

## Chemical Composition and Fuel Properties of Alternative Jet Fuels

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The chemical composition and fuel properties of nine alternative jet fuels (named as AJF 1-9) and three commercial jet fuels (named as CJF 1, 2 and 3) are reported in this work. The fuels were characterized by GC/MS, SEP-GC/MS (for quantification of oxygenated molecules), viscosity, density, water content, water solubility at 0 °C, carbonyl content, total acid number, elemental composition, calorific value, flash point, differential scanning calorimetry, and surface tension. The content of n-paraffins, iso-paraffins, olefins, naphthenes, and aromatics are reported. The fuel rich in aromatics (AJF 1) has the highest density (0.90 g/mL), C content (over 90 wt. %), and water solubility, lowest calorific value, and high surface tension. The fuels with high contents of light molecules have the lowest flash points (AJFs 1, 6, and 8). AJF 2 is the most viscous fuel due to the presence of a single relatively heavy molecule. The content of oxygenated compounds measured was in all the cases very low and comparable with the amount found in commercial jet fuels. Overall, these fuels comply with most of ASTM requirements and offer opportunities to develop specialized products.

*Keywords:* Alternative jet fuels; Fuel properties; Bioenergy

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### INTRODUCTION

The aviation industry is in fast expansion, with the number of passengers expected to increase from 2.4 billion in 2010 to approximately 16 billion in 2050 (IATA 2011). Nevertheless, the concern with increasing levels of carbon emissions, crude oil price volatility, and its impact on global warming is a serious concern for the aviation sector.

Although the aviation industry contribution to CO<sub>2</sub> emissions is much lower than other segments of the transport industry (only contributes to 2% of total GHG emissions) (Rosillo-Calle *et al.* 2012), this contribution is likely to increase 2 to 3% per year (Hong *et al.* 2013), as the industry is growing to meet the transportation demand (Hileman and Stratton 2014).

Therefore, in order to address this problem, the International Air Transportation Association (IATA) established a challenging goal of reducing the net CO<sub>2</sub> production of the aviation industry by 50% by 2050, compared with 2005 levels (Hileman *et al.* 2013). One promising approach to achieve this goal is the use of alternative jet fuels derived from renewable resources (Popp *et al.* 2014).

In the United States, Jet A is the main commercial jet fuel. In Europe Jet A-1 is the main civil jet fuel used (Maurice *et al.* 2001; Lenz and Aicher 2005). These fuels have similar properties, but the limit value for freezing point of Jet A is higher (-40 °C) than for Jet A-1 (-47 °C) (Lenz and Aicher 2005). Jet fuel produced from petroleum refining typically comply with ASTM requirements and its production is very reliable.

Until now, five alternative jet-fuels have been approved by ASTM (Maurice *et al.* 2001): Fischer-Tropsch; Hydro processed Synthesized Paraffinic Kerosene (FT-SPK) (Marano and Ciferno 2001; Spath *et al.* 2005; Wright *et al.* 2008; Henrich *et al.* 2009; Swanson *et al.* 2010; Staples *et al.* 2014), Fischer Tropsch Synthetic Kerosene Containing Aromatic (FT - SKA), Synthesized Paraffinic Kerosene from Hydroprocessed Esters and Fatty Acids (HEFA) (Pearlson 2011; Pearlson *et al.* 2013; Seber *et al.* 2014; Staples *et al.* 2014;), Direct Sugar to Hydrocarbon (DSHC) (Total and Amyris 2013), and Alcohol to jet. These fuels can be blended with commercial petroleum-based jet fuel up to 10 wt. % for DSHC, up to 30 wt. % for Alcohol to Jet and up to 50 wt. % for HEFA, FT-SPK and FT-SKA. Other processes that are under ASTM investigation are: Catalytic Hydrothermolysis (CH); Synthesized Kerosene (SK) Synthesized Aromatic Kerosene (SAK), and Hydrotreated Depolymerized Cellulosic Jet (HDCJ).

Several papers have been published on properties of alternative jet fuels (Starck *et al.* 2016). Corporan *et al.* (2011) studied the chemical, thermal stability, seal swell, and emission of six alternative jet fuels (three from Fischer Tropsch and three from hydroprocessing). Zhang *et al.* (2016) have recently reviewed the recent studies on alternative jet fuel combustion of alternative jet fuels. Hui *et al.* (2012) reported experimental studies on the derived cetane number, autoignition response, laminar flame speed, and extinction stretch rate for premixed combustion of alternative jet fuels. Won *et al.* (2016) reported some correlations to predict the global combustion *behavior* of petroleum derived and alternative jet fuels by simple fuel property measurements.

Most of the AJF pathways of interest to the Federal Aviation Administration (FAA), ASTM, CAAFI, and the industry rely on a final deoxygenation step through catalytic hydrotreatment (hydrogenation, hydrocracking, hydrodeoxygenation). Under certain circumstances (catalyst deactivation, changes in the composition of the feedstock, operational problems), the deoxygenation efficiency may decrease; this could cause some residual oxygenated compounds to remain in the fuel. There are several papers (Zabarnick 1994; Grinsted and Zabarnick 1999; Balster *et al.* 2006; Sobkowiak *et al.* 2009; Corporan *et al.* 2011; West 2011; Chuck and Donnelly 2014b) on the presence of polar fractions in petroleum derived jet fuels. Balster *et al.* (2006) studied the role of polar molecules in the autoxidative deposit formation of jet fuels. The polar fraction of fuels they investigated were mainly composed of phenols and other oxygenated molecules, which demonstrated that they were related to surface deposit. West (2011) studied the effect of potential homogeneous catalytic sources on autoxidation chemistry of jet fuel. When naphthenic acids are added alone to fuel, there is little effect on the rate of hydroperoxide decomposition. The authors were not able to find any paper on the nature and the content of oxygenated compounds in alternative jet fuels.

Thus, the main goal of this paper is to report the chemical composition and fuel properties of alternative jet fuels derived from different feedstocks focusing on the content of residual oxygenated compounds.

## EXPERIMENTAL

### Materials and Methods

#### *Source of jet fuels*

The Alternative Jet Fuels (AJF) herein studied were produced by different processes: DSHC, HEFA, FT, Alcohol to Jet (ATJ), Catalytic Hydrothermolysis (CH), and Hydrotreated Depolymerized Cellulosic Jet (HDCJ). Description of these technologies can be found elsewhere (Staples *et al.* 2014; De Jong *et al.* 2015; Mawhood *et al.* 2016; Wang and Tao 2016). The fuels studied in this project were kindly provided by the US Air Force Research Laboratory. The commercial jet fuels (CJF) were obtained from Shell, Valero, and NuStar. The nomenclature used to designate each of the fuels studied is listed in Table 1.

**Table 1.** Nomenclature Used to Designate Each of the Fuels Studied

Nomenclature	Source	Comments
AJF 1	Kior	Hydrotreated Kerosene, produced by HDCJ technology. Sample shipped from Air Force Research Laboratory (AFRL)
AJF 2	Amyris	Farnesane, produced by DSHC technology. Sample shipped by AFRL
AJF 3	ARA	ReadiJet (Jet A), produced by CH technology. Sample shipped by AFRL
AJF 4	Gevo	Gevo Jet Blend Stock, produced by ATJ technology. Sample shipped from University of Washington
AJF 5	UOP	Camelina, produced by HEFA technology. Sample shipped by AFRL
AJF 6	Sasol	FT-Coal, produced from FT technology. Sample shipped from University of Washington
AJF 7	Syntroleum	FT-Methane, produced from FT technology. Sample shipped from University of Washington
AJF 8	UOP	HEFA Camelina, produced from HEFA technology. Sample shipped from University of Washington
AJF 9	UOP	HEFA Tallow, produced from HEFA technology. Sample shipped from University of Washington
CJF 1	Shell	Jet A, conventional civil jet fuel. Sample shipped from AFRL
CJF 2	Valero	JP-5, conventional military jet fuel. Sample shipped from University of Washington
CJF 3	NuStar	JP-8, conventional military jet fuel. Sample shipped from University of Washington

#### *Chemical Characterization GC/MS*

Quantification and identification of individual compounds is important for understanding fuel composition and characteristics. Besides, the presence of aromatics and olefins must be known, as they can relate to problems in fuel properties and must be controlled.

The fuels studied were analyzed using an Agilent Technologies 7890A Gas Chromatograph linked to Agilent 5975C Mass Selective Detector with NIST 2.0 f Mass Spectral Search Program. GC was equipped with Restek Rtx-170 column with dimensions of 60m x 250 $\mu$ m x 0.25 $\mu$ m. 1  $\mu$ L of sample was injected with split ratio 30:1. Front inlet parameters were set as: 250  $^{\circ}$ C, 9.5 psi, total flow He 21.6 mL/min, septum purge flow. Column flow (0.6 mL/min, 9.5 psi, 19.9 cm/s, 5.0 min hold time). Oven

temperature was set at 45 °C for 10 min and then increased to 250 °C at the rate of 3 °C/min and final hold time was 5 min.

The internal standards method was used in this analysis (phenanthrene was used as internal standard). For the response factor calculation, solutions of internal standard, n-C7 to n-C18 compounds, xylene, toluene, naphthalene, and ethyl-benzene, all in a concentration of about 1 mg of compound per 1 g solvent (dichloromethane), were prepared. 1 g of each solution was then weighted and mixed. The sample mixture was then analyzed by GC-MS to calculate the response factors. Four different concentrations (0.1, 0.5, 1 and 5 mg/g) were prepared using HPLC grade methanol as solvent. The compounds quantified by each of the standards are listed on Table 2 below.

**Table 2.** Standards Used to Analyze the Peaks in the GC-MS Analysis of the Jet Fuels

Standard	Peaks analyzed with the same response factor
n-C7	Non-aromatic compounds, with 7 carbons or less
n-C8 to n-C17	Non-aromatic compounds, with 8 to 17 carbons, respectively
n-C18	Non-aromatic compounds, with 18 carbons or more
toluene	Toluene
xylene	Polysubstituted benzenes (one ring)
naphthalene	Polycyclic aromatic hydrocarbons
ethyl-benzene	Monosubstituted benzenes (one ring)

#### *Elemental Composition (CHN-O)*

This method is important to quantify the content of individual elements from which the ratio C:H can be calculated. The analysis for carbon, hydrogen, and nitrogen was conducted in a 630-100-300 RFB TRUSPEC CHN, serial number 4299, software version 2.71. First 5 empty blank foils were analyzed, and the blank correction was assigned in the software. After that, 3 conditioned samples (approx. 0.1 g of EDTA) were run before the next step. 3 standards (approx. 0.15 g of EDTA) were then run, and the drift correction was made in the software. Finally, the samples were prepared using 0.15 g of the fuel and 0.15 g of the standard, placed in the Carousel and analyzed (ASTM D5291 (2010)). The hydrogen content data collected by the US Air Force Research Laboratory (AFRL, kindly provided by Dr. Tim Edwards) obtained by the ASTM D7171 (2005) and D3701 (2001) methods was compared with our data.

#### *Water content*

The presence of water is undesirable and needs to be quantified. According to ASTM D7566 (2017), the maximum allowed in AJF is 75 ppm. Water content in the jet fuel was measured using Karl Fischer titration with a Mettler Toledo C20 Compact Karl Fischer Coulometer that has a measurement range of 1 ppm to 5% of water in samples (ASTM D6304 (2007)). The data collected by AFRL was also obtained by this method, and it is described in ASTM D6304 (2007).

#### *Identification and quantification of oxygenated molecules*

The identification and quantification of oxygenated molecules is important for understanding if the deoxygenation step is being efficient and what kind of oxygenated molecules remain in the fuels. The polar molecules were concentrated through Solid Phase Extraction (SPE) using a 6 mL Agilent SampliQ silica SPE cartridge. 10 mL

sample of jet fuel was analyzed per run. A volume of 12 mL hexane was used to rinse the cartridge and, after that, 11 mL of methanol eluted the polar species (Balster *et al.* 2006). The sample collected from SPE was analyzed by GC-MS. Both internal and external standards were used in this analysis and compared to have a good estimate of the accuracy of each method. Phenanthrene was used as internal standard at a concentration of 0.05 mg/g. For the response factor calculation, solutions of the internal standard with 2,2-dimethoxy-propane; hydroxy-acetic acid (glycolic acid); 2,5-dimethyl-2-hexanol; 3,4-dimethyl-3-hexanol; 5-methyl-3-hexanol, 2,4,4-trimethyl-1-pentanol; 2-ethyl-1-hexanol, 2-(2-ethoxyethoxy)-ethanol; cyclohexyl-ethanol; 3,4-dimethyl-phenol; 2,3,5-trimethyl-phenol, 2,4,6-trimethyl-phenol; 2-propyl-phenol, 3,4,5-trimethyl-phenol; 4-methoxycinnamic acid; tropic acid; 4-butyl-phenol; 2-hydroxyphenylacetic acid; 4-pentyl-phenol; phytol; 2-methyl-phenol (*o*-cresol); 2-(2-methoxyethoxy)-ethanol; 2,4-dimethyl-phenol, and 2-ethyl-phenol were prepared. All were prepared in a concentration of about 1 mg of compound per 1 g solvent (methanol). One gram of each solution was then weighted and mixed. The sample mixture was then analyzed by GC-MS to calculate the response factors. The analysis was performed in the same Agilent Technologies 7890A Gas Chromatograph used for the analysis of the oils.

#### *Total acid number*

Fuel corrosion problems are associated with the presence of acids. According to ASTM D1655 (2004), the acid number of jet fuels should be less than 0.1 mg KOH/g. The method used at WSU to measure acid number is described elsewhere (Christensen *et al.* 2011; Wu *et al.* 2014; Shao and Agblevor 2015). Briefly, a Mettler Toledo T50 titrator with a Mettler Toledo Rondolino was used to test the samples. Acetone was used as solvent and 0.1 M KOH in DI water standardized with potassium hydrogen phthalate was used as titrant (Shao and Agblevor 2015). The data collected by the AFRL was obtained following the ASTM D3242 (2001) standard method.

#### *Content of carbonyl groups*

The content of carbonyl groups was determined using a spectrophotometric technique (ASTM E411 (2012)). A series of standards using 2-butanone diluted in methanol was used for calibration. First a stock solution was prepared adding approximately 0.064 g of 2-butanone (Assay 99.8%) to a 100 mL glass stoppered volumetric flask and completing the volume to the mark with methanol. Then a sequence of 2, 4, 6, 8 and 10 mL aliquots of this stock solution was transferred to five 100 mL glass stoppered volumetric flasks and the volume completed with methanol, forming the standards. 2 mL aliquots of each standard were transferred to five 25 mL glass stoppered volumetric flasks.

An additional 2 mL sample of jet fuel was transferred to others 25 mL volumetric flasks to be analyzed and 2 mL of methanol were transferred to another 25 mL volumetric flask to serve as blank. To each flask, 2 mL of 2,4-dinitrophenylhydrazine was added and approximately 30 min were waited before completing the volume with a 100 g/L KOH solution and mixing well. After adding the KOH solution, a 12 min interval was allowed for color to develop and then, the absorbance was measured using a Shimadzu UV-2550PC UV/Vis Spectrophotometer at 480 nm, using a 1-cm cell.

## Fuel Properties

### *Density*

Fuel density is very important to quantify aircraft weight, as fuel is usually metered by volume. According to ASTM D1655 (2004), the density of Jet A / Jet A-1 fuel must be in the range of 0.775 g/mL to 0.840 g/mL at 15 °C. The density was determined using a cleaned and dried 10-mL Gay-Lussac pycnometer. The pycnometer was weighed and tared. The pycnometer was completely filled with fuel and closed with a stopper. The outside was carefully wiped and the filled pycnometer was weighed. The density of the liquid was calculated dividing the mass obtained by the volume of the pycnometer. The data collected by the US Air Force Research Laboratory was obtained following the ASTM D4052 (2011) method.

### *Viscosity*

High viscosity values can cause problems in fuel pumpability and filter plugging. Besides, viscosity is related to the size of droplet in sprays generated by burner nozzles. ASTM D1655 (2004) establishes a viscosity limit at -20 °C of 8 mm<sup>2</sup>/s for Jet A/Jet A-1, and 8.5 mm<sup>2</sup>/s for JP-5. The ASTM D445 (2006) method was followed. In this method, calibrated glass viscometers were used immersed in a temperature-controlled water bath filled with distilled water. The viscosity was measured at eight different temperatures (15 °C to 50 °C, in intervals of 5 °C). A viscometer with a range covering the estimated viscosity was selected. 7 mL of sample was inserted in each glass viscometer and time was allowed for the sample to reach bath temperature. Using air to apply pressure, the level of the fuel sample was adjusted to about 7 mm above the first timing mark in the instrument arm. The total time that the sample meniscus took to flow from the first to the second timing mark was measured and recorded. The kinematic viscosity is calculated by multiplying the measured time (in seconds) by the viscometer calibration constant (in mm<sup>2</sup>/s<sup>2</sup>). The procedure was repeated three times and the kinematic viscosity reported was an average of the three values obtained<sup>40</sup>. The viscosity data at -20 °C collected by the US Air Force Research Laboratory was also obtained following the ASTM D445 (2006) method.

### *Surface tension*

Surface tension has an important effect in atomization and ignition characteristics of jet fuels. There is no ASTM specification for jet fuel surface tension. The method used was the Du Noüy Ring Method with a LAUDA TD 2 Tensiometer. The ring used has dimensions  $R = 9.55$  mm and  $r = 0.2$  mm. Before and after every measurement, the ring was washed with solvent (acetone) and heated with a mini-torch unit. This is a very important step, as a small quantity of impurities (especially if they are surfactants) can cause a considerable change in the values of surface tension. Before the measurements, the du Noüy Ring was tared with standard deviation of 0.1 mg and then calibrated at standard deviation of 0.1 mg using a calibration weight of 500.00 mg. Measuring parameters (Mov. Speed = 5; Mov. Opt. = 20%; Pause = 1 min; Max. time = 15 min; Points of Stdv = 5; Stdv = 0.01 mN/m). Each fuel surface tension was measured twice and the average reported (ASTM D1331 (2014)).

### *High heating value*

ASTM D1655 (2004) specifies the lower limit for the low heating value (LHV) as 42.8 MJ/kg for Jet A and Jet A-1. The ASTM D4809 (2013) method was followed. An

IKA C200 Calorimeter was used in this analysis. The instrument was calibrated by combusting two tablets of certified benzoic acid (IKA C 723, Lot SZBD2180V, gross cal. val 26461 J/g). This process is repeated three times, and the average value obtained is inserted in the instrument for reference. The samples analyzed were prepared using around 4 g of jet fuel and the pressure in the vessel was set to 30 bar (ASTM D4809 (2013)). The heat of combustion data collected by AFRL and kindly provided by Dr. Tim Edwards for comparison purposes was also obtained by the ASTM D4809 (2013) method.

#### *Flash point*

Flash point relates to volatility, hence affects the combustibility of the fuel. It is crucial to determine fire safety in fuel handling. ASTM D1655 (2004) establishes a minimum flash point of 38 °C. This method was performed using the Small Scale Closed-Cup Apparatus, based on ASTM D3278 standard (ASTM D3278 (1996)). A Koehler K16200 instrument was used in the analysis. 2 mL sample was placed in the cup for testing and the initial temperature was set to the expected flash point for each fuel. The test flame was adjusted to a diameter of approximately 4 mm. The ignition source was applied, and when the flash was observed, the sample was cooled down by 5 °C and the flame was again applied every 1 °C after this temperature, until a flame was observed. If the flash was not observed at the first expected flash point, 5°C higher temperature was applied and the same procedure repeated. The temperature at which the flame was observed was recorded. The data collected by AFRL and kindly provided by Dr. Tim Edwards for comparison purposes was obtained by the ASTM D93 method.

#### *Equilibrium water content*

The equilibrium water content represents how much water a fuel can absorb from a saturated ambient in a certain temperature. There is no ASTM standard for equilibrium water content. Approximately, 80 mL of each fuel was placed in beakers and stored in desiccators containing silica gel for at least 24 h to assure that there was no free water left in the fuel. After 24 h, the beaker containing the fuel was transferred to a bigger beaker containing a vial with 1 mL of distilled water. This beaker was placed inside a refrigerator with controlled temperature, sealed, and kept in constant stir with a magnetic stirrer for at least 16 hours to achieve water saturated equilibrium. Equilibrium water content in the jet fuel was then measured using Karl Fischer titration with a Mettler Toledo C20 Compact Karl Fischer Coulometer that has a measurement range of 1ppm to 5% of water in samples (Lam *et al.* 2014).

#### *Cold flow properties*

The freezing point has influence in the pumpability of fuels at low temperatures. ASTM D1655 (2004) freezing specification limit for Jet A is -40 °C and -47 °C for Jet A-1. Differential scanning calorimetry (TA Instruments DSC Q2000) was performed to study the cold flow properties. Approximately 20 µg of each fuel was placed in aluminum sample pans and the mass recorded. As reference, an empty sample pan was used (Widmor *et al.* 2003; Zabarnick and Widmor 2001). The sample was initially equilibrated at 25 °C for 1 min. After this initial step it was cooled down to -40 °C at a cooling rate of 10 °C/min. The sample was kept at this temperature for 1 min and then was further cooled down to -90 °C at a heating rate of 1.5 °C/min. The sample was kept at -90 °C for 1 min before allowing its temperature to increase to 25 °C. The freeze point

data collected by AFRL and kindly provided by Dr. Tim Edwards for comparison purposes was obtained by the ASTM D5972 (2005) method.

## RESULTS AND DISCUSSION

### Chemical Characterization

#### *GC/MS results*

Figures 1 and 2 show the chromatograms of alternative and commercial jet fuels, respectively. The major compounds identified are marked with numbers, and the name, residence time, molecular form and classification of these molecules are listed on Table 3. The main compounds have between 9 and 12 carbon atoms (C9 to C12), followed by C13 to C15 compounds, although compounds in the range from C6 to C 18 were found.

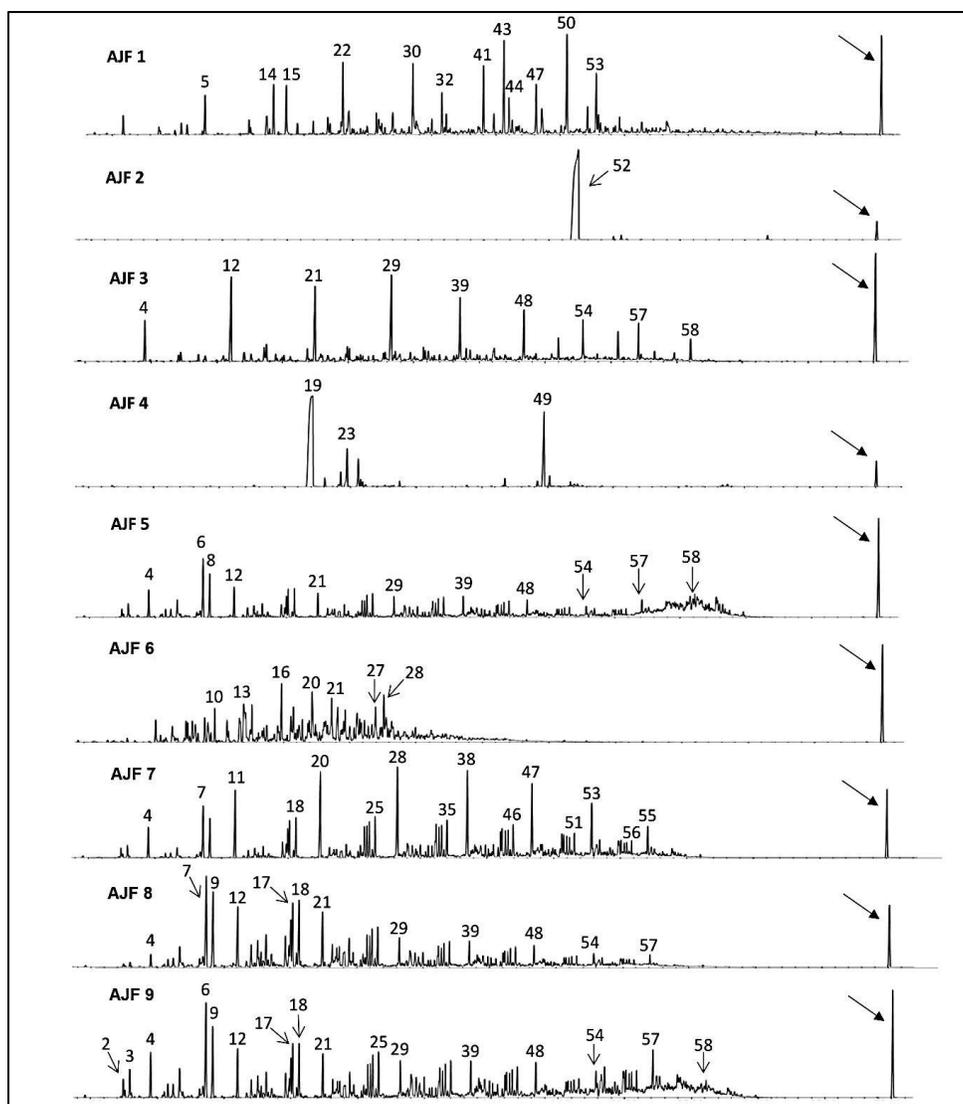


Fig. 1. GC/MS chromatograph of alternative jet fuels

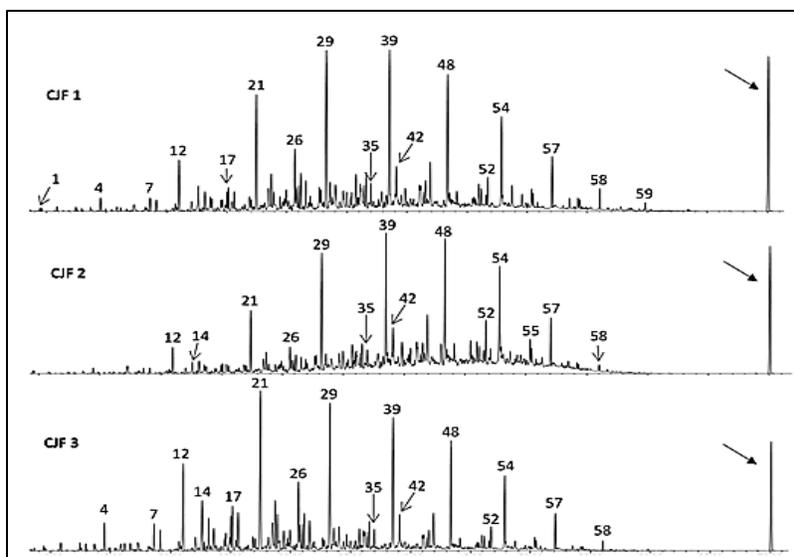


Fig. 2. GC/MS chromatograph of Commercial Jet Fuels.

Table 3. Main Compounds Identified in Each of the Fuels

No	RT (min)	Compound	MF	Classification
1	9.448	Heptane	C <sub>7</sub> H <sub>16</sub>	Paraffin
2	12.457	Heptane, 2-methyl	C <sub>8</sub> H <sub>18</sub>	Paraffin
3	12.945	Heptane,3-methyl	C <sub>8</sub> H <sub>18</sub>	Paraffin
4	14.496	Octane	C <sub>8</sub> H <sub>18</sub>	Paraffin
5	17.267	Cyclohexane, ethyl-	C <sub>8</sub> H <sub>16</sub>	Naphthene
6	18.65	Octane, 4-methyl-	C <sub>9</sub> H <sub>20</sub>	Paraffin
7	18.684	Octane, 2-methyl	C <sub>9</sub> H <sub>20</sub>	Paraffin
8	19.156	Heptane, 2,5-dimethyl-	C <sub>9</sub> H <sub>20</sub>	Paraffin
9	19.189	Octane, 3-methyl	C <sub>9</sub> H <sub>20</sub>	Paraffin
10	19.874	Heptane, 2,2,4-trimethyl-	C <sub>10</sub> H <sub>22</sub>	Paraffin
11	20.531	Cyclopentane, butyl-	C <sub>9</sub> H <sub>18</sub>	Naphthene
12	21.012	Nonane	C <sub>9</sub> H <sub>20</sub>	Paraffin
13	22.057	Hexane, 3-ethyl-2,5-dimethyl-	C <sub>10</sub> H <sub>22</sub>	Paraffin
14	22.624	Benzene, 1,3-dimethyl-	C <sub>8</sub> H <sub>10</sub>	Aromatic
15	23.621	Cyclohexane, propyl-	C <sub>9</sub> H <sub>18</sub>	Naphthene
16	24.899	Octane, 2,5,6-trimethyl-	C <sub>11</sub> H <sub>24</sub>	Paraffin
17	25.193	Nonane, 2-methyl-	C <sub>10</sub> H <sub>22</sub>	Paraffin
18	25.666	Nonane, 3-methyl-	C <sub>10</sub> H <sub>22</sub>	Paraffin
19	27.084	Heptane, 2,2,4,6,6-pentamethyl-	C <sub>12</sub> H <sub>26</sub>	Paraffin
20	27.202	Nonane, 2,3-dimethyl-	C <sub>11</sub> H <sub>24</sub>	Paraffin
21	27.445	Decane	C <sub>10</sub> H <sub>22</sub>	Paraffin
22	28.044	Cyclohexane, 1-methyl-2-propyl-	C <sub>10</sub> H <sub>20</sub>	Naphthene
23	28.666	Heptane, 5-ethyl-2,2,3-trimethyl-	C <sub>12</sub> H <sub>26</sub>	Paraffin
24	28.667	Benzene, 1-ethyl-2-methyl-	C <sub>9</sub> H <sub>12</sub>	Aromatic
25	29.439	Decane, 3-methyl-	C <sub>11</sub> H <sub>24</sub>	Paraffin
26	30.862	Benzene, 1,2,3-trimethyl-	C <sub>9</sub> H <sub>12</sub>	Aromatic
27	31.977	Decane, 3,7-dimethyl-	C <sub>12</sub> H <sub>26</sub>	Paraffin
28	32.599	Undecane, 4-methyl-	C <sub>12</sub> H <sub>26</sub>	Paraffin
29	33.278	Undecane	C <sub>11</sub> H <sub>24</sub>	Paraffin
30	33.512	Benzene, 1-ethenyl-2-methyl-	C <sub>9</sub> H <sub>10</sub>	Aromatic
31	33.549	Benzene, 1,2-diethyl-	C <sub>10</sub> H <sub>14</sub>	Aromatic

**Table 3.** Main Compounds Identified in Each of the Fuels (Continuation...)

Number	RT (min)	Compound	MF	Classification
32	35.778	Benzene, 1-methyl-4-(2-propenyl)-	C <sub>10</sub> H <sub>12</sub>	Aromatic
33	35.856	Benzene, 1-ethyl-2,4-dimethyl-	C <sub>10</sub> H <sub>14</sub>	Aromatic
34	35.894	1-Methyl-2-(4-methylpentyl)cyclopentane	C <sub>12</sub> H <sub>24</sub>	Naphthene
35	36.996	Undecane, 3-methyl-	C <sub>12</sub> H <sub>26</sub>	Paraffin
36	37.641	Benzene, 1,2,3,5-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	Aromatic
37	38.283	1,1'-Bicyclohexyl, 2-methyl-, cis-	C <sub>13</sub> H <sub>24</sub>	Naphthene
38	38.513	Z-1,6-Tridecadiene	C <sub>13</sub> H <sub>24</sub>	Olefin
39	38.542	Dodecane	C <sub>12</sub> H <sub>26</sub>	Paraffin
40	39.029	Benzene, 1-ethenyl-4-ethyl-	C <sub>10</sub> H <sub>12</sub>	Aromatic
41	39.032	Benzene, 1-methyl-2-(2-propenyl)-	C <sub>10</sub> H <sub>12</sub>	Aromatic
42	39.101	Undecane, 2,6-dimethyl	C <sub>13</sub> H <sub>28</sub>	Paraffin
43	40.595	Naphthalene, 1,2,3,4-tetrahydro-	C <sub>10</sub> H <sub>12</sub>	Aromatic
44	40.989	Benzene, 2-ethenyl-1,3,5-trimethyl-	C <sub>11</sub> H <sub>14</sub>	Aromatic
45	41.091	Cyclohexane, hexyl-	C <sub>12</sub> H <sub>24</sub>	Naphthene
46	41.952	Dodecane, 3-methyl-	C <sub>13</sub> H <sub>28</sub>	Paraffin
47	43.117	Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	C <sub>11</sub> H <sub>14</sub>	Aromatic
48	43.378	Tridecane	C <sub>13</sub> H <sub>28</sub>	Paraffin
49	44.736	Nonane, 2,2,4,4,6,8,8-heptamethyl-	C <sub>16</sub> H <sub>34</sub>	Paraffin
50	45.523	Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	C <sub>11</sub> H <sub>14</sub>	Aromatic
51	46.557	Tridecane, 3-methyl-	C <sub>14</sub> H <sub>30</sub>	Paraffin
52	46.738	Dodecane, 2,6,10-trimethyl-	C <sub>15</sub> H <sub>32</sub>	Paraffin
53	47.81	Naphthalene, 1,2,3,4-tetrahydro-2,7-dimethyl-	C <sub>12</sub> H <sub>16</sub>	Aromatic
54	47.869	Tetradecane	C <sub>14</sub> H <sub>30</sub>	Paraffin
55	50.386	Pentadecane, 7-methyl-	C <sub>16</sub> H <sub>34</sub>	Paraffin
56	50.867	Tetradecane, 3-methyl-	C <sub>16</sub> H <sub>34</sub>	Paraffin
57	52.079	Pentadecane	C <sub>15</sub> H <sub>32</sub>	Paraffin
58	56.051	Hexadecane	C <sub>16</sub> H <sub>34</sub>	Paraffin
59	59.825	Heptadecane	C <sub>17</sub> H <sub>36</sub>	Paraffin

The overall fraction of the oils quantified by GC/MS varied from 48 to 180 wt. % (CJF 1: 117.20 wt. %, CJF 2: 101.06 wt. %, CJF 3: 69.72 wt. %, AJF 1: 58.68 wt. %, AJF 2: 58.40 wt. %, AJF 3: 93.84 wt. %, AJF 4: 48.56 wt. %, AJF 5: 114.63 wt. %, AJF 6: 73.18 wt. %, AJF 7: 180.37 wt. %, AJF 8: 116.90 wt. %, AJF 9: 120.48 wt. %). This poor closure was mostly due to the fact that the number of standards used was unable to provide accurate quantification. So, all the data presented in this section were prorated from the raw data collected. The ideal would have standards that match as much as possible the physical and chemical characteristics of the compounds of interest. However, due to the complexity of some compounds, there were no standards commercially available. Therefore, non-aromatic compounds, with 7 carbons or less and the ones with 18 carbons or more were quantified using C-7 and C-18 standard, respectively. For those with 8 to 17 carbons, C-7 to C-18 standards were used, respectively. Monosubstituted and polysubstituted benzenes (one ring) were quantified using ethyl-benzene and xylene as standard, respectively. The polycyclic aromatic hydrocarbons were quantified with naphthalene as standard. The inaccuracy of the standard for many of the compounds

made some fuels show values above 100%, while some showed quantification less than 100%.

To get a better understanding of the composition of the fuels, a hydrocarbon distribution plot was made, and corresponding results are shown in Figs. 3 and 4. It was observed that the alternative jet fuels tend to concentrate one kind of molecule. For example, AJF 2, 4, 5, 6, 7, 8 and 9 are basically composed of paraffin, and the content of aromatics is very low. Fuel AJF 1 is rich in aromatic compounds with very low content of paraffins. Jet fuels contain all the groups of compounds. Although high contents of aromatics will increase the formation of soot, aromatics are necessary (until a certain level) to avoid leaks in the seals of fuel systems. The content of aromatics in jet fuels for engine certification is typically between 15 and 23 vol. % (Brem *et al* 2015). Because some of the alternative Jet fuels tested contain lower quantities of aromatics (sometimes less than 0.5 wt. %), they should be blended with commercial fuels to reach the targeted level. Commercial jet fuels presented a better distribution between the different classes of hydrocarbons, although the fuel CJF 3 did not present n-paraffins in it. It's important to emphasize that the presence of olefins in jet fuels is undesirable, as these are the most reactive class of hydrocarbons. The compounds selected as representing these peaks were made based on the author's interpretation of the best fitted spectra. However, the distinction between naphthenes and olefins is especially difficult. Several of the alternative jet fuels studied do not have a balanced composition as such, and therefore they cannot be used alone as fuel. They need to be blended with other AJFs or with CJFs.

**Table 4.** Overall Content of the Fractions (wt. % of total quantified oil)

Fuel	n-paraffin	Iso-paraffin	Olefin	Naphthene	Aromatic	Total
AJF1	-	0.2	4.3	34.4	59.4	98.3
AJF2	-	96.4	0.2	1.3	-	97.9
AJF3	44.0	6.9	5.1	32.9	8.8	97.7
AJF4	-	99.8	-	0.2	-	100
AJF5	11.7	87.3	0.1	0.9	-	100
AJF6	4.0	82.9	12.4	0.6	0.1	100
AJF7	19.6	79.9	0.1	0.1	-	99.7
AJF8	9.1	89.4	0.1	0.7	-	99.3
AJF9	12.8	86.9	0.1	0.3	-	100.1
CJF1	28.1	38.8	1.2	15.1	14.4	97.6
CJF2	37.5	42.2	6.6	11.5	2.6	100.4
CJF3	-	81.2	0.3	4.9	13.0	99.4

#### *Identification and quantification of oxygenated molecules*

Tables 5 and 6 reports the concentration of oxygenated molecules found in the alternative and commercial fuels, respectively. AJF 7 and CJF 1 did not have quantifiable oxygenated compounds. As expected, the amount of oxygenated compounds was very low, accounting for far less than 1% wt. of the fuels. The most abundant molecule was 2-(2-methoxyethoxy)-ethanol, followed by 2-methylphenol. 2-(2-Methoxyethoxy)-ethanol is used as a fuel system icing inhibitor in military fuels (and is also known as diethylene glycol monomethyl ether (di-EGME)). Its presence in JP-5, JP-8, and some of the alternative fuels is due to deliberate addition, not as a byproduct of production. This additive is required in commercial military JP-5 and JP-8 fuels, and can be used in Jet A

or Jet A-1 by agreement with the customer. Therefore, it is possible to verify the presence of this molecule in both military fuels.

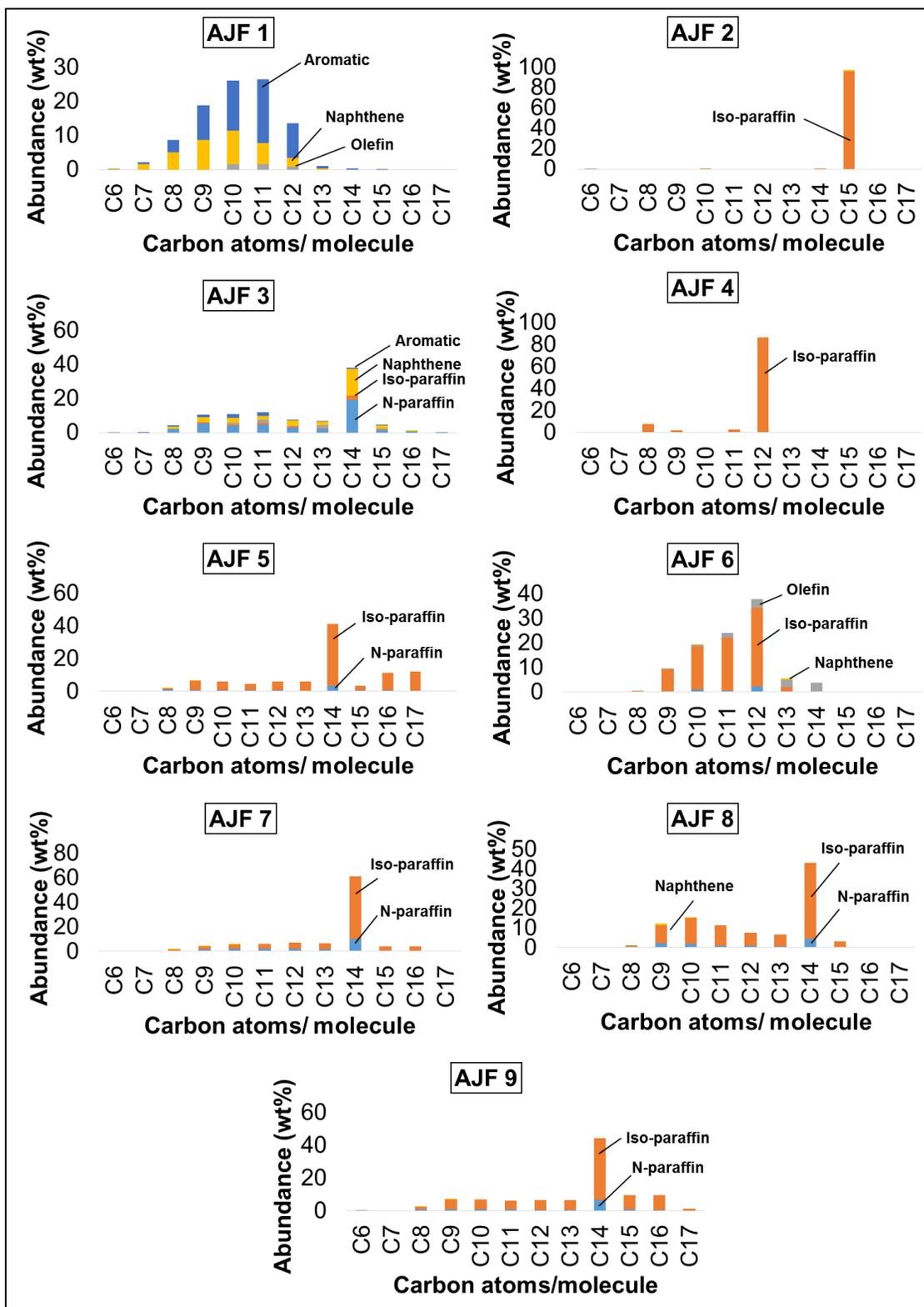
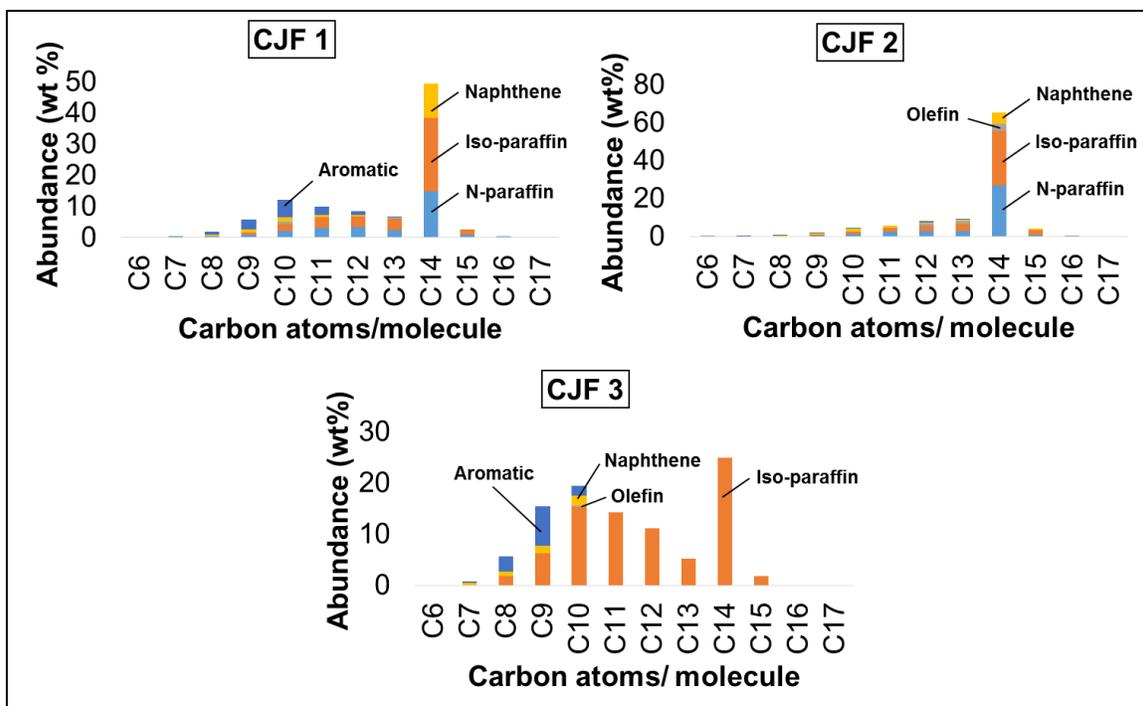


Fig. 3. Weight percentage of each class of hydrocarbons identified in the alternative jet fuels by GC-MS



**Fig. 4.** Weight percentage of each class of hydrocarbons identified in the commercial jet fuels by GC-MS

The class of oxygenated compounds that stands out is phenols, followed by alcohols. Many phenols are approved for use as antioxidants in jet fuel; however, their presence in the fuel is related to thermal and oxidative deposit (Sobkowiak *et al.* 2009). The large amount compared to other oxygenated compounds can be explained by the low reactivity in hydrodeoxygenation (Grange *et al.* 1996; Furimsky 2000). It is important to conduct an investigation on the effect of phenols on jet fuel properties because, if this molecule could be allowed in the fuel, the amount of hydrogen used in the hydroprocessing could be reduced, optimizing the process (Christensen *et al.* 2011). Ketones, ethers and acids were also encountered, but in lower quantities. These compounds were not quantified. The fact that they are present in trace amount, associated to the limitation of mass spectral library, made it difficult to get conclusive identification.

#### Total acid number

Table 7 shows the total acid number, *i.e.*, the mass of KOH consumed to neutralize the acids of the fuels, per gram of fuel. The presence of acids potentially causes corrosion problems. Different samples of jet fuels, including 10 alternative fuels and 3 commercial fossil-derived jet fuel were analyzed to study the general presence of acids in fuels. ASTM establishes a maximum of 0.1 mg KOH/ g fuel (Exxon 2005), and all the samples investigated were in accordance with the requirement. Observe that AJF 1 was the fuel with a higher value of TAN. This can be related to the higher aromatic content in this fuel, compared to the other analyzed items.

**Table 5.** Oxygenated Molecules Identified in Alternative Jet Fuels and Quantified.

	AJF1	AJF2	AJF3	AJF4	AJF5	AJF6	AJF8	AJF 9
2-Butanone, 3-methoxy-3-methyl-	-	-	-	N/S	-	N/S	-	-
2,5-dimethyl-2-hexanol	-	-	-	0.02	-	-	-	-
3,4-dimethyl-3-hexanol	-	-	-	0.01	-	-	-	-
3-Pentanol, 2,3,4-trimethyl-	-	-	-	0.01	-	-	-	-
3-Hexanol, 5-methyl-	-	-	-	0.01	-	-	-	-
2,4,4-Trimethyl-1-pentanol	-	-	-	0.01	-	-	-	-
Ethanol, 2-(2-methoxyethoxy)-	-	-	-	-	1.3	2.04	0.36	0.31
Ethanol, 2-(2-ethoxyethoxy)-	-	-	-	-	-	0.07	-	-
Phenol	-	-	0.02	-	-	-	-	-
Cyclohexane-ethanol	-	0.06	-	-	-	-	-	-
Phenol, 2-methyl-(o-cresol)	0.64	-	0.33	-	-	-	-	-
Phenol, 2,6-dimethyl-	-	-	0.16	-	-	-	-	-
Phenol, 2,4-dimethyl-	0.21	-	-	-	-	-	-	-
1-Pentanol, 2,2,4-trimethyl-	-	-	-	0.01	-	-	-	-
1-Hexanol, 4-methyl-	-	0.04	-	-	-	-	-	-
Phenol, 4-methyl-(p-cresol)	0.07	-	-	-	-	-	-	-
Phenol, 2-ethyl-	0.2	-	0.2	-	-	-	-	-
3,4-dimethyl-phenol	0.5	-	0.1	-	-	-	-	-
Phenol, 2,4,6-trimethyl-	0.1	-	-	-	-	-	-	-
Phenol, 2-propyl-	0.2	-	0.12	-	-	-	-	-
Phenol, 3,4,5-trimethyl-	0.2	-	-	-	-	-	-	-
4-Methyl-2-propylphenol	0.2	-	-	-	-	-	-	-
Phenol, 4-butyl-	-	-	0.23	-	-	-	-	-
Phenol, 4-pentyl-	-	-	0.37	-	-	-	-	-

N/S = the molecule was found but no standard was available for quantification. Concentration unit: mg/g

**Table 6.** Oxygenated Molecules Identified on Commercial Jet Fuels and Quantified (concentration unit: mg/g)

	CJF 2	CJF 3
Ethanol, 2-(2-methoxyethoxy)-	4.1	6.827
1-Hexanol, 2-ethyl-	-	0.024
3,4-dimethyl-phenol	0.003	-
Phenol, 2,3,5-trimethyl-	0.031	-
Phenol, 3-(1-methylethyl)-	0.002	-
Phenol, 3,4,5-trimethyl-	0.046	-
Phenol, 4-(1-methylethyl)-,	0.004	-

The oxygenated compounds may be attracted to the localized electron density. It is consistent with the quantification of oxygenated molecules. AJF 1 is the fuel with a higher amount of oxygenated compounds if the additive Ethanol, 2-(2-methoxyethoxy) is not taking into consideration. Therefore, it is expected that the amount of organic acids will also be higher in this fuel, as observed.

**Table 7.** Total Acid Number Results

Jet Fuel	TAN (mg KOH/g fuel) (WSU)	TAN (mg KOH/g fuel) (AFRL)	Difference between WSU and AFRL results
CJF 1	0.010	0.006	0.004
CJF 2	0.000	0.006	-0.006
CJF 3	0.000	0.008	-0.008
AJF 1	0.021	-	-
AJF 2	0.005	0.002	0.003
AJF 3	0.005	0.012	-0.007
AJF 4	0.004	0.001	0.003
AJF 5	0.016	0.005	0.011
AJF 6	0.010	0.001	0.009
AJF 7	0.010	0.004	0.006
AJF 8	0.010	0.002	0.008
AJF 9	0.010	0.002	0.008

*Carbonyl content*

Table 8 shows the carbonyl content of the jet fuel samples analyzed. The concentration of carbonyl compounds was lower than 0.000246 wt. %. The content of carbonyl groups in alternative jet fuels is comparable with the content measured in commercial fuels (Christensen *et al.* 2011).

**Table 8.** Carbonyl Content of Fuels\*

	CO ( $\mu\text{g/g}$ )	$\sigma$ ( $\mu\text{g/g}$ )
CJF 1	1.5	0.3
CJF 2	1.0	-
CJF 3	1.0	-
AJF 1	1.8	0.4
AJF 2	1.2	0.2
AJF 3	2.5	0.4
AJF 4	0.4	-
AJF 5	0.3	0.2
AJF 6	0.6	-
AJF 7	0.6	-
AJF 8	0.6	-
AJF 9	0.6	-

\*Six samples were tested in triplicate, and the standard deviation associated is also related in this table. By means of saving sample, the experiment was conduct once for the other seven fuels.

*Water content*

Table 9 shows the water content of the commercial and alternative jet fuels determined at WSU and the one obtained at the Air Force Research Laboratory. The limit of water content is not in the specifications for aviation turbine fuels; however, water in fuel is undesirable, as its presence can cause acceleration of corrosive processes and favor microbial growth (Webster *et al.* 2015). The presence of even minor quantity of water can cause filter plugging at high altitudes, where the low temperature causes water to freeze. The typical water solubility in commercial jet fuel varies between 40 and 80 ppm, at 21°C (70 °F) (Hemighaus *et al.* 2006). The standard ASTM D7566 (2017) establishes

a maximum of 75 ppm of water in the AJF (DSHC, Fischer-Tropsch, ATJ, and HEFA). None of the studied fuels presented more than 75 ppm of water in its composition. The high hydrophobicity of the fuels (hydrocarbons with only residual amounts of polar compounds) explain this low water content.

**Table 9.** Water Content of Fuels (ppm)

	Data collected at WSU	Data collected at the AFRL
CJF 1	23.8 ± 3.3	-
CJF 2	40.2 ± 1.3	-
CJF 3	38.8 ± 1.0	-
AJF 1	58.8 ± 3.9	-
AJF 2	47.6 ± 5.6	46
AJF 3	39.0 ± 4.4	8
AJF 4	20.6 ± 2.5	14
AJF 5	22.2 ± 1.7	-
AJF 6	28.9 ± 8.0	25
AJF 7	21.5 ± 0.2	22
AJF 8	0.0	14
AJF 9	22.8 ± 0.5	-

## Fuel Properties

### Density

Table 10 shows density analysis of the fuels, at room temperature obtained at WSU and at the AFRL. According to ASTM D1655 (2004) and IATA specifications (Zabarnick and Widmor 2001; ExxonMobile Aviation 2005), the density of a Jet A / Jet A-1 kerosene fuel must be in the range of 0.775 to 0.840 g/mL and the density of JP-5 kerosene, according to US Navy specification must be in the range of 0.788 to 0.845 g/mL, at 15 °C. The measurements listed were performed at room temperature. AJF 1, AJF 5, AJF 6, and AJF 8 do not qualify by this specification. In a same class of hydrocarbons, the density increases with the number of carbons.

**Table 10.** Density of Fuels, at Room Temperature (g/mL)

	Data collected at WSU	Data collected at the AFRL	Difference between WSU and AFRL results
CJF 1	0.819	0.803	0.016
CJF 2	0.836	0.827	0.009
CJF 3	0.800	0.780	0.02
AJF 1	0.904	0.888	0.016
AJF 2	0.786	0.773	0.013
AJF 3	0.826	0.803	0.023
AJF 4	0.786	0.761	0.025
AJF 5	0.762	0.764	-0.002
AJF 6	0.757	0.761	-0.004
AJF 7	0.786	0.756	0.03
AJF 8	0.766	0.751	0.015
AJF 9	0.777	0.758	0.019

At the same number of carbon atoms, the density of aromatics is higher than the density of naphthenes, which is higher than the density of paraffins (Hemighaus *et al.* 2006). Note that the fuels with higher content of aromatic compounds showed density closer to the upper limit. The high amount of aromatics in AJF 1 increased the density value to above the upper limit. As for the fuels with low content of aromatics, the density is closer to the lower limit, going a little under it in some fuels.

### Viscosity

Figure 5 shows the viscosity of fuels as a function of temperature in an Arrhenius plot. By analyzing this figure it is possible to verify that for all fuels, viscosity decreases with the increase in temperature (Berkhous 2007; Balster *et al.* 2008; Chuck and Donnelly 2014a). According to the literature, the value of viscosity is directly related to the number of carbons (Knothe and Steidley 2005; Hemighaus *et al.* 2006) or to the molecular weight (Detusheva *et al.* 1986). This relationship was not clearly verified in this experiment as, for instance, fuels with higher content of carbon (AJF 1, CJF 1, and AJF 3) presented lower viscosity values. However, viscosity is also related to the nature of the fuel. All of the fuels had approximately the same range of viscosity; however AJF 2 had a higher value. The higher value of AJF 2 was related to the presence of a single heavy compound (2,6,10-trimethyl-dodecane, neglecting the minor compounds encountered) in the fuel. This result is consistent to the low freezing point of AJF 2 (see item *Cold Flow Properties*), Materials with higher viscosity values present lower freezing points. These two properties are used to characterize jet fuel fluidity (Hemighaus *et al.* 2006). High viscosity values can result in problems with pumping and of filter plugging (Berkhous 2007). That is the reason why there is a specification for jet fuel maximum viscosity of 8 mm<sup>2</sup>/s for Jet A/ Jet A-1, and 8.5 for JP-5, both at -20 °C (ASTM D1655 2004). We were not able to conduct the viscosity tests below room temperature. So it was decided to carry out tests between 15 and 50 °C and then correlate the data with an Arrhenius plot following ASTM D371 (1996) (Schruben 1985) to estimate the viscosity at -20 °C (see Annex A1). The results obtained at WSU and the AFRL are listed in Fig. 5

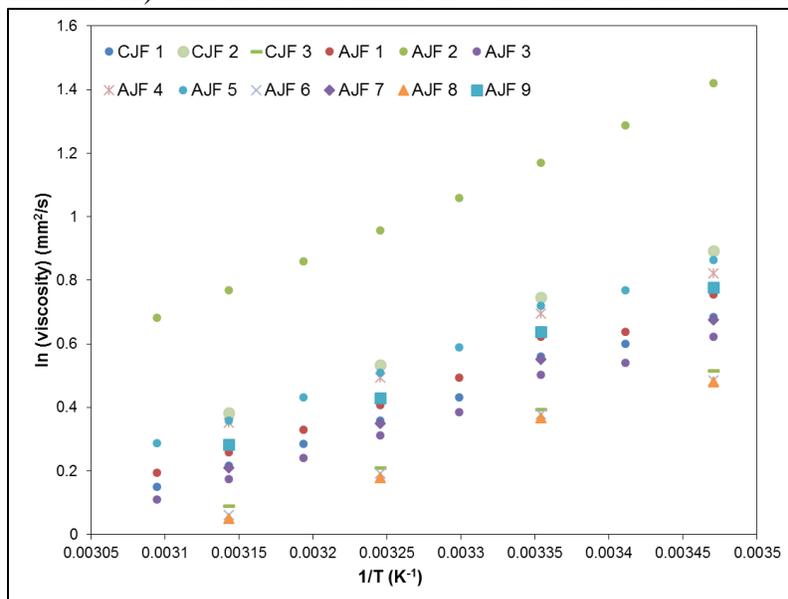


Fig. 5. Logarithmic plot of the viscosity (mm<sup>2</sup>/s) in function of 1/T [K<sup>-1</sup>].

Only one fuel, AJF 2, did not comply with the specification for viscosity at -20 °C (it was higher than 8 mm<sup>2</sup>/s). This high viscosity value is explained by the presence of only one major component on the fuel, with high molecular weight. Once more, this is not a major issue for the utilization of this fuel, as it can be blended with commercial jet fuel.

#### Surface tension

Table 11 shows the average surface tension of fuels with standard deviation.

**Table 11.** Average Surface Tension of the Jet Fuels and the Associated Standard Deviations

	$\sigma$ average (mN/m)	Stdv
CJF 1	25.8	0.2
CJF 2	26.7	0.1
CJF 3	24.6	0.1
AJF 1	25.0	0.1
AJF 2	24.2	0.2
AJF 3	24.1	0.1
AJF 4	22.2	0.1
AJF 5	23.6	0.2
AJF 6	23.0	0.1
AJF 7	24.0	0.1
AJF 8	23.5	0.00
AJF 9	24.0	0.1

The measurements were conducted at a sample temperature of  $22.7 \pm 0.36$  °C. There are no specification for surface tension; however, the Handbook of Aviation Fuel Properties (Coordinating Research Council Incorporated 1983), report an average of 23.5 mN/m at the test temperature. Commercial jet fuels CJF 1 and CJF 2, and that with higher content of aromatic, AJF 1, had the higher surface tension. Besides, AJF 1 and CJF 2 are the fuels with higher density.

#### Hydrogen content and heating value

Table 12 shows hydrogen content of the fuel samples obtained at WSU and at the AFRL. It is interesting to notice that the fuels with higher content of aromatic compounds presented lower content of hydrogen. The High Heating Value (HHV), in kJ/g, of jet fuels is also reported in Table 12. The specification for fuels is in terms of low or net heat of combustion (LHV), *i.e.*, the HHV discounted the energy released on water condensation. The limit established by ASTM D1655 (2004) is a minimum of 42.8 MJ/kg for Jet A and Jet A-1, and 42.6 MJ/kg for JP-5, by US Navy.

It is calculated based on the mass of water formed, which can be obtained by the hydrogen content of fuel, as each two moles of hydrogen are necessary to form one mole of water (2 grams of H forms 18 grams of water). Equation (1) below shows the calculation of LHV from HHV:

$$LHV = HHV - \left(\frac{\%H \times 9}{100}\right) \times \Delta H_v \quad (1)$$

where %H refers to the hydrogen concentration in fuel, and  $\Delta H_v$  is the (latent) heat of vaporization of water, equal to 2.44 kJ/g.

Table 12 shows the value of HHV from the experiment and the calculated LHV of fuels. CJF 2 and AJF 1 have a low heating value, which is lower than the specification. Blending the fuels to the commercial may solve this problem. The H content determined at the AFRL is higher than the H content measured at WSU. AJF 2 is mostly farnesane (C<sub>15</sub>H<sub>32</sub>). The hydrogen content estimated by the molecular formula is 15.06 mass % which is closer to the value obtained by the AFRL.

**Table 12.** Hydrogen Percentage, High Heating Value and Low Heating Value of Jet Fuel Samples

	H (mass %) (WSU)	H (mass %) (AFRL)	HHV (KJ/g) (WSU)	LHV (KJ/g) (WSU)	LHV (kJ/g) (AFRL)
CJF 1	12.0	13.8	46.1	43.6	43.1
CJF 2	11.9	13.5	44.5	42.0	43.0
CJF 3	12.0	14.3	46.1	43.4	43.1
AJF 1	10.4	11.8	44.3	42.2	41.6
AJF 2	13.4	15.2	47.1	44.5	44.0
AJF 3	12.0	-	46.2	43.6	-
AJF 4	12.8	15.4	47.2	44.3	43.9
AJF 5	12.6	15.1	47.2	44.4	44.0
AJF 6	12.5	15.4	47.1	44.2	44.0
AJF 7	12.6	15.6	46.2	43.2	43.9
AJF 8	12.8	15.1	46.8	43.9	43.9
AJF 9	13.1	15.1	47.3	44.4	44.5

#### *Flash point*

Table 13 shows the flash point of fuels and the spec data from AFRL, for comparison. The ASTM D1655 (2004) requirement is a minimum of 38 °C. According to US Navy specification, flash point of JP-5 fuel must be more than 60 °C<sup>47</sup>. This is a very important property because it is directly related to fire safety when handling the fuel. Two alternative fuels, AJF 1 and AJF 6, did not meet the requirements, and both military fuels did not qualify according to this specification. However, the values were according to the defined in the material safety data sheet received with the fuels. These fuels have high content of very light molecules, increasing the volatility and, consequently, decreasing the flash point. AJF 2 presented the best performance for this test, with a flash point of 96.2 °C. This is due to the composition of this fuel, which has basically only one compound, decreasing the volatility of the fuel.

**Table 13.** Flash Point for the Different Jet Fuel Samples (°C)

	Collected at WSU	Collected at the AFRL
CJF 1	43 ± 0.1	48
CJF 2	41 ± 0.7	60
CJF 3	46 ± 0.1	42
AJF 1	38 ± 2.0	-
AJF 2	96 ± 0.6	108
AJF 3	41 ± 0.6	48
AJF 4	46 ± 0.6	50
AJF 5	40 ± 0.1	43
AJF 6	36 ± 0.1	42
AJF 7	42 ± 1.0	48
AJF 8	39 ± 1.0	42
AJF 9	41 ± 0.6	55

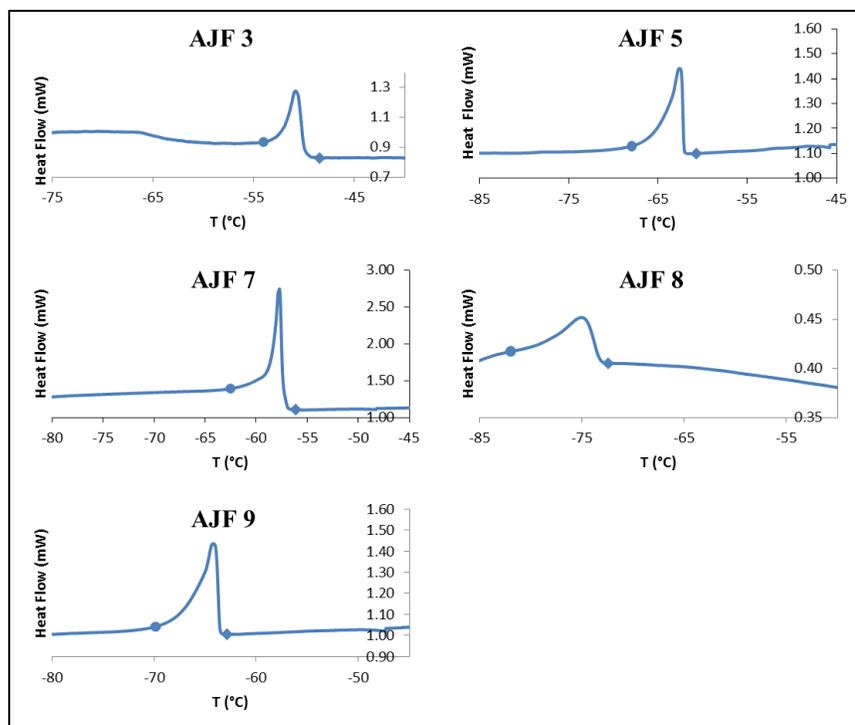
#### *Equilibrium water content*

The presence of water in fuel contributes to corrosion on fuel system, filter clogging, and poor performance of filter separators. The equilibrium water content of the fuels studied at 0 °C was 21, 25, 24, 37, 25, 30, 15, 17, 14, 18, 14, and 15 ppm for CJF1-3 and AJF1-9, respectively. According to the Handbook of Aviation Fuel Properties (Coordinating Research Council Incorporated 1983), at the temperature of the test, Jet A, Jet A-1, JP-5, and JP-8, together with JP-7 and TS, solubilize between 0.002 and 0.003 wt. % (20 to 30 ppm) of water. All fuels, except AJF 1, were in the specified range. This result can be explained by the high content of aromatics in this fuel (Hemighaus *et al.* 2006).

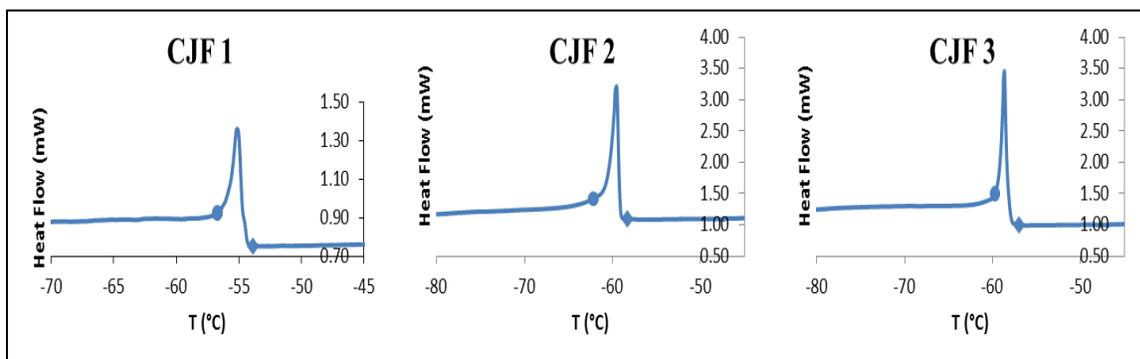
#### *Cold flow properties*

Figures 6 and 7 show the cold flow properties analysis, by DSC, for alternative and commercial fuels, respectively. Investigation of cloud point and pour point temperatures were conducted, as the reproducibility of freezing point tests is suggested to be low and to rely greatly on the operator ability (Chuck and Donnelly 2014a). Cloud point temperatures are represented by the beginning (“shoulders”) of the peaks (identified by a diamond on the figures), where the crystallization starts and, therefore, where the heat flow changes begins. The crystallization in fuel samples continues and achieves the pour point (identified by a circle on the figures) when the peaks return to the baseline (Lam *et al.* 2014). At the pour point, the fuel is not completely solidified, but it loses the flow characteristics. The cloud point and pour point are estimated by tracing a tangent to the left and right sides of the curve, respectively, at the point the line meets the base. AJF 1, AJF 2, AJF 4 and AJF 6 did not show any peak in this experiment, meaning that the cloud point must be lower than the minimum temperature tested. They have excellent cold flow characteristics.

The results are listed in Table 14. AJF 3 had the worst performance, compared to the other fuels. As the freezing point is generally higher than the cloud point, this fuel is just at the ASTM D1655 (2004) specification limit for Jet A/ Jet A-1, which is -40 °C for Jet A, and -47 °C for Jet A-1 (Exxon 2005).



**Fig. 6.** DSC results for the alternative jet fuel samples. The base (“shoulder”) of the peaks, indicated by diamond mark, represents the measured cloud point temperatures. Fuels AJF 1, AJF 2, AJF 4 and AJF 6 did not show any peaks within the range of temperature used in this analysis.



**Fig. 7.** DSC results for commercial jet fuel samples. The base (“shoulder”) of the peaks, indicated by diamond mark, represents the measured cloud point temperatures. The pour point estimation is indicated by a circle mark.

**Table 14.** Cloud Point and Pour Point of Fuels, in °C, Obtained by DSC Analysis, Data from AFRL of Freezing Point, in °C, is also showed for analysis.

	Cloud Point (°C) (WSU)	Pour Point (°C) (WSU)	Freezing Point (°C) (AFRL)
CJF 1	-53	-57	-52
CJF 2	-58	-62	-50
CJF 3	-57	-60	-51
AJF 1	< -80	< -80	-
AJF 2	< -80	< -80	<-100
AJF 3	-48	-54	-49
AJF 4	< -80	< -80	-90
AJF 5	-61	-68	-54
AJF 6	< -80	< -80	<-75
AJF 7	-56	-63	-49
AJF 8	-72	-83	-67
AJF 9	-62	-70	-62

## CONCLUSIONS

1. Phenols are the most common oxygenated compound in jet fuels and represent the class of oxygenated compounds, which are resistant to hydrotreatment. The deviation from specifications caused by phenols can be compensated by blending the AJF to the commercial fuel. This can result in reduction of amount of hydrogen used in deoxygenation process, leading to reduction in production cost of these fuels. However, more studies must be conducted to investigate the interaction between different classes of oxygenated compounds and their effect on fuel properties.
2. Alcohols, ketones, ethers, and acids were found in smaller quantities. The total acid number and carbonyl content in AJFs compared well with the content in commercial products. Likewise, the fuel properties of these new fuels are close to those recommended in the literature for jet fuels. All the deviations from current jet fuel specifications are likely to be compensated by blending the alternative jet fuels to the commercially available jet fuels.
3. GC/MS analysis indicated that the composition of the fuels is very diverse. For instance, AJF 2 contains one only component, while fuels like CJF 1 contain hundreds of compounds. Furthermore, the hydrocarbon distribution varies between different fuels. The difference between the compositions is related to the different feedstocks and processes used to produce them.
4. Elemental analysis indicates a high content of carbon in fuels with high aromatic content. The water content was above 80 ppm for AJF 1, due to the higher aromatic content. This is an indication that the amount of aromatic compounds in fuels must be controlled.

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