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SYNERGIES BETWEEN RENEWABLE KEROSENE AND FISCHER-TROPSCH SYNTHETIC PARAFFINIC KEROSENE (FT-SPK)

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ABSTRACT

Fossil-derived fuels have been the source of transportation energy for many decades, but with the increase in fuel prices, environmental concerns and government regulations, the interest in alternative fuels has escalated. The future of the aviation industry, including that of the rest of the transportation industry, will inevitably be driven to the use of sustainable renewable fuels in increasing quantities. This drive is based on the carbon footprint of the aviation industry and the critical need to slow down the growth rate of greenhouse gas (GHG) emissions.

Fuel producers have a mandate to explore, develop, and demonstrate future renewable fuel technology options that will ensure sustainability over the long term. The aviation industry's experience with alternative jet fuel has mainly been focused on Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK). FT-SPK derived from coal, natural gas or biomass is now generically approved for commercial use as a blend component with petroleum-derived jet fuel across the world. This approval became effective in September 2009 with the publication of ASTM D 7566. In July 2011, Hydroprocessed Esters and Fatty Acids (HEFA) fuel was approved for commercial aviation use as a second annex in ASTM D 7566. The "greening" of FT-SPK and/or crude-derived jet fuel is a critical action that could become mandatory in the future, when a minimum proportion of renewable carbon atoms in the fuel may be required by legislation.

Synergies between Gas-to-Liquid (GTL)-derived SPK and HEFA fuel, or other renewable jet fuel molecules, could potentially exist. This paper summarises the technical feasibility of a FT-SPK with enough renewable carbon content such that it will be acceptable from a "green" perspective. Property analysis of the blends is reported according to the ASTM D 7566 and DEF STAN 91-91 specification with special emphasis on thermal oxidative stability.

Keywords: Fischer-Tropsch Synthetic Paraffinic Kerosene (FT-SPK), Hydroprocessed Esters and Fatty Acids (HEFA), Thermal oxidative stability

1. INTRODUCTION

Fossil fuels (e.g. petroleum, coal and natural gas) are currently the main source of the world's energy requirements, even though all of these fuels are considered to be non-renewable sources of energy. The use of any fossil fuel as an energy source is becoming increasingly controversial from an environmental impact point of view, as it potentially contributes to climate change effects. Environmental concerns, depleting fossil fuel resources and energy security are the major drivers leading to the search for alternative energy sources that will reduce our reliance on petroleum.

There is enormous political push for the introduction of renewable fuels into the fuel market causing considerable research activity in this emerging area. This is already a common reality for road transportation where bioethanol from corn and sugarcane and biodiesel from soya and rapeseed are used commercially in gasoline and diesel vehicles respectively. The aviation industry has just recently started using Hydroprocessed Esters and Fatty Acids (HEFA), previously known as Hydroprocessed Renewable Jet fuel (HRJ), as renewable jet fuel approved by ASTM International for aviation use in July 2011.¹ The main driver for introducing renewable jet fuel in aviation is the need to reduce greenhouse gas (GHG) emissions.

Although aviation only contributes 2 – 2.5% of global carbon emissions according to the Intergovernmental Panel on Climate Change (IPCC), this is expected to increase with continuous air traffic growth (which is anticipated to double in the next 20 years).² The reduction in emissions due to technological effects to improve fuel efficiency alone will *not* make a significant impact on aviation carbon dioxide (CO₂) emissions.³ Sustainable low carbon fuels are essentially required to make a greater impact and are considered to represent a promising alternative to petroleum-derived fuels to mitigate GHG emissions. The existing infrastructure of aviation favours the continued reliance on liquid hydrocarbon fuels and this may be the case for many more decades to come.

The European Union (EU) has considered placing a 10% renewable energy target for transportation (including aviation) in the Renewable Energy Directive (RED) by 2020.⁴ Additionally, CO₂ emissions on a life cycle basis are required to be at least 35% less than for petroleum fuels and 60% lower by 2018. Introduction of the aviation industry into the EU Emission Trading Scheme (EU ETS) in 2012 is another means to assist with the introduction of low carbon jet fuels into the aviation industry.⁵ This entails capping of aviation emissions at 97% (then 95% from 2013 onwards) of their level in 2005. It will also require that airlines flying to and from European airports will have to add the cost of CO₂ emission allowances to the cost of jet fuel. In June 2009, the International Air Transport Association (IATA), representing most international airlines, set a number of goals to reduce aviation GHG emissions which included:⁶

- An average improvement in fleet fuel efficiency of 1.5% per year from 2009 to 2020,
- A cap on aviation CO₂ emissions from 2020 (to achieve carbon neutral growth),
- A reduction in CO₂ emissions of 50% by 2050 relative to 2005 levels.

In October 2010, the first two goals were also included in International Civil Aviation Organisation (ICAO) Resolution on Climate Change.⁷

ASTM D 7566 (“Aviation Turbine Fuel Containing Synthesized Hydrocarbons”) enables the use of Fischer-Tropsch (FT)-derived fuels up to a 50 vol% blend with petroleum jet fuel.⁸ FT fuels can be derived from different feedstocks such as coal (coal-to-liquids (CTL)), natural gas (gas-to-liquids (GTL)) and biomass (biomass-to-liquids (BTL)). Currently, renewable jet fuel is rare and expensive compared to conventional jet fuel and not economical for airlines to use. Renewable jet fuel will become more attractive when the price of conventional jet fuel increases and it is also expected that governmental-imposed policies will add significant cost to fossil fuel users in the future. FT fuels, however, do provide an opportunity to diversify aviation fuel supply to meet world demand and circumvent increasing crude oil price or depleting resources. Additionally, FT fuels (and HEFA fuels), reduce the level of particulate emissions of the turbine engine due to their negligible aromatics content, and also result in a lower aromatic content of the blended Jet A-1.⁹ There is also an improvement in air quality due to reduced sulphur emissions as well as reduced contrails formation.¹⁰

Tough emissions-driven penalties may be imposed in the future on companies producing jet fuels containing no renewable or low carbon intensity jet fuel components. Therefore Sasol Technology Fuels Research is investigating the use of renewable fuels as part of Sasol’s FT-based future product slates.

2. EXPERIMENTAL PROCEDURE

2.1. Description of fuel components

2.1.1. Gas-to-Liquids (GTL) kerosene

At the heart of the Oryx GTL plant in Ras Laffan, Qatar, is the Low Temperature Fischer-Tropsch (LTFT) unit which utilises the Sasol Slurry Phase Distillate™ (SPD™) process. The plant design consists of three major processing steps (shown schematically in Figure 1);

- Natural gas reforming produces synthesis gas.
- LTFT technology converts synthesis gas to waxy hydrocarbons using a cobalt-based proprietary catalyst in the Sasol SPD™ process.
- Upgrading (hydrocracking) of waxy hydrocarbons produces hydrocarbons boiling in the naphtha to diesel fuel boiling range, while olefins and oxygenates are also converted to paraffins in the same process. The distillate is fractionated into GTL naphtha and GTL diesel products. Product upgrading is executed with ChevronTexaco *iso*-cracking technology which makes use of a Chevron hydrocracking catalyst.

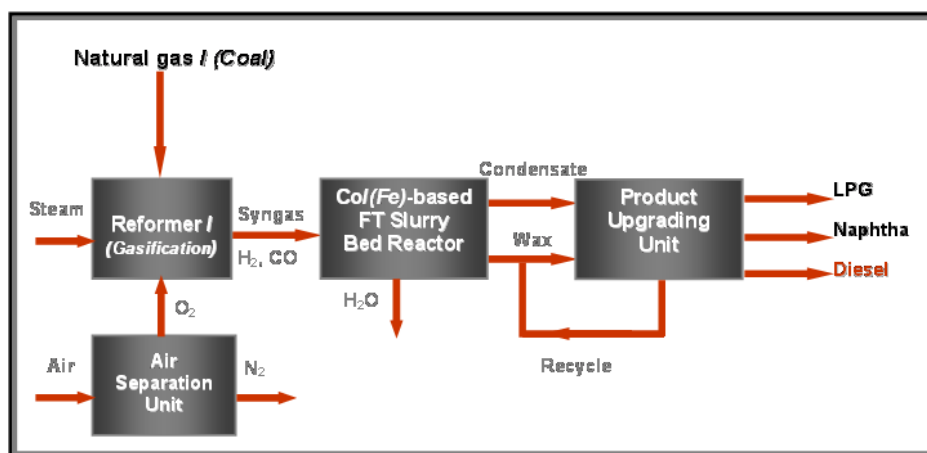


Figure 1. Block flow diagram of the Oryx GTL process in Qatar.¹¹

The Oryx GTL plant was commissioned in 2006.¹² In the current plant configuration, diesel fuel is produced predominantly, with naphtha as a co-product. A limitation of the LTFT process is that it does not produce a final diesel fuel meeting the current European minimum density specification (EN590); hence, it is mostly used as a diesel blend component. GTL kerosene is currently not part of the product slate of this facility and is thus not produced on commercial scale. For the purpose of the current study, GTL diesel and naphtha produced at Oryx GTL was therefore blended in an 80/20 ratio respectively and fractionated at the Sasol Technology R&D pilot plants to produce a GTL kerosene fraction. GTL kerosene is characterised by its highly paraffinic composition, with negligible sulfur and aromatics content, and has inherently a low fuel density.¹³

2.1.2. Hydroprocessed Esters and Fatty Acids (HEFA)

HEFA, also referred to as HRJ or bio-SPK,¹⁴ can be produced from vegetable and algal oils by hydroprocessing. ASTM International has recently changed the HRJ definition to the more encompassing name: “Hydroprocessed Esters and Fatty Acids” or HEFA, in order to include most renewable feedstocks. HEFA is not biodiesel; although the same feedstock is used, the process for the production is different, thereby yielding different products. In biodiesel production, vegetable oil is treated with methanol in a trans-esterification process step to produce fatty acid methyl ester (FAME) and a by-product, glycerol. Glycerol is a low value product with a limited market. The production of HEFA is a more complicated process than the typical production process for biodiesel. A simple schematic illustration of the production of HEFA is shown in Figure 2.

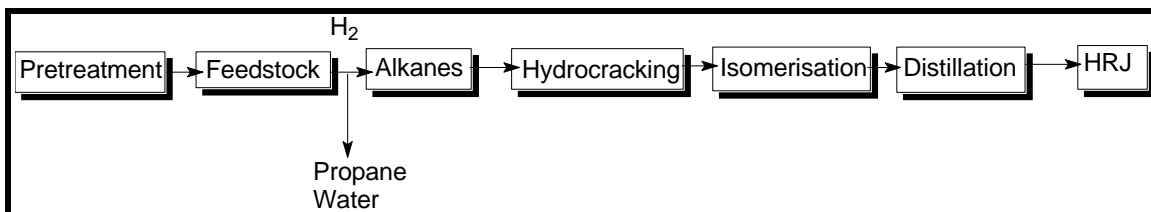


Figure 2. A simplified flow scheme for the production of HEFA.

In HEFA production, the first step is a pre-treatment step of the vegetable oil to remove trace metal contaminants such as phosphorus, sodium, potassium and cadmium. In the second step, the triglycerides present in the bio-oils are hydrotreated under appropriate conditions over a suitable catalyst to deoxygenate the oil and form normal paraffins, propane and $\text{H}_2\text{O}/\text{CO}/\text{CO}_2$. Additional conventional refinery processes such as hydrocracking, isomerisation, and distillation eventually yield kerosene range material (the so-called HEFA product). The HEFA produced from these bio-oils is similar in its chemical properties to FT-SPK and would also require blending with conventional jet fuel to meet Jet A-1 specifications (in particular minimum aromatics and density requirements).¹⁵ **In this study, two HEFA samples were evaluated in blends with GTL kerosene. Universal Oil Products' (UOP) HEFA sample was derived from camelina feedstock whereas Syntroleum's HEFA sample was derived from animal fat.**

UOP has a renewable jet fuel process where processing techniques similar to those mentioned above are used to convert bio-oil to HEFA with their specially-formulated catalysts (as shown in Figure 3). UOP's renewable jet fuel process was developed in 2007 and was used to produce HEFA for various commercial flight tests and for the United States Air Force (USAF) aircraft certification process.¹⁶ They have successfully converted bio-oils derived from algae, vegetable oil, jatropha, camelina and halophytes to jet fuel. UOP is also currently developing a pyrolysis technology to convert biomass into renewable jet range aromatics which will enable the possibility of 100% fully synthetic, but renewable Jet A/A-1.¹⁷

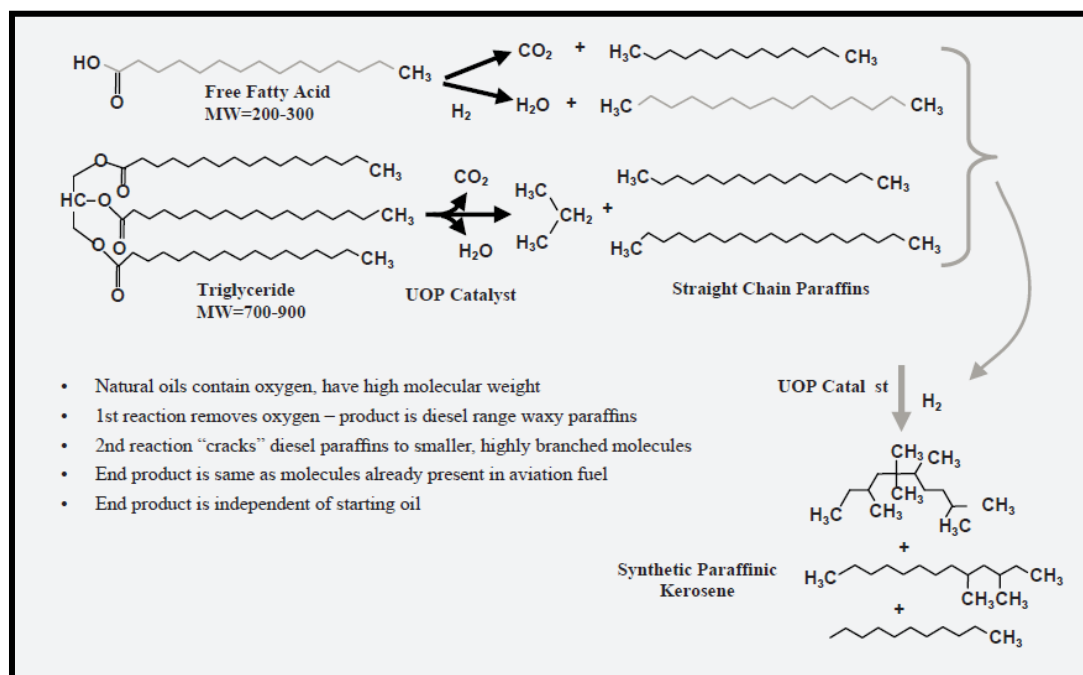


Figure 3. UOP's HEFA process.¹⁸

Syntroleum has a renewable jet fuel process called the Bio-Synfining™ technology that converts triglycerides derived from tallow or animal fats (which are obtained from Tyson Foods) to HEFA.¹⁹ A joint venture between Syntroleum and Tyson Foods yielded a company called Dynamic Fuels in 2007, who began commercial production of renewable fuels (jet fuel and diesel) in November 2010 at their Geismar, Louisiana facility.

2.1.3. Model renewable aromatics/cycloparaffins

Model renewable molecules (in the jet fuel boiling range) such as those produced by Amyris' genetically engineered microbes were purchased from commercial sources (*not from Amyris Biotechnologies*) and tested in blends with GTL kerosene. Types of potentially renewable molecules falling in the jet fuel range are shown in Figure 4 below. **Of these compounds, only *p*-cymene (99%, Sigma-Aldrich) and pinane (>98%, Merck) were commercially available. These two compounds were thus evaluated in this blending study with GTL kerosene.** The other compounds are only commercially available in their alkene terpenoid precursor form (such as limonene, carene and sabinene) and would need to be hydrogenated to obtain the desired saturated compounds. **The terpenoid precursor, limonene (97%, Merck) was purchased for this study and hydrogenated at Sasol Technology R&D to limonane for use in this blending study.** Farnasane, a C₁₂ branched paraffin, is Amyris' primary renewable diesel blending component.²⁰

These were all single molecules blended into GTL kerosene with the aim of producing a final Jet A-1. The aviation industry has no experience in blending single molecules into jet fuel. This paper may therefore provide some additional insight into the blending of the single aromatics and cycloparaffins into kerosene.

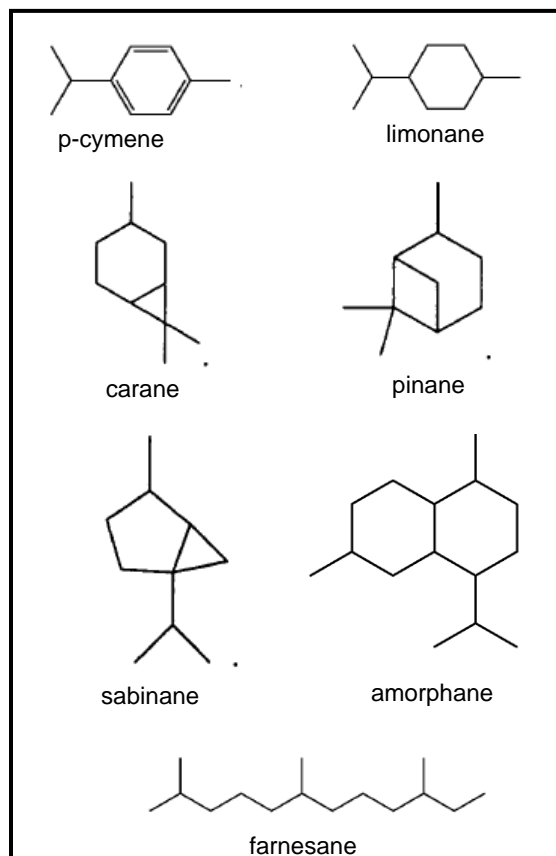


Figure 4. Renewable molecules in the jet fuel boiling range potentially produced by genetically engineered microbes (such as from Amyris Biotechnologies' fermentation process).

Limonene hydrogenation to limonane

Limonene, also known as 1-methyl-4-isopropenyl-1-cyclohexene (97 %, Merck), was purchased and hydrogenated at Sasol Technology R&D to produce limonane for use in the blending study with GTL kerosene. The hydrogenation reactions were conducted in a fixed bed reactor using 40 – 55 % Ni/Al₂O₃ BASF catalyst at a hydrogen pressure of 50 bar and reaction temperature of 120 °C. The limonene conversion was about 98% with 1.09% unprocessed limonene remaining in the sample (*Limonane Product 1*, as indicated in Table 1). A smaller quantity of the *Limonane Product 1* was further processed to provide complete hydrogenation of limonene yielding *Limonane Product 2*. Both products also contained *p*-cymene. The product composition of the two limonane products used in the blending study with GTL kerosene is shown in Table 1.

Table 1. The composition of the limonane product (as measured by GC-MS) after limonene hydrogenation using a Ni catalyst (50 bar, 120 °C).

Product components	Limonane Product 1 / wt%	Limonane Product 2 / wt%
2,6-dimethyloctane	1.03	1.03
<i>Cis</i> and <i>trans</i> -limonane	89.17	92.95
<i>p</i> -Cymene	6.83	4.65
Limonene	1.09	0.03
<i>p</i> -Menth-1-ene	0.65	0
γ -terpinene	0.01	0.04
Unknown	1.22	1.31

Amyris Biotechnologies is a renewable products company that was founded in 2003 and is based in California, USA.²¹ They also have a sister company in Sao Paulo, Brazil named Amyris Brasil where commercial piloting takes place to produce their Amyris products from Brazil's sugar cane. Products from Amyris not only include renewable diesel and jet fuels (not commercially available as yet), but also anti-malarial drugs such as artemisinin. Amyris Biotechnologies have stated that their renewable fuels can reduce life-cycle GHG emissions by 80% or more compared to conventional petroleum fuels.²² They make use of a proprietary technology based on synthetic biology using genetically engineered yeast to transform sugar into these renewable jet fuel and diesel-range molecules as shown in Figure 5.

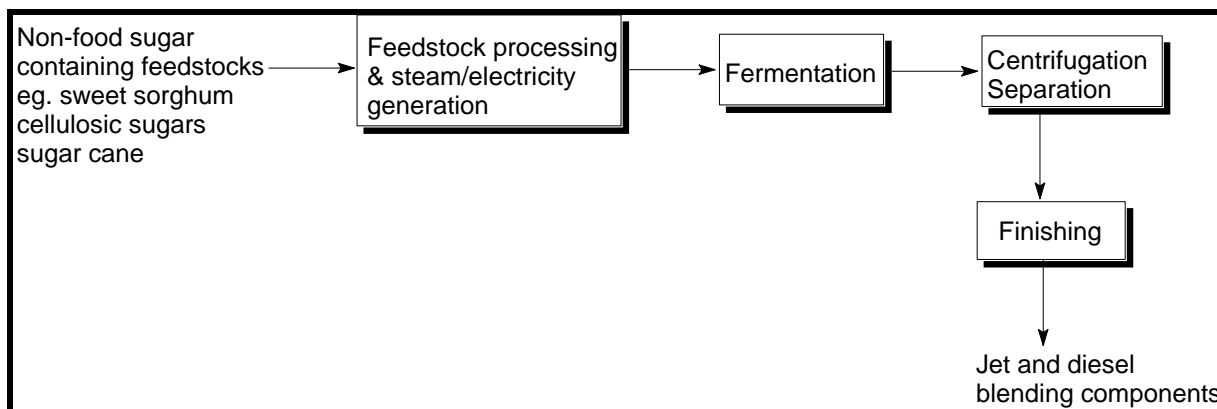


Figure 5. Amyris fermentation technology.²³

Amyris Biotechnologies have patented the use of genetically engineered microbes or yeasts to produce bio-derived jet fuel molecules through sugar/starch fermentation.²⁴ These bio-derived renewable jet fuel molecules are unique in the sense that they are aromatic and cyclic in nature, rather than the paraffinic molecules normally found in HEFA. These bio-derived compounds could have a positive effect on density and also on the seal swell propensity of the final jet fuel blend. The genetically engineered microbes can however also produce paraffinic molecules such as farnesane, which can be used in both renewable jet fuel and diesel production. In the Amyris patents, the renewable jet fuel compounds were blended with petroleum-derived jet fuel (50/50 vol%) and met all the Jet A specifications. Further applied testing such as light-off and lean blow-out tests of the renewable-petroleum blends was also covered in the patent.²⁵

The Amyris renewable jet fuel components (structures are shown in Figure 4) as listed in the Amyris patent are shown in Table 2.²⁵

Table 2. Amyris renewable jet fuels components.

Fuel blend #	Amyris Fuel ID	Amyris fuel components
1	AMD200	99.76% farnesane
2	AMJ300	97.1% limonane + 1.6% <i>p</i> -cymene + 1.3% unknowns
3	AMJ310	81.0% limonane + 17.5% <i>p</i> -cymene + 1.5% unknowns
4	AMJ700	50.0% limonane + 10.0% <i>p</i> -cymene + 40.0% farnesane

2.1.4. Byogy renewable jet fuel (Alcohol-to-jet (ATJ) process)

Byogy Renewables has developed a four step process to convert ethanol or other alcohols to a 100% fully synthetic renewable jet fuel consisting of mainly *iso*-paraffins and some aromatics with very little *n*-paraffins. It is claimed that the process can be adjusted to produce any percentage of aromatics that may be typically required for Jet A (*i.e.* up to 25%). Their renewable fully synthetic jet fuel is a 100% stand-alone drop-in replacement fuel for petroleum-derived jet fuel. The Byogy process makes use of processes that are widely used on commercial scale and does not rely on the use of genetically modified organisms (GMO) or enzymes.

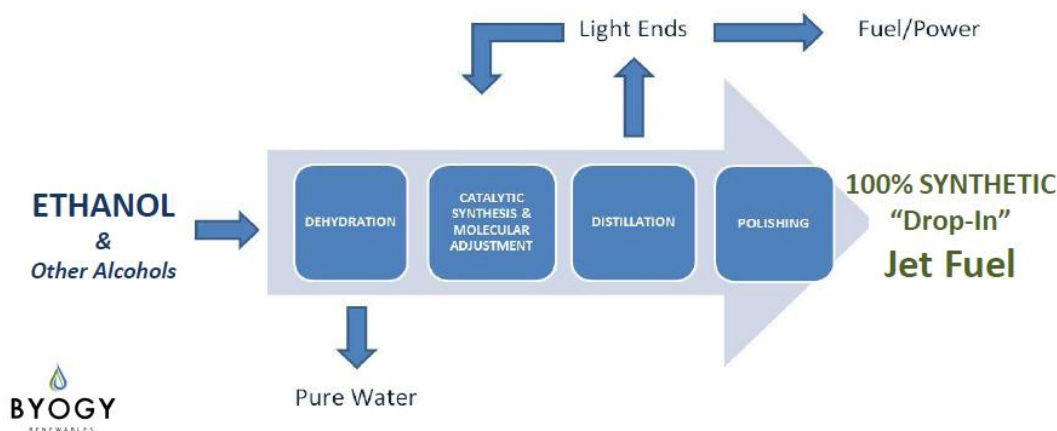


Figure 6. Byogy’s renewable jet fuel process.²⁶

Byogy Renewables, together with other leading companies such as Gevo, LanzaTech, Logos Technologies, and others, have formed an Alcohol-to-Jet (ATJ) ASTM Task Force at the June 2010 ASTM meeting. Byogy Renewables, Logos Technologies and Virent are the only companies that have thus far claimed to produce significant quantities of renewable aromatics. Blending GTL kerosene with renewable aromatics is an attractive way to produce a final Jet A-1 fuel containing a portion of renewable molecules.

2.2. Specified fuel properties

A full specification analysis and characterisation of the GTL kerosene, renewable kerosene and the resulting blended fuels were carried out according to the ASTM International test methods as contained in the British DEF STAN 91-91 specification for Jet A-1 and in ASTM D 7566 for FT-SPK and HEFA. The blending envelope between GTL kerosene and the HEFA fuel was investigated across the whole range, from 0% HEFA to 100% HEFA. Since these two products (FT-SPK and HEFA) were known to be quite similar in physical properties, the expectation was that the blending envelope will be unconstrained across the full range. The model renewable compounds were blended into GTL kerosene to meet the minimum density specification for Jet A-1. The Byogy renewable jet fuel containing aromatics was blended into GTL kerosene to also meet the minimum density specification for Jet A-1.

Two-dimensional gas chromatography (2D GC or GCxGC) was also performed on the individual fuels and blended fuels to provide insight into the hydrocarbon composition of the fuels.

2.3. Jet Fuel Thermal Oxidation Tester (JFTOT) evaluation

The thermal stability of the test fuels were investigated by means of the JFTOT procedure according to ASTM D3241²⁷ through evaluation of the break point temperatures of GTL kerosene, renewable fuels and the resulting blended fuels. The current Jet A-1 specification requires the fuel to pass the JFTOT procedure at a test temperature of 260 °C. According to ASTM D 7566, FT-SPK and HEFA needs to pass the JFTOT procedure at a significantly more severe test temperature of 325 °C. The break point temperatures of the fuel evaluated by JFTOT are defined as the highest temperature at which the fuel still passes the specification rating criteria. This is normally a good practice when comparing the thermal stability of jet fuels. JFTOT was therefore measured at 40 °C intervals from 260 °C until the break point temperature of the fuel was reached (in the following order: 260, 300, 340 and 360 °C). Within the 40 °C break point interval, the test temperature was increased by 5 °C increments until the JFTOT failure was detected by either tube colour rating or pressure drop. The maximum operating temperature of the JFTOT apparatus is 380 °C, but for safety and quality reasons, the maximum operating temperature was set at 360 °C.

3. RESULTS AND DISCUSSION

3.1. GTL kerosene/HEFA blends

a) Properties of kerosenes

The hydrocarbon composition of the GTL kerosene and HEFA samples as determined by 2-dimensional gas chromatography (referred to in short as GCxGC) is shown in Figure 7. GTL kerosene consists predominantly of *n*-paraffins and to a lesser extent, *iso*-paraffins, causing the fuel to have a good cetane number but less optimal cold flow properties. The HEFA from UOP and Syntroleum was highly isomerised in nature and contained few *n*-paraffins. This allowed the HEFA to contain higher carbon number chains (i.e. heavier *iso*-paraffins), while still conforming to the required freezing point and final boiling point limits. The absence of aromatics and reduced levels of cycloparaffins resulted in GTL kerosene and HEFA both having a lower fuel density.

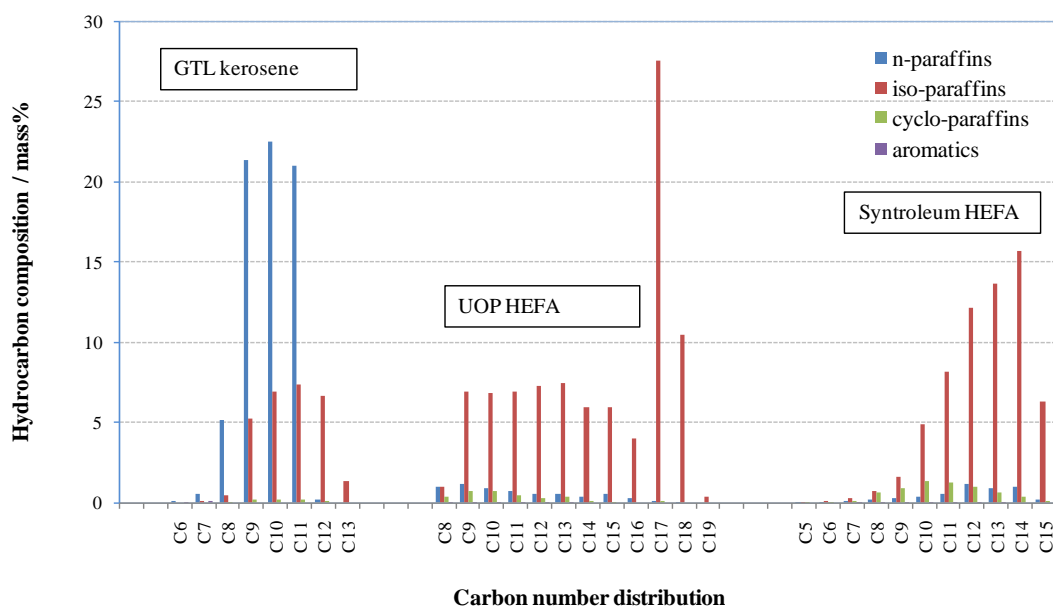


Figure 7. The hydrocarbon composition of GTL kerosene and HEFA samples as determined by GCxGC.

Critical jet fuel analyses of GTL kerosene and HEFA samples from UOP and Syntroleum are shown in Table 3. The test fuels were evaluated against the requirements of ASTM D 7655, “Table A1.1 Detailed Batch Requirements; Hydroprocessed SPK”.

Table 3. Critical jet fuel analysis of GTL kerosene and HEFA from UOP and Syntroleum.

Line No.	Property	Limits	GTL kerosene	UOP HEFA	Syntroleum HEFA
COMPOSITION					
1	Acidity, mg KOH/g	0.015 (max)	0.003	0.003	0.001
2	Mercaptan sulphur, mass%	0.003 (max)	1	<1	<1
3	Total sulphur, mass%	0.3 (max)	1	<1	<1
VOLATILITY					
4	Initial boiling point, °C	Report	137.6	146.8	145.3
5	10% recovered, °C (T10)	205 (max)	155.6	170.8	177.9
6	50% recovered, °C (T50)	Report	168.1	235.7	221.8
7	90% recovered, °C (T90)	Report	184.3	275.7	257.8
8	Final boiling point, °C	300 (max)	194.1	280.6	270.4
9	T ₉₀ – T ₁₀ , °C	22 (min)	28.7	104.9	79.9
10	Flash point, °C	38.0 (min)	38.5	49.0	45.5
11	Density @ 15 °C, kg/L	0.730 – 0.770	0.734	0.764	0.761
FLUIDITY					
12	Freezing point, °C	-40.0 (max)	-50.5	-51.8	-48.7
13	Viscosity @ -20 °C, cSt	8.0 (max)	2.1	6.8	5.8
COMBUSTION					
14	Net heat of combustion, MJ/kg	42.8	43.8	44.1	44.2
15	Smoke point, mm	25.0 (min)	26.0	28.0	25.0
16	Naphthalenes, vol%	3.0 (max)	<1	<1	<1
CORROSION					
17	Copper strip, 2hrs @ 100 °C	1 (max)	1A	1A	nd
THERMAL STABILITY					
18	Control temperature, °C	325 (min)	360	360	360
19	Filter pressure drop, mm Hg	25 (max)	0	0	0
20	Tube deposit rating @ 360 °C	<3	1	1	1
CONTAMINANTS					
21	Microseparometer without SDA	85 (min)	93	97	nd
22	Existent gum	7.0 (max)	0.3	1.2	0.3
OTHER TESTS					
23	Conductivity, pS/m	50 – 600	7	275	nd

nd = not determined.

The HEFA material from UOP and Syntroleum represent examples of very good quality kerosenes with a higher density than GTL kerosene due to their higher average chain length. Due to the presence of high concentrations of *iso*-paraffins, a higher carbon chain length could be accommodated in the boiling point distribution, which increased the yield of the kerosene material while still conforming to the freezing point requirement. The HEFA from UOP, unlike GTL kerosene, contained static dissipater additive (SDA) causing the conductivity to be within the required specification.

b) Blending study

Critical jet fuel analysis of GTL kerosene blended with UOP's HEFA and Syntroleum's HEFA are shown in Table 4 and Table 5 respectively. Note that these blends were also evaluated against the requirements of ASTM D 7655, "Table A1.1 Detailed Batch Requirements; Hydroprocessed SPK". The implication is that these blends would still be required to be blended at up to 50 vol% with conventional or synthetic Jet A/A-1, to be used as semi-synthetic Jet A/A-1 or fully synthetic Jet A/A-1.

Table 4. Critical jet fuel analysis of UOP's HEFA and GTL kerosene blends.

Line No.	Property	Limits	75/25 HEFA/GTL	50/50 HEFA/GTL	25/75 HEFA/GTL
COMPOSITION					
1	Acid number, mg KOH/g	0.015 (max)	0.003	0.003	0.003
VOLATILITY					
2	Initial boiling point, °C	Report	175.7	144.9	147.1
3	10% recovered, °C (T10)	205 (max)	189.5	161.4	160.9
4	50% recovered, °C (T50)	Report	215.6	189.4	180.6
5	90% recovered, °C (T90)	Report	261.4	269.7	240.0
6	Final boiling point, °C	300 (max)	289.2	279.9	278.6
7	T ₉₀ -T ₁₀ , °C	22 (min)	72.0	108.0	79.0
8	Flash point, °C	38 (min)	44.0	42.5	41.0
9	Density @ 15 °C, kg/L	0.730 - 0.770	0.757	0.749	0.741
FLUIDITY					
10	Freezing point, °C	-40.0 (max)	-56.3	-61.9	-55.3
11	Viscosity @ -20 °C, cSt	8.0 (max)	5.0	4.1	3.1
COMBUSTION					
12	Net heat of combustion, MJ/kg	42.8	44.2	44.2	44.3
13	Smoke point, mm	25.0 (min)	29.0	30.0	29.0
CORROSION					
14	Copper strip, 2hrs @ 100 °C	1 (max)	1A	1A	1A
THERMAL STABILITY					
15	Control temperature, °C	325 (min)	360	360	360
16	Filter pressure drop, mm Hg	25 (max)	0	0	0
17	Tube deposit rating @ 360 °C	<3	<1	1	<1
CONTAMINANTS					
18	Microseparometer without SDA	85 (min)	99	98	98
19	Existent gum	7.0 (max)	1.0	1.1	0.8
20	Water content, mg/kg	75 (max)	11	13	10

Table 5. Critical jet fuel analysis of Syntroleum's HEFA and GTL kerosene blends.

Line No.	Property	Limits	75/25 HEFA/GTL	50/50 HEFA/GTL	25/75 HEFA/GTL
COMPOSITION					
1	Acid number, mg KOH/g	0.015 (max)	0.003	0.002	0.001
VOLATILITY					
2	Initial boiling point, °C	Report	148.3	143.6	145.6
3	10% recovered, °C (T10)	205 (max)	159.1	161.7	170.2
4	50% recovered, °C (T50)	Report	180.4	189.8	207.1
5	90% recovered, °C (T90)	Report	222.3	247.6	255.1
6	Final boiling point, °C	300 (max)	262.8	266.7	269.6
7	T ₉₀ -T ₁₀ , °C	22 (min)	63.2	85.9	84.9
8	Flash point, °C	38 (min)	39.0	40.0	44.0
9	Density @ 15 °C, kg/L	0.730 - 0.770	0.740	0.747	0.754
FLUIDITY					
10	Freezing point, °C	-40.0 (max)	-55.1	-58.6	-53.0
11	Viscosity @ -20 °C, cSt	8.0 (max)	3.0	3.6	4.6
COMBUSTION					
12	Net heat of combustion, MJ/kg	42.8	44.3	44.2	44.2
13	Smoke point, mm	25.0 (min)	27.0	26.0	26.0
THERMAL STABILITY					
14	Control temperature, °C	325 (min)	360	360	360
15	Filter pressure drop, mm Hg	25 (max)	0	0	0
16	Tube deposit rating @ 360 °C	<3	<1	<1	<1
CONTAMINANTS					
17	Existent gum	7 (max)	0.4	0.7	0.9
18	Water content, mg/kg	75 (max)	17	16	13

Of special interest in this blending study was the quantification of any synergetic blending behaviour that might be uncovered, apart from the obvious benefit of increased renewable carbon atoms with an increase in the HEFA content of the blend. One possible example is that if the HEFA product has been converted to predominantly *iso*-paraffins by effective isomerisation in its production process, its resultant low freezing point will enable the GTL kerosene to be cut heavier, potentially leading to an increased yield of kerosene from the GTL plant. The wider range of boiling point distributions in the combined blend may also lead to an increased density for the GTL kerosene plus HEFA blend, making it possible to blend with lighter petroleum-derived Jet A-1 at the maximum allowable blend ratio of 50 vol%.

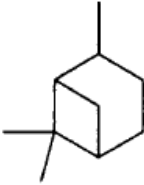
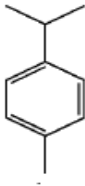
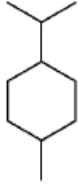
There are definite synergies in blends of GTL kerosene and HEFA besides introducing renewable carbons into GTL kerosene. The density of the blends increase as more HEFA is added; this will allow more of the synthetic material to be added to petroleum-derived jet fuel while still meeting the minimum density requirement. The freezing points of the blends are also enhanced, when compared to the individual test fuels.

3.2. GTL kerosene/model renewable compounds

a) Properties of renewable model compounds

The physical properties of pinane, limonane and *p*-cymene are shown in Table 6. Pinane and *p*-cymene has similar densities, whereas limonane's density is considerably lower.

Table 6. Properties of potential renewable jet-range molecules.

Property	Pinane	<i>p</i> -Cymene	Limonane
Structure			
Chemical formula	C ₁₀ H ₁₈	C ₁₀ H ₁₄	C ₁₀ H ₂₀
Density at 20 °C / kg/L	0.8595	0.8591	0.8025
Viscosity at -20 °C / mm ² /s	6.79	1.68	2.92
Freezing point / °C	<-70	<-70	<-70
Boiling point / °C	165	177	168
Derived Cetane Number (DCN)	22.7	7.8	Not measured due to sample limitation

b) Preliminary blending study

Critical jet fuel properties such as density, freezing point, viscosity and cetane number were evaluated in blends of GTL kerosene with pinane and *p*-cymene in a wide spectrum of blending ratios. This preliminary evaluation was done in order to cover the full range of blending ratios and evaluate any anomalies in physical behaviour *i.e.* identifying possible non-linearity in the blending behaviour of physical properties. Table 7 shows the blending ratios of pinane and *p*-cymene that were evaluated. **Renewable blends 1 to 4 were then further blended into GTL kerosene in blending ratios of 75:25, 50:50 and 25:75 and the critical properties of these resulting blends were evaluated.**

Table 7. Blend ratios of pinane and *p*-cymene for blending study.

Renewable Blend No.	Pinane / vol%	<i>p</i> -Cymene / vol%
Blend 1	75	25
Blend 2	50	50
Blend 3	25	75
Blend 4	100	0

Due to the limited volume of limonane available, this type of extensive study was not done for GTL/limonane/*p*-cymene blends. The effect of the renewable blends (Blend 1 to 4) on the critical properties of GTL kerosene is discussed below.

Density

The density of the fuel is impacted by the presence of aromatics or cycloparaffins. GTL kerosene does not contain aromatics and its density is therefore below the minimum density specification for Jet A-1. The renewable blends contain an aromatic molecule, *p*-cymene, and a cycloparaffinic molecule, pinane, and have a positive effect on the density of GTL kerosene as shown in Figure 8. The density of *p*-cymene and pinane are similar with a value of 0.860 kg/L causing the different blend ratios to have similar densities. More than 25% of renewable molecules are required in a blend with GTL kerosene to meet the Jet A-1 density specification.

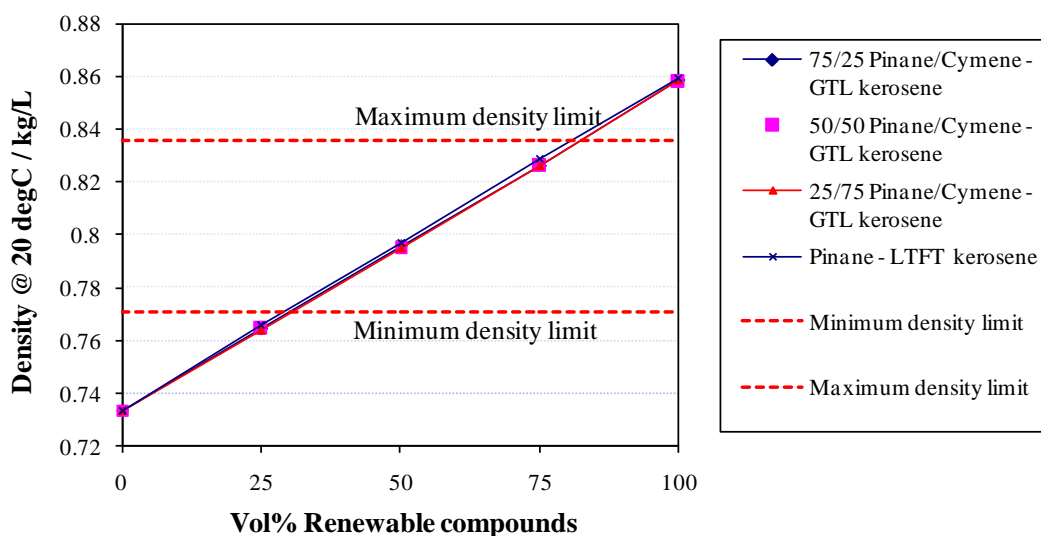


Figure 8. The effect of renewable molecules on GTL kerosene's density.

Freezing point

The operation of aircraft above 12 000 meters can cause jet fuel in aircraft fuel tanks to be subjected to very low temperatures. This could result in the fuel freezing or solidifying which reduces the fuel flow and could plug filters. The resultant fuel starvation could be catastrophic, resulting in engine failure. The freezing point of the fuel is impacted by its hydrocarbon composition, especially by the presence of *n*-paraffins. *Iso*-paraffins have a positive impact on jet fuel freezing point whereas *n*-paraffins have a negative impact. As the jet fuel cools, normal paraffins precipitate out of solution forming nucleation sites which enable further crystal growth. GTL kerosene has the correct ratio of *iso*- and *n*-paraffins to enable the fuel to meet the freezing point specification of $<-47^{\circ}\text{C}$. The renewable fuel molecules have excellent beneficial freezing points due to their cyclic nature. It is observed that by increasing the volume% of renewable molecules in GTL kerosene, the blended fuel had significantly improved cold flow properties.

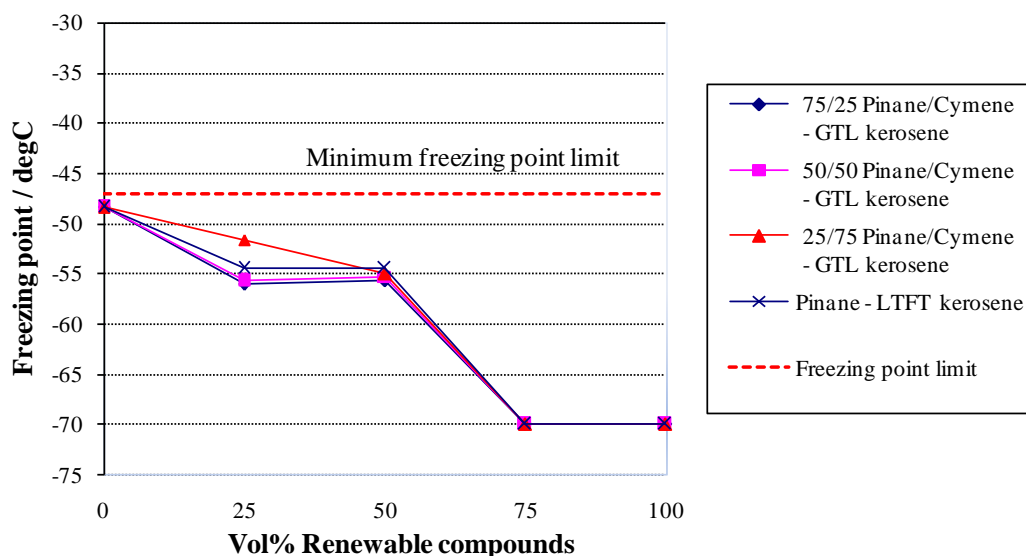


Figure 9. The effect of renewable molecules on GTL kerosene's freezing point.

Viscosity

Low temperature properties of jet fuel are critical in ensuring effective operation of the aircraft. Engine starting is one of the critical performance properties influenced by the fuel's low temperature properties. On cooling the fuel, the viscosity of the fuel increases. A maximum viscosity of 8 cSt is required at -20 °C to enable the fuel to effectively start the engines on the ground. A higher fuel viscosity could hinder effective engine starting due to increases in fuel droplet sizes of the combustor fuel spray, leading to poor atomization and ignition propensity.

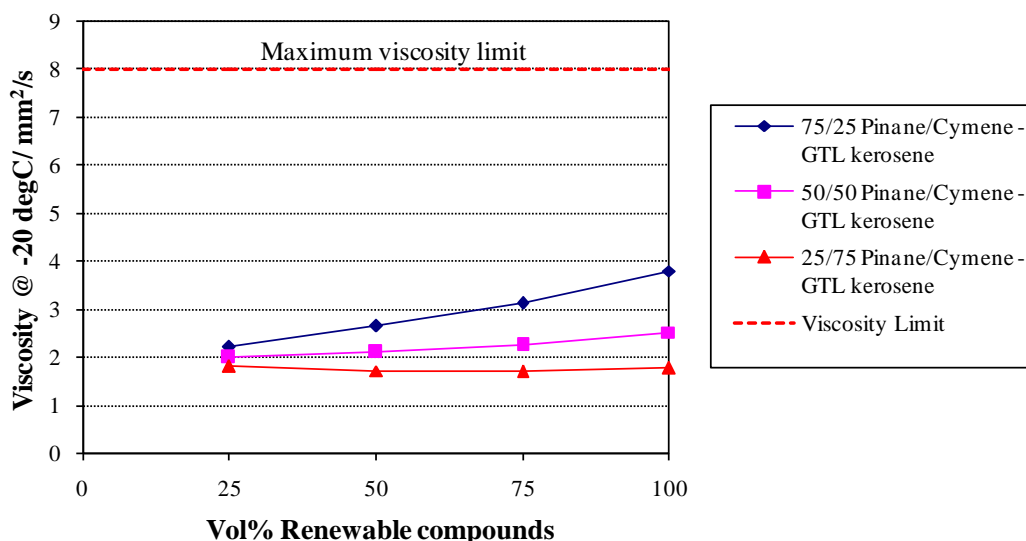


Figure 10. The effect of renewable molecules on GTL kerosene's viscosity.

Blends of renewable jet-range molecules with GTL kerosene are well within the maximum viscosity specification as shown in Figure 10. The viscosity of *p*-cymene is similar to GTL

kerosene but significantly less than the viscosity of pinane, causing the blending slopes to be different.

Derived Cetane Number (DCN)

Cetane number is a measure of the ignition delay of diesel during compression ignition *i.e.* the time period between the start of injection and start of combustion (ignition) of the fuel. Linear paraffins have very good cetane numbers but poor cold flow properties. Fuels with a high cetane number have shorter ignition delays, thereby providing more time for the combustion of the fuel to be completed. The Derived Cetane Number (DCN) was determined by the Ignition Quality Tester™ (IQT) method for the various renewable jet fuel blends (results are shown in Figure 11). The GTL kerosene used in this study had a high cetane number of 62.8. In the current jet fuel specifications, there is no cetane requirement. There has however been increasing interest in the aviation industry in understanding the role of cetane quality on high altitude re-light and lean blow-out (LBO) characteristics of jet fuel.

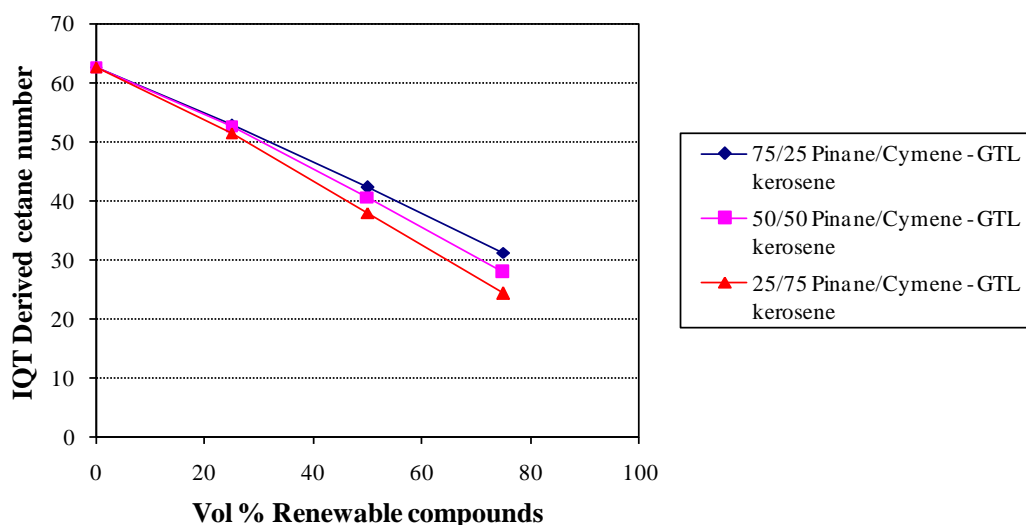


Figure 11. The effect of renewable compounds on the derived cetane number of GTL kerosene.

The renewable molecules have a negative effect on the cetane number of GTL kerosene, as is expected from the resultant reduction in the concentration of linear paraffins. An increasing *p*-cymene concentration lowers the cetane number at a slightly greater extent compared to the increasing pinane concentration due to its lower cetane number. *p*-Cymene has a lower DCN of 7.8 compared to pinane (22.7). Aromatics and cyclics are known to have a negative impact on cetane number with aromatics having the worst impact. The 50/50 blends of renewable molecules and GTL kerosene still has adequate cetane numbers of around 40 which is considered to be acceptable and compares well with conventional jet fuel. Higher concentrations of model renewable molecules in GTL kerosene (75 vol%) caused the cetane number to drop to around 30.

c) Final fuel blending study

Mixtures of pinane and *p*-cymene were blended with GTL kerosene to meet final Jet A-1

specifications according to DEF STAN 91-91. Also, mixtures of limonane and *p*-cymene were blended with GTL kerosene to meet final Jet A-1 specifications according to DEF STAN 91-91. Six renewable jet fuel (RJ1 to RJ6) blends were evaluated as shown in Table 8.

Table 8. Blends of renewable jet-range compounds and GTL kerosene.

Blend ID	GTL kerosene + model renewable molecules	Blend ratios / vol%	Blend details
RJ1	GTL kerosene + <i>Pinane</i>	68 : 32	Meets the density specification
RJ2	GTL kerosene + <i>Pinane</i> + <i>p</i> -Cymene	68 : 23 : 9	Meets the 8 % aromatic specification
RJ3	GTL kerosene + <i>Pinane</i> + <i>p</i> -Cymene	68 : 14 : 18	Meets the normal 18 % aromatic content
RJ4	GTL kerosene + <i>Limonane</i> Product 2	40 : 60	Meets the density specification
RJ5	GTL kerosene + <i>Limonane</i> Product 1 + <i>p</i> -Cymene	45 : 50 : 5	Meets the 8 % aromatic specification
RJ6	GTL kerosene + <i>Limonane</i> Product 1 + <i>p</i> -Cymene	52 : 33 : 15	Meets the normal 18 % aromatic content

Renewable jet fuel blend 1 (RJ1) only contains the cyclic molecule pinane, in order to observe the effect of aromatic-free jet fuel that still meets the density specification, but not the minimum 8 vol% aromatic specification. Renewable jet fuel blend 2 (RJ2) contains the minimum 8 vol% aromatic molecule, *p*-cymene as well as pinane to meet the minimum jet fuel density specification. Typical conventional petroleum jet fuel from the Natref Refinery in South Africa usually contains 18 vol% of aromatics, renewable jet fuel blend 3 (RJ3) was therefore also produced to meet the typical 18 vol% aromatic content. A blend of *p*-cymene alone and GTL kerosene will be able to meet the minimum density specification, but requires 32 vol% of cymene. This blend will however fail the jet fuel maximum aromatic specification of 25 vol% and was therefore not tested.

Renewable jet fuel blend 4 (RJ4) only contains the completely hydroprocessed Limonane Product 2 with a small quantity of *p*-cymene (4.65%) already present in the renewable limonane. Renewable jet fuel blend 5 and 6 (RJ5 and RJ6) were blended to meet the minimum jet fuel density but to also meet the 8% and 18% aromatic contents, respectively. The Limonane Product 1 already contained 6.83% *p*-cymene which resulted in additional *p*-cymene that had to be added to meet the aromatic specifications required.

A full specification analysis of GTL kerosene and the blended fuels (GTL kerosene with *p*-cymene and pinane) were evaluated according to the ASTM test methods as contained in DEF STAN 91-91 for Jet A-1 and are summarized in Table 9.

Table 9. Full specification properties of GTL kerosene and the renewable blended fuels containing pinane and *p*-cymene.

Property	Units	Limits	Results			
			GTL kerosene	RJ1	RJ2	RJ3
BLEND RATIO	GTL:Pin:Cym		100:0:0	68:32:0	68:23:9	68:14:18
APPEARANCE						
Visual			PASS	PASS	PASS	PASS
Colour, Saybolt	-	Report	>+30	>+30	>+30	>+30
Particulate Contaminants	mg/L	1.0 max	0.2	0.3	0.2	0.3
COMPOSITION						
Total Acidity	mgKOH/g	0.015max	0.003	0.004	0.004	0.004
Olefins	vol %	5.0 max	0.3	1.1	2.7	2.2
Paraffins	vol %		99.6	98.9	89.4	82.0
Total Aromatics	vol %	26.5 max	0.1	0	8.0	15.8
Total Sulphur	mg/kg	3000	<1	<1	<1	<1
Total Nitrogen	mg/kg		<1	<1	<1	<1
Bromine No	gBr/100g		<0.5	<0.5	<0.5	<0.5
VOLATILITY						
IBP	°C	Report	137.6	150.9	151.0	153.4
10 %	°C	205.0max	155.6	158.1	158.9	160.3
20 %	°C		158.6	161.0	161.4	162.7
30 %	°C		161.8	163.0	163.7	164.6
40 %	°C		164.9	165.0	165.7	166.6
50 %	°C	Report	168.1	167.1	167.6	168.6
60 %	°C		171.2	169.4	169.9	170.7
70 %	°C		175.0	172.1	172.5	173.3
80 %	°C		179.0	175.6	175.8	176.1
90 %	°C	Report	184.3	181.7	181.1	181.1
95 %	°C		189.3	187.6	186.3	186.1
FBP	°C	300.0max	194.1	193.1	193.6	192.3
Recovery	vol %		98.0	98.5	98.4	99.0
Residue	vol %		0.6	1.0	1.0	0.5
Loss	vol %		0.5	0.5	0.6	0.5
T ₅₀ -T ₁₀	°C	> 15	12.5	9.0	8.7	8.3
T ₉₀ -T ₁₀	°C	> 40	28.7	23.6	22.2	20.8
Flash Point	°C	38.0 min	38.5	45.0	41.5	41.0
Density @ 15 °C	kg/L	0.775 – 0.840	0.734	0.775	0.775	0.775
Density @ 20 °C	kg/L	0.771 – 0.836	0.730	0.771	0.771	0.771
FLUIDITY						
Freezing Point	°C	-47.0 max	-50.5	-58.5	-58.1	-58.4
Viscosity@ -20 °C	mm ² /s	8.0 max	2.5	3.1	2.8	2.8
Viscosity@ 40 °C	cSt		0.97	1.14	1.03	0.97
COMBUSTION						
Specific Energy	MJ/kg	42.8 min	44.3	43.8	43.6	43.14

Property	Units	Limits	Results			
			GTL kerosene	RJ1	RJ2	RJ3
BLEND RATIO	GTL:Pin:Cym		100:0:0	68:32:0	68:23:9	68:14:18
Smoke Point	mm	25.0 min	26.0	25.0	26.0	25.0
Naphthalene	vol %	3.0 max	<0.1	<0.1	<0.1	<0.1
Derived cetane number ex IQT™			62.8	51.1	51.0	49.8
CORROSION						
Copper Corrosion	-	1 max	1A	1A	1A	1A
THERMAL STABILITY (JFTOT) 260 °C						
Filter Pressure Differential	mmHg	25.0 max	0	0	0	0
Tube Deposit Rating		<3	<1	<1	<1	<1
CONTAMINANTS						
Existent gum	mg/100mL	7.0 max	0.3	0.9	0.9	0.2
Water reaction: interface rating		1b max	1b	1b	1b	1b
Water content	mg/kg	80 max	51	35	35	38
MSEP RATINGS						
Microsep – w/o Static Dissipator Additive		85 min	93	90	89	93
CONDUCTIVITY						
Conductivity	pS/m	50 – 450	7	0	0	5
LUBRICITY						
BOCLE, WSD	mm	0.85 max	0.68	0.67	0.68	0.82

* Red coloured properties means outside of limits.

The renewable jet fuel blends (containing *p*-cymene and pinane) conform to almost all Jet A-1 specifications except the conductivity and distillation gradient specifications. The conductivity of the renewable jet fuel blends is very low (0 – 5 pS/m), and would therefore need the addition of a static dissipater additive such as Stadis® 450, which is already a common practise during jet fuel dispatch. The density specification conformance of the renewable jet fuel blends is marginal, which indicates that perhaps a higher concentration of the renewable molecules is needed for real world implementation. The cetane number of the renewable jet fuel blends was comparable to that of conventional jet fuel.

A full specification analysis of GTL kerosene and the renewable blended fuels (GTL kerosene with *p*-cymene and limonane) were evaluated according to the ASTM test methods as contained in DEFSTAN 91-91 for Jet A-1 and are summarized in Table 10.

Table 10. Full specification properties of GTL kerosene and the blended fuels containing *p*-cymene and limonane.

Property	Units	Limits	Results			
			GTL kerosene	RJ4	RJ5	RJ6
BLEND RATIO	GTL:Lim:Cym		100:0:0	40:60:0	45:50:5	52:33:15
APPEARANCE						
Visual			PASS	PASS	PASS	PASS
Colour, Saybolt	-	Report	>+30	>+30	>+30	>+30
Particulate Contaminants	mg/L	1.0 max	0.2	0.5	0.7	0.9
COMPOSITION						
Total Acidity	mgKOH/g	0.015max	0.003	0.004	0.004	0.004
Olefins	vol %	5.0 max	0.3	0.0	0.0	0.0
Paraffins	vol %		99.6	98.0	92.0	85.4
Total Aromatics	vol %	26.5 max	0.1	2.0	8.0	14.6
Total Sulphur	mg/kg	3000	<1	<1	<1	<1
Total Nitrogen	mg/kg		<1	<1	<1	<1
Bromine No	gBr/100g		<0.5	<0.5	0.61	<0.5
VOLATILITY						
IBP	°C	Report	137.6	159.1	158.0	153.9
5 %	°C		152.4	167.1	166.9	164.9
10 %	°C	205.0max	155.6	168.0	167.8	166.3
20 %	°C		158.6	170.9	170.9	170.0
30 %	°C		161.8	172.2	172.3	171.9
40 %	°C		164.9	173.3	173.7	173.6
50 %	°C	Report	168.1	174.3	174.9	175.1
60 %	°C		171.2	175.3	176.2	176.5
70 %	°C		175.0	176.8	177.4	178.2
80 %	°C		179.0	178.5	179.4	180.3
90 %	°C	Report	184.3	181.5	183.2	183.9
95 %	°C		189.3	185.5	187.9	188.0
FBP	°C	300.0max	194.1	198.9	200.5	196.4
Recovery	vol %		98.0	98.5	98.7	98.8
Residue	vol %		0.6	0.6	0.5	0.7
Loss	vol %		0.5	0.5	0.5	0.4
T ₅₀ -T ₁₀	°C	> 15	12.5	6.3	7.1	8.8
T ₉₀ -T ₁₀	°C	> 40	28.7	13.5	15.4	17.6
Flash Point	°C	38.0 min	38.5	41.5	41.5	41.0
Density @ 15 °C	kg/L	0.775 – 0.840	0.734	0.776	0.776	0.776
Density @ 20 °C	kg/L	0.771 – 0.836	0.730	0.774	0.773	0.773
FLUIDITY						
Freezing Point	°C	-47.0 max	-50.5	-67.6	-66.1	-62.8
Viscosity@ -20 °C	mm ² /s	8.0 max	2.5	2.7	2.6	2.4
Viscosity@ 40 °C	cSt		0.97	nd	1.01	0.96
COMBUSTION						

Property	Units	Limits	Results			
			GTL kerosene	RJ4	RJ5	RJ6
BLEND RATIO	GTL:Lim:Cym		100:0:0	40:60:0	45:50:5	52:33:15
Specific Energy	MJ/kg	42.8 min	44.3	43.7	43.6	43.4
Smoke Point	mm	25.0 min	26.0	32.0	32.0	31.0
Naphthalene	vol %	3.0 max	<0.1	<0.1	<0.1	<0.1
Derived cetane number ex IQT™			62.8	nd	nd	nd
CORROSION						
Copper Corrosion	-	1 max	1A	1A	1A	1B
THERMAL STABILITY (JFTOT) 260 °C						
Filter Pressure Differential	mmHg	25.0 max	0	0	0	0
Tube Deposit Rating		<3	<1	<1	<1	<1
CONTAMINANTS						
Existent gum	mg/100mL	7.0 max	0.3	1.3	1.5	0.9
Water reaction: interface rating		1b max	1b	1b	1b	1b
Water content	mg/kg	80 max	51	21	32	38
MSEP RATINGS						
Microsep – w/o Static Dissipator Additive		85 min	93	92	94	96
CONDUCTIVITY						
Conductivity	pS/m	50 – 450	7	1	1	1
LUBRICITY						
BOCLE, WSD	mm	0.85 max	0.68	0.53	0.61	0.59

* Red colored properties means outside of limits.
nd = not determined due to sample volume limitation.

The renewable jet fuel blends (containing *p*-cymene and limonane) conform to almost all Jet A-1 specification requirements, except the conductivity and distillation gradient specifications as seen previously. The lower conductivity is not a concern and can be rectified by the addition of static dissipater additive which is a general practice in jet fuel dispatching. These renewable jet fuel blends (RJ4, RJ5 and RJ6) contain significant quantities of renewable components (> 50 vol%) which in reality might not be economically feasible, even though this work had confirmed the technical feasibility of the blends.

3.3. GTL kerosene/Byogy renewable jet fuel

a) Properties of Byogy renewable jet fuel

The hydrocarbon composition of the Byogy renewable jet fuel as determined by GCxGC is shown in Figure 12.

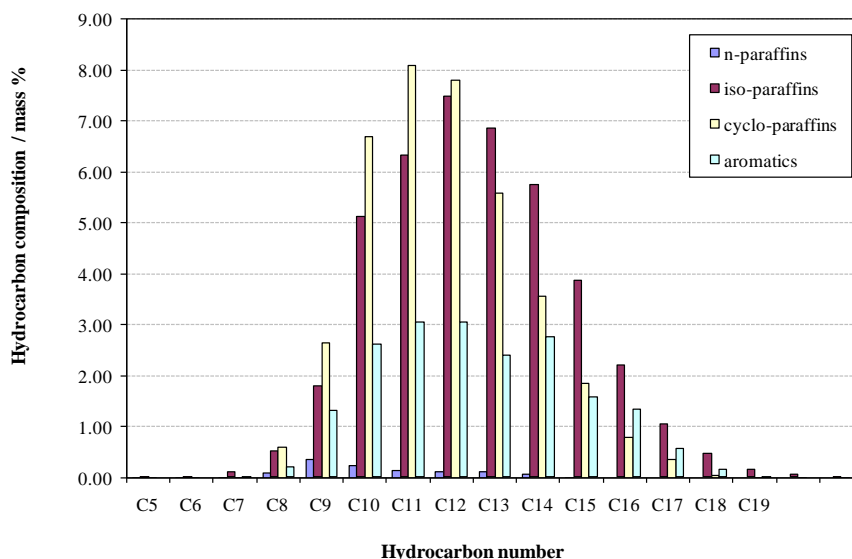


Figure 12. The hydrocarbon composition Byogy's renewable jet fuel as determined by GCxGC.

The Byogy renewable jet fuel contains mainly *iso*-paraffins and cycloparaffins and some aromatics. The *iso*-paraffins will result in the jet fuel having excellent cold flow properties and the aromatics and cycloparaffins will yield a high density jet fuel. The Byogy renewable jet fuel is a 100% renewable fully synthetic jet fuel and therefore an excellent drop-in replacement fuel for petroleum-derived jet fuel.

The blending of Byogy's renewable jet fuel with GTL kerosene would produce excellent synergies due to the presence of aromatics and cycloparaffins, besides increasing the renewable content in GTL kerosene. GTL kerosene could potentially provide sufficient volumes necessary for world jet fuel blending with renewable jet fuel.

b) Blending study

Critical jet fuel analysis of the individual test fuels and GTL kerosene blended with Byogy's renewable jet fuel are shown in Table 11. Note that the test fuels were evaluated against the requirements of ASTM D 7566, "Table A1.1 Detailed Batch Requirements; Hydroprocessed SPK".

Table 11. Critical jet fuel analysis of Byogy's renewable jet fuel and GTL kerosene blends.

Line No.	Property	Limits	GTL kerosene	Byogy Renewables	GTL/Byogy 40:60 blend
COMPOSITION					
1	Acidity, mg KOH/g	0.015 (max)	0.003	0.001	0.009
VOLATILITY					
2	Initial boiling point, °C	Report	137.6	151.5	146.3
3	10% recovered, °C (T10)	205 (max)	155.6	170.5	161.2
4	50% recovered, °C (T50)	Report	168.1	207.1	187.8
5	90% recovered, °C (T90)	Report	184.3	263.8	250.4
6	Final boiling point, °C	300 (max)	194.1	298.0	289.0
7	T ₉₀ – T ₁₀ , °C	22 (min)	28.7	93.3	89.2
8	Flash point, °C	38 (min)	38.5	45.5	40.5
9	Density @ 15 °C, kg/L	0.730 – 0.770	0.734	0.803	0.775
FLUIDITY					
10	Freezing point, °C	-40.0 (max)	-50.5	<-70.0	-65.4
11	Viscosity @ -20 °C, cSt	8.0 (max)	2.1	5.4	4.8
COMBUSTION					
12	Net heat of combustion, MJ/kg	42.8	43.8	43.4	43.6
13	Smoke point, mm	18.0 (min)	26.0	23.0	23.0
14	Naphthalenes, vol%	<3	<1	<1	<1
THERMAL STABILITY					
15	Control temperature, °C	325 (min)	360	325	325
16	Filter pressure drop, mm Hg	25 (max)	0	4	0
17	Tube deposit rating	<3	<1	>4P	1A
CONTAMINANTS					
18	Existent gum	7.0 (max)	0.3	5.3	0.5

The neat Byogy renewable jet fuel met most of the critical jet fuel analysis and can be used on its own as a renewable fully synthetic jet fuel. The Byogy renewable jet fuel contained aromatics which relates to the higher density of 0.803 kg/L. According to the GCxGC analysis, 19.1 mass% aromatics were found to be present in the Byogy renewable jet fuel. The Byogy renewable jet fuel had excellent cold flow properties due to the presence of *iso*-paraffins. A blend of 40:60 vol% GTL kerosene and Byogy renewable jet fuel was required to produce a final Jet A-1 still meeting the density requirement. The Byogy renewable jet fuel and its blend with GTL kerosene met almost all of the critical Jet A-1 analysis with the exception of the 325 °C JFTOT specification for ASTM D 7566. The stability results will be explained in detail in the next section.

3.4. Stability of test fuels

In the application of kerosene as aviation turbine fuel in modern aircraft, it is increasingly used as the primary coolant for various aircraft systems, thereby increasing the thermal stress that the jet fuel is exposed to. Fuel stability relates to the resistance of the fuel to changes in physical and/or chemical properties which could hinder aircraft performance or impact operation

negatively. Fuel stability is particularly sensitive to the presence of trace chemical species. Jet fuel stability is therefore an important performance requirement that needs to be assessed to ensure that the fuel is fit-for-use. FT kerosenes and HEFA fuel are expected to have inherently good thermal and oxidative stability due to their negligible quantities of hetero-atomic species, olefins and aromatics. The effect of adding renewables to the stability properties of FT kerosene was thus investigated.

3.4.1. JFTOT break point temperatures

The purpose of the JFTOT procedure is to measure the deposit formation tendencies of jet fuel when heated at a specified temperature, in the presence of oxygen and a metal surface. The JFTOT break point temperatures were evaluated for the GTL kerosene, HEFA's and model renewable blends. The results are shown in Table 12.

Table 12. JFTOT break point temperatures of GTL kerosene, HEFA's and renewable blends.

Entry	Blended kerosene fuel	Tube Code	Rating	JFTOT break point temperature / °C
1	GTL kerosene		1	>360
2	UOP's HEFA		1	>360
3	Syntroleum's HEFA		1	>360
4	GTL kerosene / UOP's HEFA (50:50)		1	>360
5	GTL kerosene / Syntroleum's HEFA (50:50)		<1	>360
6	GTL kerosene – Pinane (RJ1)		1	>360
7	GTL kerosene – Pinane – Cymene (RJ2)		1	>360
8	GTL kerosene – Pinane – Cymene (RJ3)		1	>360
9	GTL kerosene – Cymene (25 %)		1	>360
10	GTL kerosene – Limonane Product 1 – Cymene (RJ5)		<1	>340
11	GTL kerosene – Limonane Product 1 – Cymene (RJ6)		<1	>340
12	Byogy renewable jet fuel		>4P	<325
13	GTL kerosene / Byogy renewables (40:60)		1A	<325

From the results in Table 12, it is clear that GTL kerosene, both HEFA samples and their blended fuels have excellent JFTOT break point temperatures (greater than 360 °C) (entries 1 – 5, Table 12).

The renewable jet fuel-range molecules blended into GTL kerosene also have excellent JFTOT break point temperatures (greater than 360 °C) indicating that the model renewable molecules have no harmful effect on jet fuel stability (entries 6 – 11, Table 12). The renewable jet fuel blends containing Limonane Product 1 (RJ5 and RJ6) had a slightly lower break point temperature (greater than 340 °C) but was still excellent compared to blends containing pinane; this is believed to be due to small concentrations of di-olefinic impurities (limonene) present in the Limonane Product 1 (entries 10 – 11, Table 12). It needs to be noted that these renewable molecules are essentially pure, whereas the actual real Amyris fuels may contain impurities from the biochemical production processes that could have a negative effect on jet fuel stability. This negative effect can only be evaluated with actual Amyris fuel components produced from

genetically engineered microbes.

The Byogy renewable jet fuel by itself did not meet the JFTOT specification of 325 °C but this could be due to the presence of residual olefinic type of species as detected by GCxGC. More severe hydrogenation conditions will eliminate these olefins and produce a much more stable jet fuel that meets the JFTOT specification of 325 °C. Even though Byogy renewable jet fuel did not meet the JFTOT specification of 325 °C as required for an FT-SPK or HEFA fuel, it is highly likely that Byogy renewable jet fuel and its blend with GTL kerosene would have met the 260 °C JFTOT specification as stated in DEF STAN 91-91 or ASTM D 1655 for Jet A-1 or Jet A respectively. Insufficient sample volume prevented the testing of JFTOT at 260 °C. The blend of Byogy renewable jet fuel and GTL kerosene did not meet the JFTOT specification of 325 °C as well, but it is clear that the deposit formation tendency is less compared to the neat Byogy renewable jet fuel. This is most probably due to a dilution of the problematic olefinic species present in Byogy renewable jet fuel.

4. CONCLUSIONS

The future of the aviation industry and the rest of the transportation industry will inevitably be driven to the use of sustainable renewable fuels in increasing quantities, especially as more sources reach commercial maturity. This is due to the growing carbon footprint of the aviation industry and the critical need to slow down the growth in the rate of greenhouse gas (GHG) emissions. Tough emissions-driven penalties may be imposed in the future on companies producing jet fuels containing no renewable jet fuel components. Therefore Sasol Technology Fuels Research has been mandated to investigate the use of renewable fuels as part of Sasol's Fischer-Tropsch-based future product slates.

In this study, the “greening” of Gas-to-Liquids (GTL) kerosene with Hydroprocessed Esters and Fatty Acids (HEFA) samples as received from UOP and Syntroleum, with other potentially renewable jet-range molecules, and with Byogy renewable jet fuel were investigated, with a special focus on uncovering potential synergies. The objective of this study was to investigate and quantify any possible synergies that may exist between GTL kerosene and renewable kerosene or individual renewable molecules. The results of the study indicated the following major findings:

- The HEFA from UOP and Syntroleum was highly isomerised in nature and contained few *n*-paraffins. This allowed the HEFA to contain higher carbon number chains (*i.e.* heavier *iso*-paraffins), while still conforming to the required freezing point and final boiling point limits.
- There were discernable synergies observed in blends of GTL kerosene and HEFA besides only introducing renewable carbons into GTL kerosene. The density of the blends increased as more HEFA was added, this will allow more of the combined synthetic material to be added to petroleum-derived jet fuel while still meeting the minimum density requirement. The freezing points of the blends were also enhanced, when compared to those of the individual test fuels.
- The blended fuels containing renewable jet fuel-range molecules (*p*-cymene, pinane and limonane) met all the critical jet fuel properties as specified in DEF STAN 91-91 for Jet

A-1, except for the distillation gradient specification and conductivity. The conductivity of the renewable jet fuel can be improved by the addition of a static dissipater additive.

- The renewable jet fuel-range molecules have a number of positive effects on GTL kerosene such as improvement in freezing point and density. The renewable molecules also had no negative effect on jet fuel stability
- The Byogy renewable jet fuel had excellent cold flow properties due to the significant presence of *iso*-paraffins and lack of *n*-paraffins. It also showed a high density due to the presence of aromatics and cyclo-paraffins. The Byogy renewable jet fuel is a 100% renewable fully synthetic jet fuel and therefore an excellent drop-in replacement fuel for petroleum-derived jet fuel.
- The Byogy renewable jet fuel had a number of positive effects on GTL kerosene such as improvement in freezing point and density. A blend of Byogy renewable jet fuel and GTL kerosene met most of the critical Jet A-1 analyses.

Issues related to feedstock and production cost, life-cycle analysis (LCA), carbon footprint and sustainability of these particular HEFA's or renewable jet-range molecules have not yet been evaluated. This will be important in future work in order to determine the sustainability of each particular HEFA or renewable product.

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