend ratios), might be as a consequence of the richer oxygen contents, which, apart from minimizing the actuation of soot precursors [151], contains in the formed soot provoking soot oxidation [152]. Overall, it can be concluded that the smaller mean size of the emitted particles of GTL and its blends is basically the result of significant diminution of the largest particles, which compensates by the

small (negligible in the case of GTL-biodiesel blend) increment in the amount of the smallest particles emitted [16, 20, 153, 154].

8.6 Summary

In the consequences of the exhaust emission analysis of GTL and its blends, the following conclusions are available:

- Majority of the authors reported good emission features of GTL and its blends with diesel and bio-diesel for all parameters like Carbon monoxide, Hydrocarbon, NO_x, smoke and particulate matter emission.
- GTL fuels possess some distinctive characteristics like high H/C ratio, low aromatic content, high CN and distillation temperatures which provide good combustion that leads in to higher CO and HC emission reduction than diesel and bio-diesel. GTL-diesel blends showed higher reductions with increasing GTL content in blends. GTL-biodiesel blends also showed significant reduction but most of the authors suggested to keep biodiesel ratio in blends within 20%~30% to maintain the CO and HC emission reduction.
- Most of the researches revealed lower NO_x emission of GTL fuel than diesel and biodiesels. Higher CN and lower aromatic contents of GTL assist in maintaining the combustion temperature which provides significant NO_x reduction. GTL-diesel blends demonstrated higher NO_x decrement with the higher fraction of GTL in blends. GTL-biodiesel blends showed lower NO_x reduction compared to neat GTL, diesel and GTL-diesel blends.
- In the analysis of Smoke and PM emission, most of the authors reported lower emission for GTL than diesel and biodiesels. Blends of GTL-diesel and GTL- biodiesel showed

lower PM emission than diesel and biodiesel. Significant lower sulfur and lower aromatic contents of GTL fuel assist in PM reduction of GTL fuel. Blends of GTL with diesel or biodiesel also demonstrated lower smoke emission in most of the studies.

Table 12

Engine Emission features of GTL and GTL Blended fuels

9. Conclusion

This review encompassed in depth analysis of fuel properties, combustion, engine performance and exhaust emission in context of neat GTL fuel and its blend with conventional diesels and renewable bio-diesels.

GTL fuel both neat and in blends demonstrate emissions benefits in comparison to refinery diesel fuels over a wide spectrum of fuel specifications. The properties of the blended fuels changed in proportion to their respective blending ratios. Density, sulfur, and total aromatics of blends showed diminution while the cetane number and lower heating value increased with higher GTL fraction in blends. Cold flow characteristics (Higher pour point, cloud point) and kinematic viscosity of the GTL fuels improved with addition of diesel and bio-diesel. Lower efficacy regarding lubricity seemed improved with lubricity improver additives and also by addition of ULSD and biodiesel in GTL blends.

The use of GTL diesel fuel in unmodified engines enables significant reductions on HC, CO, and PM Emissions, without compromising NO_x emissions, when compared to diesel and bio-diesel fuels. A number of strategies implied in actual engines with retarding SOI reduces the

emission (especially NO_x) sacrificing the fuel consumption. With advancing SOI in engines associated with the shorter ignition delay of GTL fuels many studies demonstrated significant improvement of BSFC and thermal efficiency, while limiting NO_x . However, in higher compression ratio, benefits of GTL having high CN disparages as decreased pre-mixed phase of combustion results higher soot emissions. In spite of high tolerance of GTL fuel to EGR level, an abrupt increment in soot emission has been observed at higher levels of EGR. Lower distillation properties of GTL ensures improved atomization with uniform dispersion of fuel spray initiating rapid evaporation that lead towards proper combustible air-fuel ratio. Introducing pilot injection in association with common rail injection system (independent of fuel properties) favors the reduction in combustion noise with the support from lower heat release rate of GTL fuels. Pump-line–nozzle type fuel injection system (affected by fuel properties) engines fuelled by GTL demonstrates later injection timing compared to conventional diesel. The optimization of after-treatment system for zero sulfur fuel improves NO_x reduction efficiency, because the catalyst can be designed to improve a low temperature activity and heat resistance without having to consider desulfation performance. Further research implemented that low compression engines with high flow-rate injection nozzle facility significantly reduce harmful exhaust emissions and also improve engine performance in case of GTL fuels. Overall, the engine modifications, a lowered compression ratio and increased EGR rate, and optimized injection pattern, enables a significant reduction in NO_x without the deterioration of HC, PM, and CO emission.

Blends of superior GTL with conventional diesel can achieve a certain level of emissions reduction without any vehicle modifications while also consuming less petroleum fuel, which will also benefit legacy vehicles. GTL diesel blends have demonstrated simultaneous reduced emissions regarding CO, HC, NO_x , Soot and Particulate matter. The lower soot emissions of GTL fuel and its blend can facilitate significant reductions in NO_x emissions by exploiting their

higher EGR tolerance. The estimated emissions exhibited beneficial relation within the magnitude of exhaust emission reductions and the fraction of GTL comprising the blends. The linear variation of the prime properties of the GTL-diesel blends with the GTL ratio ensured this improved emission. In addition, both neat GTL and its blend with conventional diesel manifested enhanced fuel economy (gravimetric basis) associated with improved engine thermal efficiency. GTL –diesel blends of 50:50 can be preferred on account of the pronounced response in the improvement of fuel properties, engine performance and also in exhaust emissions. GTL-biodiesel blends with JBD; BSOY illustrated improved BSFC compared to diesel and bio-diesel but less than that of neat GTL. Regarding thermal efficiency similar or even higher magnitudes than diesel have been reported. Considering the engine emission significantly lowered emission including CO, smoke, Total HC and PM are demonstrated but higher NO_x emission due to higher ROHR at the premixed combustion, injection advance, and higher percentages of unsaturated fatty acids with double bonds in the carbon chain of biodiesels. GTL-JBD blends comprising 20% ~50% of JBD and GTL-BSOY blends up to 30% BSOY can be preferred analyzing in context of blend fuel properties, engine performance and emissions. Further research blending GTL fuel with plum, coconut, mustard biodiesel and also non-edible feedstock like cottonseed, calophyllum, inophyllum, waste cooking oil biodiesel can be performed to investigate further improvement.

Gas to liquid fuels and its blends seems to comply with the worldwide strict emissions legislation for vehicles and a concomitant tightening of fuel specifications. Implementation of GTL-diesel blends can decrease the depletion rate of fossil diesel reserve ensuring the improved engine performance and exhaust emission. GTL-biodiesel blends can add a renewable tag into the synthetic GTL fuel which may demonstrate utilization of both stranded gas reserves and non-edible feed-stocks with a pronounced improvement in context of engine performance and exhaust emission features. GTL fuel and its blends may demonstrate a new

era of diversification of alternative and renewable fuel sources with improved fuel properties, engine performance and emissions characteristics which can contribute to the future development of transportation sector.

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