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Using the poly-lactic acid as a fuel additive to enhance the physicochemical properties of aircraft jet fuel grade A1

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Abstract---The combustion quality and energy content of Jet fuel are important to fuel characteristics. There are some essential performance characteristics include density, flash point, freezing point, kinematic viscosity at -20o C, smoke point, and distillation temperatures should be detected and controlled. In this study, an experimental investigation was performed in order to determine the effects of polylactic acid, tetrahydrofuran, and Jet A1 fuel blends on the physical and chemical properties of blends. For this purpose, the fuel blends studied were analyzed using Miniscan IR which is a high speed for the comprehensive and automatic measurement of Jet fuels. From our results, it was found that the maximum flash point enhancement was obtained by S3 (95%Jet A1/5%THF/250ppmPLA) (42.3oC) while it was (38oC) for the blank Jet fuel A1. On the other hand, the decreasing of freezing point was achieved by S6 (95%Jet A1/5%THF/2500ppmPLA) (-65.4oC), while it was (-62.6oC) for the blank Jet fuel. The maximum net heat of combustion value was

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obtained by S2 (95%Jet A1/5%THF) (56.44 MJ/kg), while it was (55.62 MJ/kg) for the blank sample. Also, the density slightly increased for all Jet blended samples. The net heat of combustion values were enhancement, compared with blank Jet fuel A1.

***Keywords*---**biopolymers, fuel additives, fuel improvers, jet fuel, polylactic acid.

Introduction

Constant increase of aircraft fleets and exhausting crude oil deposits promote worsening of the world energy crisis. As a result we observe rise in prices for Jet fuel that today comprise about 25–30 % of passenger travel (Hileman J., et al., 2014). Moreover, the different products of Jet fuel combustion cause detrimental impact on surrounding environment (Jenkins R., et al., 2013). Aviation Jet fuel consist of hydrocarbon compounds (aromatics, olefins, cycloparaffins, and paraffins) also, contain chemical additives that are limited by the specific uses of the fuel (IARC, 1989). Jet A1's main components are paraffins and naphthenes. Paraffins burn cleaner than other hydrocarbons due to their high hydrogen-to-carbon ratio and high heat release per unit weight.

The fuel's density is increased by the cycloparaffin's that have lower H/C ratio, which results in less heat released per unit of weight. The Jet fuel's freezing point is decreased by these components. Total aromatic hydrocarbons are a good source of energy, but when burned, they produce smoke. Finally, olefins are unsaturated and have lower hydrogen-to-carbon ratios than paraffins. They are the hydrocarbons with the highest reactivity. (CRC, 1984).

Fuel additives for improving the Jet fuel physical and chemical characterizations in some cases, specific problems must be solved, while in others, additives are optional. The use of only officially approved Jet additives is permitted, and the quantity is controlled. (CRC, 1983). Due to its unique characteristics, poly-lactic acid, also known as the "polymer of the 21st century," is one of the most dynamic bio-polymers that adheres to a circular and green economy and is utilized worldwide in a wide range of applications. (Balla E., et al., 2021). Its origin from biomass such as corn, sugarcane and other renewable resources should also be remarked upon. The ring opening polymerization of lactide, which is produced by lactic acid, is one of the most sufficient methods for the production of polylactic acid; a product of the fermentation of agricultural compounds (Armentano I., et al., 2013).

PLA belongs to the group of aliphatic polyesters normally made from a–hydroxy acids, which include polyglycolic acid or polymandelic acid, and are considered as a biodegradable and compostable. PLA is a thermoplastic polymer with a high modulus and a high strength. It can be made from resources that are renewable on an annual basis to make products that can be used in the market for biocompatible/bio absorbable medical devices or industrial packaging. It can be easily processed using standard equipment for plastics to produce molded parts, films, or fibers (Jour M., et al., 1998).

PLA is thought to be a promising alternative for reducing the problem of disposing of municipal solid waste (MSW) because it offers additional end-of-life scenarios. PLA is a polymer that can be composted (J. Ren, 2011). Poly-condensation and/or ring-opening polymerization are typically used to produce high-weight, average molecular weight (Mw) PLA. (E. Rudnik, 2010).

Nature Works LLC is the main PLA producer, producing 150,000 metric tons per year (E.T. Vink, 2015). In the last 25 years, the number of published research studies and reports on PLA has increased exponentially as a result of its widespread market penetration, growing production, and increased global attention (A.S. Mirabal, 2013).

The aim of this study was experimentally investigated the physicochemical properties of Jet A1 blended with PLA (bio-polymer) as renewable chemical additive for purpose of enhancing Jet fuel properties to be safer and less harmful on the environment and to compare blended Jet fuel samples properties with American Society for Testing and Material (ASTM) standards.

Materials and Methods

Materials

Biopolymer

PLA 4060D is trade name of PLA, was purchased from Nature Works USA. It contains L-lactide content of around 88 weight% and its amorphous polymer has glass transition temperature (Tg) of 55-60°C.

Solvent

THF was purchased from Chengdu Kelong Chemical Reagent Co., China. THF appears as a transparent, colorless liquid with an ethereal scent. lower in density than water. It has 6°F as a flash point. Fumes are heavier than air.

Jet fuel

The Jet A1 fuel used in this work was obtained from Miser Petroleum Company. The Jet A1 fuel was stored at room temperature. The storage conditions did not result in any phase separation.

Instrumentation & Methodology

Samples Preparation

Four PLA levels (50, 200, 350, and 500 mg) were dissolved in a mixtures of 190 ml of Jet A1 and 10ml of THF and dissolution reaction by temperature and time set at 30 min., the following steps were used for experimental measurement:

- 190ml of Jet A1 was measured out; then it was poured into the reaction conical flask (reactor).
- 10ml of THF was measured out by pipet; then it was poured into the same conical flask.

- Desired amount of PLA, e.g. 50 mg, was poured into the mixture with stirring under suitable temperature.
- Repeated the previous steps to prepare the other samples with different mass of PLA as shown in table (1).

Table (1): represents PLA properties of the used bio-polymer (Nature Works LLC, 2022).

Sample ID	Fuel Samples contents	PLA Content (mg)	PLA concentration (ppm)
S1	Jet A1	0	0
S2	95%Jet A1+5%THF	0	0
S3	95%JetA1+5%THF+ 250ppmPLA	50	250
S4	95%JetA1+5%THF+ 1000ppmPLA	200	1000
S5	95%JetA1+5%THF+ 1750ppmPLA	350	1750
S6	95%JetA1+5%THF+ 2500ppmPLA	500	2500

- The PLA-Jet fuel blends were labeled and set aside to be stored for testing as shown in figure (1).

Figure (1): Different jet fuel samples

- Jet fuel blends samples were tested by using GC/MS and Miniscan IR instruments to determine specifications at temperature 20^{o}C and their chemical compositions.

Experimental Process

Miniscan IR instrument

The specifications of the jet fuel blended samples including: flash point, density, freezing point, smoke point, kinematic viscosity at -20^{o}C, and distillation temperatures were measured by Miniscan IR vision instrument according to ASTM specifications as shown in figure (2).

Figure (2): Minisan IR Vision instrument

It has fitted with an interferometer that can measure Jet A1's physical and chemical parameters and perform spectral analyses at wavelengths ranging from 630 to 4000 cm^{-1}. The long estimation time around 60 second. (Teixeira et al., 2008).

Advantages of IR Spectroscopy

The majority of the fuel's parameters can be determined simultaneously from a single measurement by the IR spectrum because it contains direct information about specific molecular structures. Microprocessors can automatically evaluate the spectrum and produce the final results, allowing the IR instrument to be automated. Only an electrical power line and no sample preparation are required. When compared to other types of analysis, the measurement only takes about one minute per analysis (Roland Aschauer, 2011).

Principle of IR Spectroscopy

Electromagnetic radiation with wavelengths between 0.7 μm and 100 μm is known as infrared radiation. This scope of frequency is additionally partitioned into the close IR (NIR) range (frequencies 0.7μm to generally 4μm), mid-IR (frequencies 4μm to around 20 μm), and far-IR (frequencies 20μm to 100 μm). The majority of analytical applications make use of NIR and mid-IR spectroscopy. In IR spectroscopy, the intensity of the transmitted radiation is measured as a function of wavelength when IR radiation in the desired wavelength range is directed through the sample to be analyzed. Excitation of the sample's molecule vibrations is the process that causes the sample to absorb IR radiation. Only radiation with wavelengths that correspond to the energy difference between the ground and excited vibrational states can stimulate these vibrations. These wavelengths vary depending on the molecule; besides there are normally various vibrations in a given particle. Because of this, IR spectroscopy enables the simultaneous measurement over a specific wavelength range of many distinct substances in a single sample. The intensity of the IR radiation passing through the sample at that wavelength decreases if a vibration is excited by radiation of a particular wavelength. The radiation decreases and the number of vibrations that can be excited increases with the number of molecules present. Accordingly, the convergences of various substances can be resolved quantitatively by IR spectroscopy (Roland Aschauer, 2011).

Chemical Characterization GC/MS

Understanding the composition and characteristics of fuel necessitates the identification and quantification of individual compounds in Jet fuel samples. In addition, the properties of jet A1 fuel are directly related to the presence of paraffin, naphthenes, aromatics, and olefins. The different Jet fuel samples were analyzed by an Agilent Technologies 7890A Gas Chromatograph connected with Agilent 5975C Mass Selective Detector linked to NIST 2.0 f Mass Spectral Search Program. GC was installed with Restek Rtx-170 column with dimensions of 60µm x 250µm x 0.25µm. A 10 µL syringe size was used, and a 30:1 split ratio of 1 µL of sample was injected. The parameters of the front inlet were set to: 280°C, 6.7776 psi, total flow He 54 mL/min, septum cleanse flow. Column flow (9.5 psi, 19.9 cm/s, 0.6 mL/min, 7.0 min hold time). Oven program was set temperature at 35°C for 3 min and then 2 °C/min to 50°C for 1 min and afterward 2°C/min to 75°C for 1 min. Run time was 56.667 min.

The net heat of combustion calculations

The net heat of combustion for different blended jet fuel samples, sulfur-free basis was calculated according to below equations (Bert, 1973):

$$Q_{p1} = [5528.73 - 92.6499(A) + 10.1601(T) (6) + 0.314169(AT)]/D + 0.0791707(A) - 0.00944893(T) - 0.000292178(AT) + 35.9936$$

Where:
Q_{p1}: net heat of combustion, MJ/kg, sulfur-free basis,
A: aromatics, volume %,
D: density, kg/m3 at 15°C, and
T: volatility: boiling point or average of test method D 86 10 %, 50 %, and 90 % points, °C.

To correct for the effect of the sulfur content of the fuel on the net heat of combustion, apply the following equation:

$$Q = Q_p *[1 - 0.01(S_1)] + C (S_1)$$

Where:
Q: net heat of combustion, megajoules/kilogram, of the fuel containing S_1 weight percent sulfur,
S_1: sulfur content of the fuel, mass %, and
C: 0.10166 (SI units) = a constant based on the thermochemical data on sulfur compounds.

The suitable mixes between the PLA and Jet A1 fuel were determined. The standard characteristics of the different blends were comparable to fuel properties of Jet A1 fuel as per DEF. STAN 91-091 and ASTM standards.

Results and Discussions

The Characteristic Properties of PLA

PLA is a thermoplastic monomer derived from renewable, organic sources, its properties mentioned in table (2).

Table (2): represents PLA properties of the used bio-polymer (NatureWorks LLC, 2022).

Physical Properties	Ingeo 6202D	ASTM Method
Specific Gravity	1.24	D792
Relative Viscosity	3.1	CD Internal Viscotek Method
Melt Index, g/10 min (210°C)	15-30	D1238
Melt Density (230°C)	1.08	----
Glass Transition Temp. (°C)	55-60	D3417
Crystalline Melt Temp. (°C)	155-170	D3418

Properties of the Obtained PLA - Jet A1 blends

The chromatograms of various blended jet fuel samples are depicted in figure (3). These molecules are identified in terms of their major compounds, residence time, molecular form, and classification.

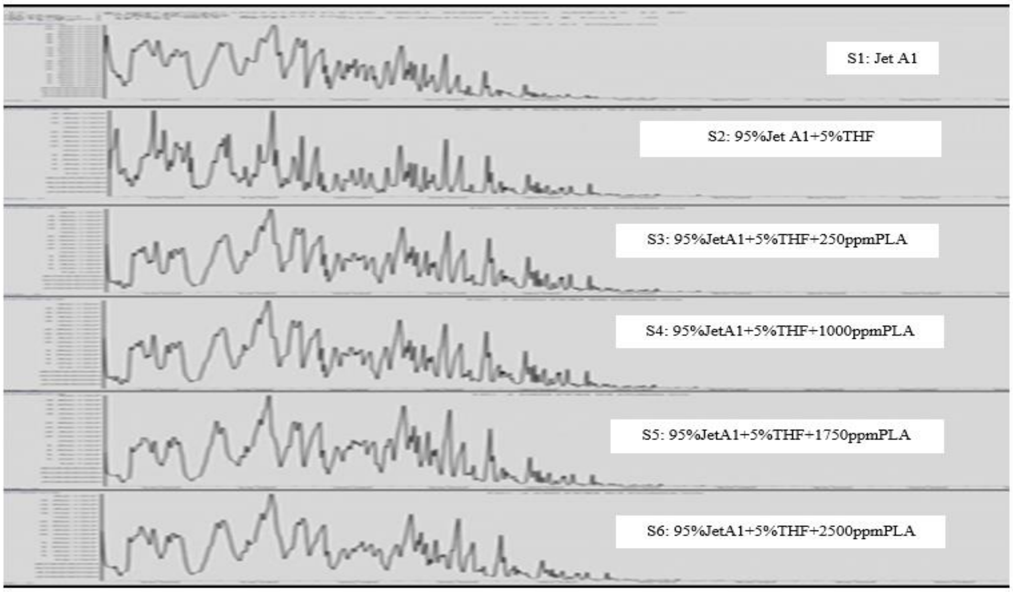

Figure (3): GC/MS chromatograph of different jet fuel samples

The main compounds in S1 (Jet A1) were between C8 and C10 (89.55%) carbon atoms, followed by C6 (5.55%), C13 (2.72%), C18 (1.17%) C16 (0.95%), and C11 (0.18%), also compounds in the range from C6 to C18 were found. The main compounds in S2 (95%JetA1/5%THF) were between C8 and C10 (82.31%) carbon atoms, followed by C7 (6.74%), C6 (2.22%), C16 (1.41%), C11 (0.74%), C12 (0.32%), C20 (0.31%), then C21 (0.25%), also compounds in the range from C6 to C21 were found. So, the Jet A1 fuel tends to concentrate the range of molecules with carbon atoms between (C8 to C10).

The main compounds in S3 (95%Jet A1/5%THF/50mgPLA) were between C8 and C10 (95.4%) carbon atoms, followed by C5 (2.27%), C11 (0.39%), C25 (0.22%),C13 (0.20%), and C16 (0.34%), also compounds in the range from C5 to C25 were found. The main compounds in S4 (95%Jet A1/5%THF/200mgPLA) were between C8 and C10 (81.62%) carbon atoms, followed by C6 (5.42%), C7 (4.92%), C12 (2.51%), C11 (0.39%), C16 (0.82%), C18 (0.81%), C11 (0.60%), C21 (0.14%), and C24 (0.21%), also compounds in the range from C6 to C24 were found.

The main compounds in S5 (95%Jet A1/5%THF/350mgPLA) were between C8 and C10 (96.17%) carbon atoms, followed by C4 (0.79%), C15 (0.8%), C16 (0.5%), C11 (0.38%), C18 (0.31%), and C21 (0.08%), also compounds in the range from C4 to C21 were found. The main compounds in S6 were between C8 and C10 (89.03%) carbon atoms, followed by C16 (4.48%), C11 (1.86%), C15 (1.18%), and C20 (0.31%), also compounds in the range from C8 to C20 were found. So, the S5 (95%Jet A1/5%THF/350mgPLA) fuel tends to concentrate the range of molecules with carbon atoms between (C8 to C10).

Table (3) represents the main compounds identified in each of the PLA- Jet A1 blends profiles. There are several parameters, which affect the physical and chemical characterizations of PLA- Jet A1 blends.

Table (3): Content of the different blended Jet A1 samples (m % of total quantified fuel)

Parameters	S1	S2	S3	S4	S5	S6
n-&iso-paraffin, m%	24.8	23.9	22.6	17.5	21.4	25.6
Olefin , m%	11.7	1.29	1.56	4.97	4.43	0.68
Sulfurous acid , m%	0.95	0	0	0.14	0.08	0
Sulfur, m%	0.37	0	0	0.05	0.03	0
Aromatics , m%	24.8	20.8	23.8	21.4	23.8	24.5
Naphthene , m%	29.1	41.9	42.5	44.63	38.2	35.8
Ester , m%	2.66	2.24	1.5	4.76	12.0	5.34
Alcohol , m%	2.74	2.12	2.76	5.89	4.19	2.81
Naphthalene , m%	0.11	0.26	0.09	0.11	0.53	0.19
Total, m%	94.4	91.2	96.6	95.1	98.3	95.2

These parameters were studied to attain the optimized characterizations of different Jet fuel samples. The specifications and characteristics of the obtained blends were detected as per ASTM standards. The measured characteristics, such as: freezing point, flash point, density, kinematic viscosity at -20°C, smoke point, and distillation temperatures were listed below in the tables and the figures.

The suitable mix between the PLA and Jet Fuel

In this work, many mixes were prepared between PLA, THF and Jet A1. The most suitable blend was S4 (95%Jet A1/5%THF/1000ppmPLA). The mixes results were in appropriate variety related to Jet A1 as per DEFSTAN 91-091 and ASTM standards.

Density

The ratio of the weight of Jet A1 fuel in grams to its volume is represented by the fuel's density. Density of Jet A1 fuel is very essential to quantify aircraft weight before landing and take-off operations, as fuel is normally metered by volume. At 15 °C, Jet A1 fuel must have a density of 0.775 to 0.840 g/mL, as specified by ASTM D1655 (2004).The Jet A1 density is one of the important properties in the ignition and processing of Jet A1. Because the fuel of high-density has an additional weight that is loaded on the aircraft engines and consumes additional amount of fuel during the ignition process. In case of S1 (Jet A1), the value of density was (0.787 g/cm^3) as per ASTM D-4052 (ASTM, 2011). The mixes densities are slightly increased but in the range of ASTM standards (0.789 to 0.791 g/cm^3) as shown in figure (4).

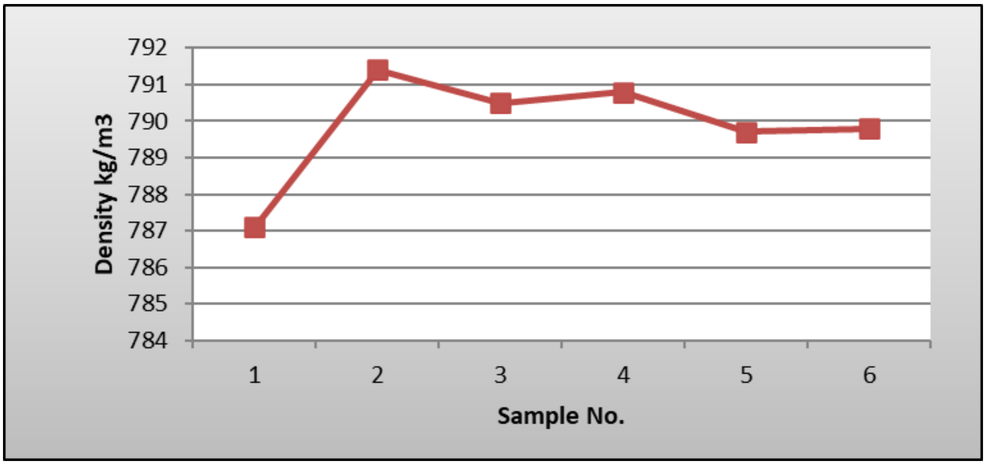

Figure (4): Density values measured for different fuel samples

Flash Point

The temperature at which a flame spark can ignite the fuel-air mixture is known as the flash point. (Sandun F., 2007). The flash point has an effect on the fuel's combustibility because it is related to volatility. Fuel handling requires fire safety detection due to the electrostatic hazards in pumping distillate fuels, so the flash point of Jet A1 should be as high as possible. ASTM D1655 (2004) determines a minimum flash point of 38°C. The obtained flash point value of the S1 (Jet A1) was 38.6 °C, while the other blended Jet fuel samples with PLA were increased within the range of ASTM (39°C – 42.3°C) except the S2 (95%Jet A1+5%THF) was 38.3°C that below Jet A1 flash point value but complying with ASTM specifications. Table (4) shows the flash point of blended Jet fuel samples. These blended Jet fuel samples have high initial boiling point than Jet A1 as shown in table (5), decreasing the volatility and, consequently, increasing the flash point.

Table (4): Flash point values measured for different fuel samples

Sample No.	ASTM Limits	Results ^{o}C	Standard Method	Off/On Specifications Jet A1
1	38^{o}C (Minimum)	38.6	ASTM D93	ON spec.
2		38.3		ON spec.
3		42.3		ON spec.
4		41.0		ON spec.
5		39.0		ON spec.
6		39.5		ON spec.

Freezing point

The ability of Jet A1 fuel to be pumped at low temperatures is influenced by the freezing point. The temperature at which crystals of hydrocarbon, formed on cooling; disappear when allowing to rise the fuel temperature under specified conditions is known as the freezing point. For Jet A1 fuel, the freezing point standard should be (maximum -47°C) as per ASTM D-7153 (ASTM, 2010). The obtained freezing point values of the prepared PLA- Jet blends were within the range of ASTM (-64.3°C to -65.4°C) and for Jet A1 sample was (-62.6) as shown in figure (5), the maximum value of freezing point for the mix of Jet A1 with THF only without adding PLA was (-57.6°C) more 5^{o}C than Jet A1 sample but within ASTM standards.

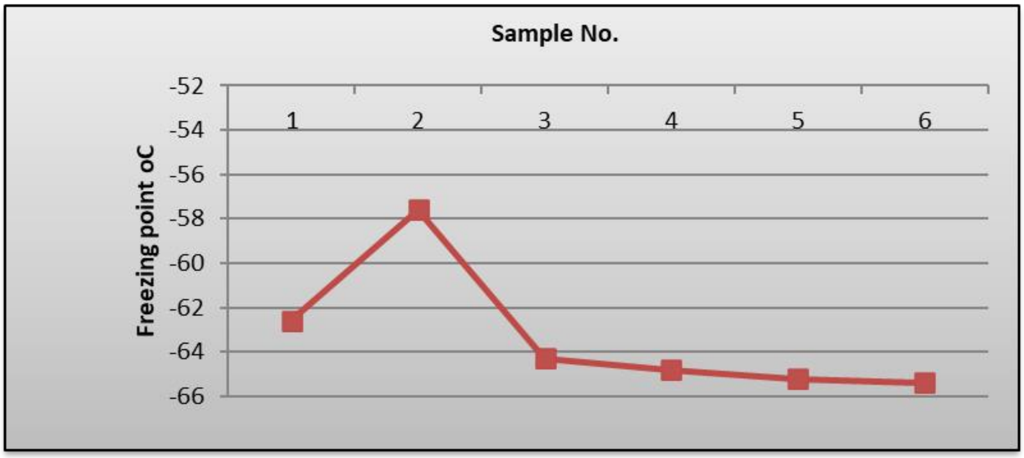

Figure (5): freezing point values measured for different fuel samples

Distillation

The "distillation" standard is one of primarily tests used to address Jet A1 fuel's vaporization characteristics and to be controlled to certain standards. Volatility is ability of Jet fuel to vaporize or change from liquid to vapour. The tendency of a fuel to vaporize is also characterized by determining a series of temperatures at which various percentages of the fuel have evaporated (boiling temperatures). The temperatures at which 10%, 50%, and 90% evaporation occurs are often used to characterize the volatility of Jet A1. The obtained distillate values of the prepared Jet blends as shown in table (5) were within the range of ASTM D 86 & D 2887 standard (ASTM, 2011).

Table (5): Distillation values measured for different fuel samples

Distillation	limits	Test method	S1	S2	S3	S4	S5	S6
Initial Boiling point	Report.	D 86 & D2887	158 °C	--- °C	164 °C	163 °C	162 °C	161 °C
recovery 10 % V/V	Max. 205°C		163 °C	164 °C	168 °C	167 °C	164 °C	166 °C
recovery 50 % V/V	Report.		186 °C	199 °C	189 °C	190 °C	187 °C	188 °C
recovery 90 % V/V	Report.		228 °C	250 °C	228 °C	230 °C	232 °C	230 °C
End Point	Max. 300°C		204 °C	237 °C	225 °C	225 °C	224 °C	224 °C
T_{50}-T_{10}	Min. 15°C		22.6°C	34.8°C	20.8°C	22.1°C	22.8°C	22.3°C
T_{90}-T_{10}	Min. 40°C		65.3°C	86.1°C	59.7°C	62.6°C	67.3°C	64.4°C

Viscosity

Fuel pumpability and filter plugging can suffer as a result of viscosity values that are too high. Furthermore, consistency is connected with the size of drop in sprays generated by burner nozzles. ASTM D1655 determines a viscosity value at -20 °C of 8 mm^2/s for Jet A1. The viscosity measured values were 2 mm^2/s for all Jet fuel blended samples at -20°C and all values were within the range of ASTM D1655 (ASTM, 2004).

Smoke point

The smoke point standard is one of the tests used to determine the maximum height in millimetres (mm) at which Jet fuel will burn without smoking (IP Standards, 1983). Table (6) shows the concentration of total aromatic compounds in different blended Jet fuel samples also an impact upon the quantity of smoke produced as shown in table (6).

Table (6): Smoke point values measured for different fuel samples

Sample No.	ASTM Limits & Method	Aromatics m%	ASTM Limits	Smoke No. mm	Off/On Specification Jet A1
1	25.5 (Max.) ASTM D 6379	18.7	18 (Min.) ASTM D 1322	24.8	ON spec.
2		18.3		20.8	ON spec.
3		19.0		23.8	ON spec.
4		18.9		21.4	ON spec.
5		19.3		23.8	ON spec.
6		18.8		24.5	ON spec.

Net heat of combustion

The net heat of combustion, which is often called specific energy or the lower heating value (LHV), is important to Jet fuel suppliers and consumers because it is the source of energy which is ultimately converted to usable power. Engine manufactures and their customers rely on determined specific energy to gage engine performance and thermal efficiency, which are quality assurance measurements done at the product level before shipping an engine for installation into an aircraft or a power generation platform (S. Kosir, 2020). The range specified by ASTM D1655, which is, "greater than or equal to 42.8 MJ/kg". Table (7) shows the values of the net heat of combustion.

Table (7): The net heat of combustion values calculated for different fuel samples

SN	Sample content	LHV (sulfur-free basis) MJ/kg	LHV (sulfur content of the fuel) MJ/kg	Off/On Specification Jet A1
1	Jet A1	55.66639	55.6208	ON spec.
2	Jet A1 (190 ml) +THF (10 ml)	56.44356	56.39729	ON spec.
3	Jet A1 (190 ml) +THF (10 ml) +PLA (50 mg)	55.80638	55.76074	ON spec.
4	Jet A1 (190 ml) +THF (10 ml) +PLA (200 mg)	55.83692	55.79125	ON spec.
5	Jet A1 (190 ml) +THF (10 ml) +PLA (350 mg)	55.77158	55.72597	ON spec.
6	Jet A1 (190 ml) +THF (10 ml) +PLA (500 mg)	55.77242	55.72682	ON spec.

Conclusion

The following conclusions can be recorded from this study's findings:

1. PLA and THF were improved Jet A1 properties as a green chemical additive; especially the flash point and the freezing point that give chance to treat and reuse Jet A1 in case of Jet A1 specifications are not met.
2. The properties and specifications of the prepared blends were combatable with ASTM standards.
3. The adequate mix between PLA and Jet A1 was S4 (95%Jet A1/5%THF/1000ppmPLA).
4. PLA may use as additive to upgrade civil aviation Jet A1 fuel to be used as military Jet B fuel due to enhancing the freezing point.
5. PLA was enhanced the net heat of combustion for different blends that is enhancing aircraft engine performance and reducing consumption of fuel.

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