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THERMAL STABILITY CHARACTERISTICS OF FISCHER TROPSCH AND HYDROPROCESSED ALTERNATIVE
AVIATION FUELS IN A FIXED BED REACTOR

by

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A thesis submitted in partial fulfillment of the requirements
for the degree of Master in Science in Aerospace Engineering
in the department of Mechanical, Materials and Aerospace Engineering
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at the University of Central Florida
Orlando, Florida

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Major Professor: Jayanta Kapat

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ABSTRACT

Growing prices, limited supply, and public concern about greenhouse gases associated with crude-derived jet fuels have led to development of renewable alternatives which must be compatible with the worldwide civilian and military aviation infrastructure, which were designed for operation with Jet-A/JP-8. Any alternative fuel should not have negative effects on the aircraft engines and fuel systems, especially from a thermal stability perspective, since any adverse effect of the physical properties, and chemical composition, including existence of trace elements, of those fuels may only be revealed after extensive operation, resulting in higher life-cycle maintenance and operation costs.

This study considered four types of alternative fuels: two derived by Fischer-Tropsch (FT) process, and two types of Hydro-processing Esters and Fatty acids (HEFA). For each of these types, both raw and 50:50 blends in volume with Jet-A samples have been prepared, thus resulting in eight different fuel blends. Fit-for-purpose ability of these alternative fuels is first investigated by studying the effects of the fuel properties and composition effects on elastomer materials, and micro-turbine performance. When elastomer o-rings, similar to those used in aircraft fuel systems were immersed in renewable fuels, smaller volume change or swelling was detected (lower than 2%), contrary to a 14% swelling observed for baseline Jet-A. Lower swelling may result into leaks during aircraft operation. This trend was reversed when renewable fuels were blended with aromatics containing Jet-A.

Lower energetic content per unit volume of the renewable fuels, resulted in a thrust reduction around 10% when compared to baseline Jet-A at full throttle settings, but other than this, no other significant effect on the engine combustion temperature or other parameters were found for short

duration testing. On the other hand at the end of the alternative fuel testing an injector issue was detected, which caused a localized heat zone at the turbine stator, and subsequent damage. The investigation of the causes of this nozzle fouling, which may be related to fuel contamination, turbine manufacture defects, or operation conditions is left for future studies.

Primary focus of this study is coking behavior of 8 different alternative fuel blends over 4 different metallic surfaces, as compared against baseline Jet-A. A specialized single tube heat exchanger apparatus was used where each fuel sample was allowed to flow through a metal tube placed inside a tube furnace. Thermal stresses caused by the break-down of hydrocarbon molecules and the catalytic effects of the tube surfaces affect thermal stability of the fuel, leading to coking deposits under the auto-oxidation and pyrolysis mechanisms.

In the results reported in this study, physical methods such as gravimetric measurements were used to obtain the deposits, while UV/VIS absorption, and GC/MS were used to study chemical changes in fuel composition and their relation with coking deposits. Thermal depositions between 16 and 46 $\mu\text{g}/\text{cm}^2$ were measured at the tubes after 3 hours of testing, finding no significant differences between the baseline Jet-A and the renewable fuels blends, even when sulfur levels, which are linked to deposits formation, were lower for the renewable fuels. Fuel bulk constituents, such as paraffins and cycloalkanes, under thermal stressing and catalytic influence of the tube metals cracked into reactive intermediates leading to surface deposits formation, like aromatic compounds. These compounds were identified by the shift towards longer excitation wavelengths of the UV-Vis absorption measurements on stressed fuels.

Blessed be God for the opportunities I have received. I also want to dedicate this thesis to my mother, CELINA and my family for the unconditional support they have always given me. I love you all!!

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LIST OF ACRONYMS/ABBREVIATIONS

FT	Fischer-Tropsch
HEFA	hydrotreated esters and fatty acids
L/D	lift to drag ratio
LHV	low heating value [MJ/kg]
R	aircraft range
SFC	engine specific fuel consumption [g/kN s]
TIT	turbine inlet temperature
UV	ultra violet
V	velocity [m/s]
W_1	aircraft maximum weight [kg]
W_e	operational empty weight [kg]
W_f	fuel weight [kg]
W_p	payload weight [kg]
W_{to}	take-off weight [kg]

CHAPTER 1: INTRODUCTION

1.1 Gas turbine fuels and thermal stability

In more than 70 years of aircraft turbine engine development, tremendous leaps in performance have been accomplished passing from the 450 kg thrust of the HeS-3 which powered the world's first turbojet aircraft, the He-178 (Meher-Homji and Prisell, 2000), to the state-of-the-art turbofan engines used by today's airliners. Remarkably the used fuel has remained essentially unchanged. After world war II, it was expected that turbines would use a variety of cheap fuels, however the effects of chemical and physical fuel properties on engine performance, and the public concern over pollution led to the requirement of high quality fuels, which are not very different of those used by Whittle (Lefebvre, 1983). Meanwhile, the ever growing aviation industry has continued pushing the fuel demand and it is not expected to diminish: forecast show that global aviation fuel usage will rise from 174 million tons (68 Mt U.S. only) consumed in 1996 to 690 Mt (167 U.S. only) in 2050 (ICAO, 2009).

Besides its use as power source, aircraft designers have used jet fuel as heat sink in supersonic airliners and military aircraft, with Environmental Control Systems (ECS), hydraulics; generators and gearboxes heat loads being taken by the fuel while on its path to the engine combustor (Maxwell, 1970, Hitzgrath, 1993). This is usually done when ram air, which is the primary source to cool down equipment onboard, is not enough, whether as consequence of additional heat loads (i.e. electronics equipment upgrade), or when the flight envelope includes extended time at supersonic speeds, when the ram air temperature is excessive. However, the fuel heat sink capacity has been limited to the maximum temperature fuel can safely reach without resulting in coke deposition and fouling of the fuel lines, which for the case of Jet-A/JP-8 is 325°F (163°C) at the combustor inlet (Hazlett, 1991). As aircraft

heat loads continuously increase, the development of effective heat management schemes remains as one of the greatest challenges for the high-speed civilian and military aircraft designers.

1.2 Motivation for renewable fuels and thermal stability research

The recent volatility in oil prices coupled with the ever-increasing fuel demand, especially by the countries under development, the uncertainty regarding the future supplies, and the geopolitical turmoil in the middle-east area where most of the oil reserves are located, have resulted in worldwide efforts, especially in the United States, which is the world's largest oil consumer, for developing alternative fuels. Environmental concerns have also contributed largely into this objective, especially in the aviation industry, which is a large producer of Green House Gases (GHG), and given the altitude, at which aircraft cruise, their contamination effects are greater than those at ground level (Lee et al., 2001). Fuels obtained under the Fischer-Tropsch (FT) and oil hydro-treatment (HEFA) processes have been the most studied alternatives, and from the consensus of the armed forces, Federal Aviation Administration (FAA), International Civil Aviation Organization (ICAO), and aircraft and engine manufacturers, FT and HEFA fuels have been authorized to be used in blends up to 50% in volume with regular Jet-A/JP-8 in the specifications for civilian and military fuels (ASTM D1655 issued in the U.S. and DEF-STAN-91-91 issued in the United Kingdom for civilian Jet A/A-1, and MIL-DTL-83133 for military JP-8). However, effects on the aircraft engines and fuel systems on the long term are yet to be studied, especially from a thermal stability perspective. Experience with Jet-A has shown that adverse effects of the physical properties, and chemical composition, including existence of trace elements, of alternative fuels may only be revealed after extensive operation, and large money expenses in unexpected repairs

(Hazlett, 1991). Similar occurrences may occur if alternative fuels enter in service without a complete understanding of their long-term fuel stability characteristics.

1.3 Objectives

The primary objective of this thesis is to study the thermal stability behavior of Fischer-Tropsch (FT) and Hydro-treated (HEFA) alternative fuels under operating conditions similar to those of state-of-the-art aircraft and engine fuel systems, using a single tube heat exchanger. Physical methods such as gravimetric measurement will be used to obtain coking deposits, while UV/VIS absorption, and GC/MS analysis will help studying chemical changes in fuel composition as result of the surface metals catalytic effects, and the thermal cracking of the hydrocarbon molecules in the transition regime. On the other hand alternative aviation fuels must be able to operate in the harsh environmental conditions of military and civilian aviation without jeopardizing flight safety, and for this reason the secondary objective of this study is to assess the suitability of the studied fuels as drop-in replacement of Jet-A/JP-8 by comparing their effects on the performance of a small scale jet-engine, and elastomer materials swelling behavior. In the long-term, lessons learnt from this project should contribute to the development of thermal management alternatives that combine of high heat transfer schemes like impingement cooling, and thermally stable fuels, required for the next generation of high speed aircraft.

CHAPTER 2: LITERATURE REVIEW

2.1 Contemporary turbine fuels

The gas turbine fuel used by aircraft is a complex hydrocarbon mixture that given the different petroleum sources, and refining processes, makes impossible to define an exact composition (ASTM, 2011). On the other hand, Jet fuels are also the product also of years of struggle between performance requirements, supply and cost considerations (Edwards, 2007); civilian operators require safe, reliable and low cost fuels, while availability, and trouble-less operation in wide range of conditions are of paramount importance for military operations (Lefebvre and Hallal, 2010). In the years after World War II, with the introduction of the gas turbine engines and the worldwide grow of commercial aviation, Jet fuel specifications were developed. These include, ASTM D1655 for the United States, Def-Stan 91-91 for the United Kingdom and GOST 10227 for Russia, which contain a series of physical and chemical properties ranges that must be met by commercially available jet fuel.

2.2 Crude oil and refinery process

Crude oil is a complex blend of thousands of individual hydrocarbons (Robbins and Hsu, 1996, Altgelt and Boduszynsi, 1994) formed as result of millions of years of pressure, heat and bacterial action, transforming organic matter from animals and plants (Robinson, 2006). The 520 millions of barrels of turbine fuels, supplied in the United States during 2011 (EIA, 2012) were derived from petroleum, which after being extracted from the ground was sent to refineries, where it was separated and converted to Jet-A and other products like gasoline, kerosene, diesel, lubes waxes and asphalt. Refining processes

may be differentiated in three elemental operations: Separation, upgrading and conversion (Lefebvre et Hallal, 2010).

Crude oil is taken to the distillation column, where it is heated up to 538 °C. As the vapors ascend through the column, lighter hydrocarbons, such as propane and butane get at the upper section to be extracted. Gasoline, kerosene, and diesel, which are heavier, condense and are successively extracted at lower locations in the column. Straight-run is the name given to products derived directly from crude distillation. (Hemighaus et al., 2006)

Distillation products are usually upgraded: mercaptans, sulfur compounds with bad odor and corrosive nature are removed by the use of catalysts, usually cobalt-based (Merox[®] process). Hydrogenation is also performed, in which a combination of hydrogen and catalyst are used to remove components such as sulfur and nitrogen, as well as upgrading olefins by adding hydrogen over the double bonds. Finally fuels are passed across a bed of clay where polar species, which perform as surfactants are removed (Hemighaus et al., 2006). Surfactants are potentially hazardous compounds, since they can harm the capability separator/filter to take the water out.

Long hydrocarbons with higher boiling points can be broken into lower boiling species by placing them under high temperatures in the presence of catalyst. A similar process can be made in the presence of hydrogen at high pressure (hydrocracking), where large molecules are broken down, and sulfur and nitrogen containing compounds are eliminated, usually resulting in kerosene and diesel boiling range products (Hemighaus et al., 2006).

Low-sulfur petroleum may have such a high quality that straight-run kerosene, could probably comply with ASTM specifications, but it is usually improved by Merox treating, clay treating, or hydro-treating before being distributed (Hemighaus et al., 2006).

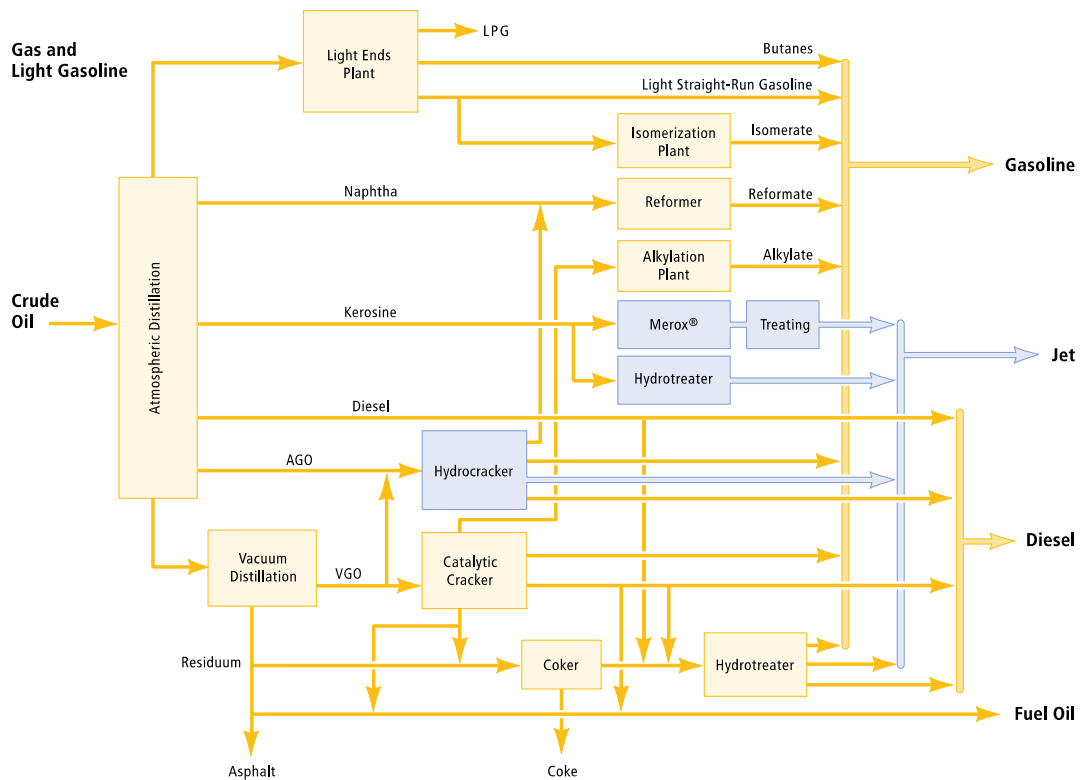


Figure 1 – Refinery layout (Hemighaus et al., 2006)

2.3 Aviation fuels composition

Gas turbine fuels are essentially composed of 4 types of hydrocarbons: paraffins, cycloparaffins, aromatics and olefins, with their proportion being a function of the crude-oil feedstock and the refining

process (CRC, 1983). In addition, the fuels also contain small amounts of heteroatoms such as sulfur and nitrogen, as well as trace metals.

Paraffins have single-bonded chains of carbon in which each carbon atom is saturated with hydrogen (CRC, 1983). Their chemical formula is C_nH_{2n+2} , and these compounds account for around 60% of the composition of aviation fuels, depending on the crude oil origin and refinery process (Lefebvre and Hallal, 2010). Their fully saturated character makes them very stable, not prone to react with materials like elastomers and metal paints, while the high hydrogen-to-carbon ratio makes them less dense, have a lower freeze point, and higher energy release per unit mass, and relatively clean burning characteristics. (Lefebvre and Hallal, 2010, CRC, 1983).

Cycloparaffins or naphthenes, are another major constituents of jet fuels, composing between 25% and 35% (Lefebvre and Hallal, 2010), in which their carbons form a saturated ring structure, with lower energy release per unit mass, and higher density, as result of their decreased hydrogen-to-carbon ratio. Cycloparaffins also have clean burning characteristics, and their freezing point is lower when compared to paraffin with the same carbon number (CRC, 1983).

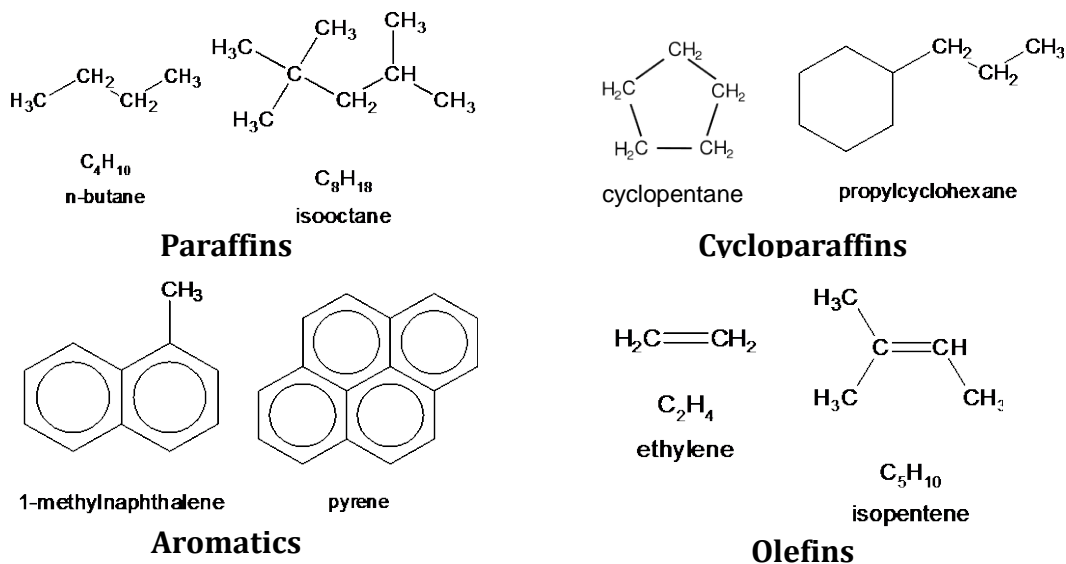


Figure 2 – Examples of hydrocarbon compounds of turbine fuels (Robinson, 2006)

While olefins are not commonly found in crude oil, those unsaturated hydrocarbons (have a carbon-carbon double bond) are usually result of several cracking steps performed during the fuel refinery process (Robinson, 2006). With a general formula of C_nH_{2n} , they have good combustion characteristics, but are also chemically active with the tendency to form gums and rubberlike materials, limiting the useful life of fuel under storage (CRC, 1983, Lefebvre and Hallal, 2010). Their content in aviation turbine fuels is usually limited in 1% or less (ASTM, 2011).

Aromatics are ring shaped species that have at least one six-element ring with the equivalent of three double bounds, and are responsible for the swelling in o-rings, helping to seal the high-pressure fuel systems (Lefebvre and Hallal, 2010). On the other hand, aromatics have the least desirable combustion properties, with a smoky flame and larger release of thermal radiation emissions than other hydrocarbons limiting their composition to 25% (ASTM, 2011). In addition their hygroscopic nature may lead to ice crystal formation at low temperatures (Lefebvre and Hallal, 2010).

2.4 Renewable aviation fuels

Pioneering developments were made in South Africa; where Sasol developed the coal derived Sasol Semi-synthetic Jet Fuel (SSJF) under the Fischer-Tropsch process, which became the first renewable fuel commercially certified under DEF STAN 91-91 and ASTM D1655 specifications (Moses, 2008). In 2006, the U.S. Department of Defense, began the developing, testing and certification of jet fuel from non-petroleum sources, beginning with synthetic paraffinic kerosenes obtained under the Fischer-Tropsch (FT) process from syngas derived from coal or natural gas (Blakey et al., 2011). Moses (2007) developed a protocol for accepting alternative aviation turbine fuels under commercial specifications, defining a series of tests and expected values of jet fuel properties, such as chemical composition, density, heating value, thermal stability, and materials compatibility. Subsequent testing concluded that Sasol IPK, Syntroleum S-8 and Shell FT fuels are fit-for-purpose, that is, interchangeable with conventional fuels when mixed up to 50% with JP-8 (Moses, 2008). All those efforts resulted in the development of the ASTM D7566 authorizing FT blends for commercial aircraft, in 2009, and the revision of the JP-8 MIL-DTL-83133 standard authorizing FT-blends for all U.S. Air Force systems in 2010 (Braun, 2012). The following family of renewable fuels considered were the Hydrotreated Esters and Fatty Acids (HEFA), as the result of efforts to further reduce environmental impact, given that, unless coupled with technologies like carbon sequestration, FT production schemes result in higher life cycle emissions compared to oil-derived Jet-A (Blakey et al, 2011). The U.S. Air force has followed a similar approach as with the FT fuels, while civil air carriers such as Virgin Atlantic, Air New Zealand, and Continental Airlines also performed demonstration flights fueled by renewable fuels, as reported by Blakey et al. (2011). An update of the ASTM D7566 specification authorizing the HEFA blends for commercial aircraft was issued

in July 2011 (Enright, 2011), while certification by the U.S. Air Force is expected for 2013 (Braun, 2012). A third family of renewable fuels based on alcohols from cellulosic materials, starches and sugars, which are subsequently hydro-processed to obtain aviation quality jet fuels are currently under development (Braun, 2012).

Unlike oil-derived jet fuels, FT and HEFA fuels are composed mostly of paraffins and do not have aromatics resulting in lower density and larger caloric power per unit mass. In addition, FT/HEFA fuels, as result of the hydro-treating process do not have sulfur compounds, leading to a cleaner combustion, as observed in emissions testing (Moses, 2008). On the other hand, the mentioned changes in density and heating value may influence aircraft performance, namely range and payload. The lack of aromatics is another concern, since their concentration and nature has a primary role in the swelling of elastomeric seals, which are thoroughly located in fuel couplings, valves, pumps, and in ground and aerial refueling lines and components. Therefore, the use of fully synthetic fuels, with no aromatic species, may result in leaks and other fuel system related issues, being this one of the main reasons for the 50% FT/HEFA concentration limit in current fuel specifications.

2.5 Land based current and alternative fuels

Land and sea based gas turbines do not present the challenging operational and environmental conditions of aircraft engines, and for this reason the most important fuel requirement is low price to maintain competitively with other energy sources (Lefebvre and Hallal, 2010), with natural gas as the most used fuel, and light petroleum distillates (#2) as alternative. Liquid fuels such as kerosene (Jet-A), and petroleum distillates (ASTM D396, D2880 No. 2 distillate, Grade No. 2 diesel) are also used as back-

up fuels, although hundreds of industrial turbines run with them in a regular basis (Campbell et al., 2008). Vegetable oils, which are partially unsaturated fatty acids with carbon chains varying between C12-C22 have also been used as fuel, presenting higher hydrogen content, density and flash point than diesel. However, their unsaturated nature makes them prone to oxidation and they exhibit a low storage life as well as low cold flow properties (Campbell, 2008). On the other hand, fuel flexibility has become more complicated in modern gas turbine engines with the introduction of low emissions combustors, which were optimized for operation with natural gas (Campbell, 2008).

2.6 Turbine fuels thermal stability

While it serves as coolant fluid, jet fuel is heated, and reactions between reactive trace species and dissolved oxygen result in coking deposits precursors which ultimately adhere to heat exchanger surfaces, or clog filters and injectors. As the fuel temperature is increased (usually above 430°C), dissolved oxygen is depleted, and the dominant reaction mechanism in the deposits formation is pyrolysis (Spadaccinie et al., 2001).

In the autoxidation regime, which spans from 150°C to 350°C, deposit formation behavior is affected by the fuel temperature, composition and oxygen concentration (Wong, 2010), therefore important reductions in the deposit formations may be obtained by deoxygenating the fuel. Regarding the oxidation mechanism, it has been suggested that autoxidation starts when dissolved oxygen reacts with fuel, resulting in free radicals, with hydroperoxides the most important intermediate species, and precursors to deposit formation (Hazzlett, 1991). A soluble macro-molecular oxidatively reactive species (SMORS) mechanism, with polar compounds as precursors for insoluble deposits was also proposed

(Beaver et al., 2005). While the SMORS theory details insoluble formation and deposition, the hydroperoxide theory emphasizes liquid fuel autoxidation (Wong, 2010).

At temperatures above 400 °C, dissolved oxygen has already reacted and fuel suffers pyrolytic decomposition, where the deposition rates increase exponentially with temperature and linearly with residence time (Balster et al., 2008). At those temperatures, hydrocarbon chains will undergo cracking into C1-C4 gases and cycloalkanes, eventually leading to aromatic compounds (Andrésen et al., 2001). Oxygen is expected to have a limited effect, since it is supposed to be consumed at lower temperatures (Hazlett, 1991). In future aircraft, with increased thermal loads, heat absorbing (endothermic) chemical reactions will be required, posing challenges in the fuel systems since it will have to handle two-phase fluids.

Polar species with weak O-H, N-H and S-H bonds, such as phenols, arylamines and thiols were believed to be beneficial natural antioxidants. On the other hand the resultant radicals with heteroatoms would react quickly with oxygen, resulting in deposits. Thus fuels with higher polar species concentrations should be less thermally stable for the autoxidation regime. (Heneghan and Zabarnick, 1994).

Regarding the surface deposition mechanisms, the insoluble particles may move from the bulk liquid towards the hot wall, where they get attached, or may form directly on the hot wall surface as result of reactions catalyzed by the surface metal, or by both mechanisms (Ervin 2003, Wong, 2010).

2.7 Fixed bed reactor thermal stability studies

Since the early days of the jet fuel development, a series of apparatuses to investigate thermal stability have been designed and built. Single tube testers use different tube lengths, diameters, wall thicknesses and materials, passing fuel through the tube, which is usually heated by electrical means. Fuel performance is then determined by changes in heat transfer, by following pressure changes through an associated filter, or by measuring the deposits after the testing (Hazlett, 1991). Heat transfer, or pressure changes across a filter are more physically relevant to engine operational problems, and also provide data while testing, but require high temperatures and longer test times to provide notable changes. Deposits determination, on the other hand, serves as measurement of fuel degradation, supplying only one data point per run, but realizable in shorter runs, and more sensitive, compared to heat transfer, or pressure changes (Hazlett, 1991).

In single tube thermal stability studies, variation of temperature, Reynolds number, passage size, residence time, pressure and heat flux rate may produce significant changes in the coking deposition as explained by Spadaccini et al, (2001):

- **Temperature:** Deposition increases with temperature increases up to 600°F. Since at this point the coking deposition comes from the dissolved oxygen reaction with the fuel, increasing temperature increases the reaction rate, up to a point where the dissolved oxygen is depleted.
- **Reynolds and Passage Size:** Increasing Diameter (thus reducing Re) reduces carbon deposition, which reflects a balance of mass-diffusion length scale, turbulence-enhanced mass-diffusion rates and residence time influence.

- **Residence Time and Space Velocity:** For a constant outlet temperature, deposition increases when increasing the fuel flow rate. Thus, the enhanced diffusion effect is stronger than the impact of residence time. At higher Re, turbulent mixing is enhanced and residence time is decreased. Here it is expected that deposit formation will be controlled by reaction kinetics instead of mass transfer.
- **Pressure:** Its variation has a minor impact on the autoxidation coke deposition.
- **High Heating Rate:** Carbon deposition is reduced significantly increasing heat flux, while increasing flow rate (Re) and decreasing the residence time, reflecting the changing balance between heating, mixing and kinetics, despite the high wall temperatures.

2.8 Fuel thermal stability and aircraft thermal management schemes

In the early 1990's a joint effort between the Air Force, the Academia and the Industry resulted in the development of an additive package, with the mind of reaching the best compromise between performance requirements, fuel cost and availability without the need of developing a new fuel (Edwards, 2006). The result of this effort was the JP-8+100, which is capable of reaching 425°F (218°C) without fouling, meaning a 50% increase in the heat sink capacity (Heneghan and Harrison, 1997), which for current aircraft, like the F/A-18, may allow to eliminate environmental control system (ECS) heat air exchanger resulting in weight savings, reduced drag and improved cooling capabilities at higher velocities (Ho et al., 1997). Future use of fuel in aircraft cooling schemes depends, however on the ability of managing coking deposits, especially in the future hypersonic aircraft when it will be likely for fuel to be heated at temperatures above 900°F (482°C) (Huang and Spadaccini, 2005).

CHAPTER 3: EXPERIMENTAL METHODOLOGIES

3.1 Single tube fixed bed reactor

The fuel thermal stability experiments were performed using Blair's lab fixed bed catalytic reactor, modified for coking purposes, shown photographically in fig. 3 and schematically in fig. 4. The apparatus was designed in such a fashion that all components in contact with fuel are either stainless steel or plastic, and as shown in in fig. 4 consists of: (1) fuel reservoir; (2) a fuel delivery system based in an Eldex 5984 Optos Series metering pump; (3) a test section comprised of a 0.25 m long, 3.175 mm outer diameter (OD), specimen tube, made either of 316 stainless steel, 3003 aluminum alloy, Alloy 600 Inconel, or Grade 2 titanium, heated in a Supelco 2-3800 tube furnace; (4) an air cooled loop.



Figure 3 – Photograph of fuel thermal stability rig

System pressure was manually adjusted by means of a Swagelok backpressure regulator. Fuel and tube wall temperatures are measured with nickel-chromium thermocouples, while inlet and outlet pressure are monitored using two 300 Series Noshok pressure transducers, all connected through a data acquisition system to a LabView® equipped computer where the information is stored. The apparatus is capable of continuous operation at maximum furnace temperatures of 580 °C and pressures up to 20.7 MPa (3000 psi) for fuel flow rates up to 80 mL/min.

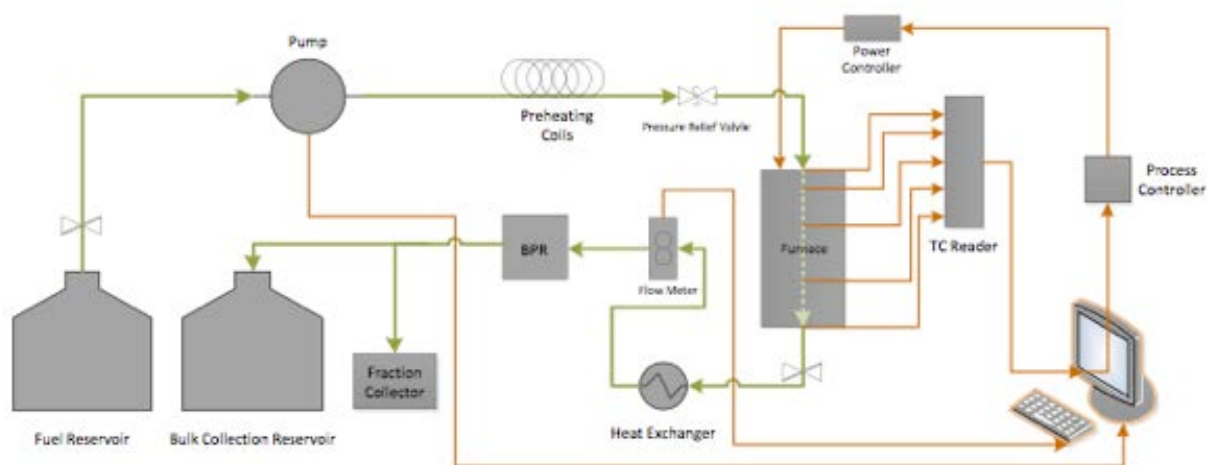


Figure 4 – Fuel thermal stability rig layout

A standard procedure was developed for tube handling. Tubes were fabricated from 1.83 m (6 ft.) tubing, and prior to installation in the furnace were rinsed with isopropyl alcohol and dried overnight in an oven at 90 °C. During handling, care was taken to avoid contamination, with the operators using nitrile gloves at all times. Routine test preparation consisted of cleaning the glass fuel reservoir with isopropyl alcohol, and checking the pump and furnace for proper condition. Then tubes were placed in the test section, and a new fuel was supplied. After test pressure and flow rate were established the system was inspected for fuel leaks, and power was provided to the electric furnace, provided no leaks

were present. System operation was not automated, therefore an operator had to be present at all times, periodically monitoring system parameters, shutting down the furnace and pump in case any critical parameter (flow rate, pressure or temperature) varied out of range. After 3 hours, which was the nominal testing time, the shutdown was initiated by turning off the electrical power to the furnace, while maintaining fuel flow to cool down. Once the fuel pump was shutdown, test tubes were removed, and again dried overnight at 90 °C, to be later labeled and stored for analysis. After the testing, fuel samples were taken for GC/MS and UV-VIs absorption testing, while the remnant fuel was discarded. Coking deposits were obtained by measuring the mass of the test tube before and after each experiment with a Mettler AT-20 high precision analytical balance. In addition to experimental data such as fuel flow rate, temperature and pressure were recorded for analysis. All test were conducted at a nominal pressure of 4.1 MPa (600 psi), and fuel inlet temperature of 20 °C. Furnace temperature was set to 325 °C, and flow rate at 2 mL/min, in an effort to reproduce conditions similar to the environment of modern gas turbine fuel systems (Giovanetti and Szetela, 1985).

3.2 Fuel samples

Table 1 lists the fuels used for during the present thesis. For the FT fuels production, natural gas is partially oxidized to obtain syngas (carbon monoxide and hydrogen), which is later fed in FT reactors. For the Shell FT process, or Shell middle distillate synthesis (SMDS), syngas passes through multi-tubular fixed bed reactors, with subsequent hydrocracking, isomerization and fractionation processes resulting in long-chain paraffins. For the Syntroleum fuel, syngas is liquefied with cobalt-based catalysts, obtaining c5-c20 paraffins and oleofins, which are further processed by hydrocracking and hydro-isomerization in order to obtain a close to Jet-A/JP-8 fuel (Moses, 2008, Corporan et al, 2011). On the other hand, the

tested HEFA fuels were manufactured by UOP taking Camelina and beef tallow as feedstock, which is pressurized and mixed with hydrogen in order to remove oxygen and produce n-paraffins, which are later hydrocracked and isomerized to obtain a freezing point and boiling distribution similar to Jet-A/JP-8 fuel (Klingshirn et al, 2011). Synthetic and hydro-treated, renewable jet fuel samples, were supplied by the Air Force Research Laboratory, and relevant properties for this study, such as density, heating value and aromatics content are listed in table 1, with S-8 data adapted from the reported values of Syntroleum S-5, which only differs in its higher flash point. Baseline Jet-A was acquired at a local FBO in the Orlando area.

Table 1 – Selected properties of tested fuels (Klingshirn et al., 2011, Corporan et al. 2011 and Lamprecht, 2007)

	Standard	JP-8 / Jet-A-1	Shell FT	Syntroleum S-8	UOP Camelina	UOP Tallow
Distillation Initial Boiling Point °C	Report	152	146	182	151	165
10% Recovered °C	Max 205	173	162	195	161	179
20% Recovered °C	Report	179	162		166	185
50% Recovered °C	Report	198	169	228	182	210
90% Recovered °C	Report	239	184		237	243
Final Boiling Point °C	Max 300	260	198	280	259	255
Freeze Point °C	Max -47	-49	-55	-50	<-77	-62
Existent Gum mg/100 mL	Max 7.0	0.4	0.4	0.4	<1	<1
Viscosity at -20°C cST	Max 8.0	4.1	2.6	7.0	3.3	5.3
Specific Gravity	0.775-0.840	0.799	0.736	0.767	0.758	0.76
Smoke Point, mm	Min 19.0	25	40	>43	50	>40
Flash Point °C	Min 38	48	44	62	43	55
Heat of Combustion, MJ/kg	Min 42.8	43	44.1	44.1	44.1	44.1
Hydrogen, % Mass	Min 13.4	13.9	15.6	15.1	15.3	15.4
Aromatics %	Max 25	17.2	0.0	0.0	0.0	0.4
Sulfur %	Max 0.3	0.064	<0.0003		0.0018	<0.0003

3.3 Micro-turbine

For the engine performance analysis, a SR-30 micro-turbine, shown in fig. 5 was used. The engine is located at the Siemens Energy Center at the University of Central Florida, and is used to

evaluate renewable fuels in a realistic operational environment, without the large fuel consumption of larger engines. A Data Acquisition Unit connected to a computer through an USB interface, provides real time information of engine parameters such as temperature and pressure for Compressor Inlet (T1/P1), Compressor Exit (T2/P2), Turbine Inlet (T3/P3), Turbine Exit (T4/P4), fuel flow, engine rotational speed and thrust. Engine specifications are provided in table 2. Performance data was collected for the turbine running with the different fuels, both raw and in 50% mixes with Jet-A. For the present study, the turbine was operated from idle to full throttle at several RPM settings, while recording performance data. After shut down, the fuel tank was drained, and a new fuel was supplied.



Figure 5 – Photograph of SR-30 engine used in testing

Table 2 – SR-30 engine specifications

Compressor type	Single stage centrifugal
Turbine type	Single stage axial
Maximum RPM	87,000
Maximum Thrust	18 kgf.
Maximum Turbine inlet Temperature	870 °C
Pressure Ratio	3.4:1

3.4 Elastomer compounds compatibility

Fuel seals are thoroughly located in fuel couplings, valves, pumps, and in ground and aerial refueling lines and components are of great importance in the fuel system, since prevent leaks, contributing to the safety since fuel is inherently volatile (Kalt, 1997). Nitrile O-ring N602-70 M29513, samples, measuring 53 mm internal diameter and 5 mm width supplied by Parker-Hannifin were chosen for the present study. The selection of the material was based on two reasons: It is representative of the types of elastomer materials found in aircraft fuel systems (Muzzell et al., 2007), and its sensitivity to changes in fuel aromatic species content, when compared to fluorinated carbon polymers (Muzzell et al., 2007, 2005, Corporan et al., 2011). Two o-ring samples were placed in glass beakers containing each one of the mentioned FT and HEFA fuels and their 50/50 volume blends with Jet-A at ambient temperature. Mass and volume measurements, based on the water-displacement technique were made at 0, 3, 9 and 28 days to determine the changes caused by the fuels. Data from control samples immersed only in Jet-A were used as reference.

3.5 Uncertainty analysis

Uncertainties were calculated using the second power method (Kline and McClintock, 1953) for deposits formation, elastomer volume swelling, gas turbine SFC and single tube heat exchanger Reynolds Number, as seen in table 3. Highest error is found in the Reynolds number calculation, as consequence of the flow rate uncertainty +/- 3% in the pump setting. A more precise flow meter was going to be used, but failed during the system tuning-up. Deposits error was inherent to the balance, and may be reduced by using alternative ways to obtain carbon deposits, such as temperature-

programed oxidation (TPO). During the gas turbine operation, it was noted a non-zero thrust, up to 8 N, after the first test run of the day, suggesting a temperature induced error in the thrust load cell. For this reason a “warm-up” period was added before performing test runs with renewable fuels.

Table 3 – Experimental uncertainty contributions

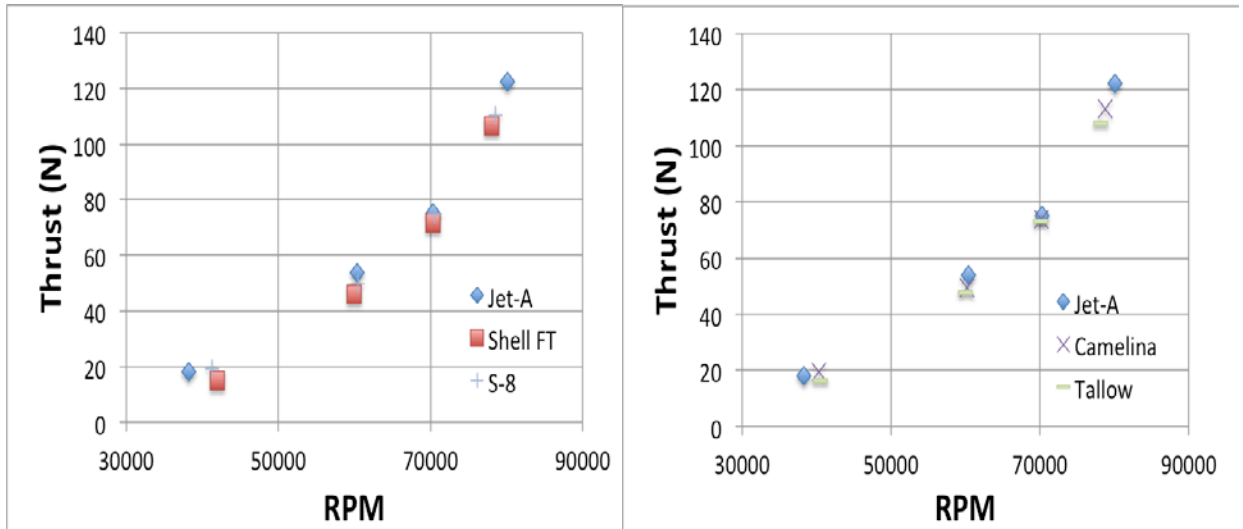
	Deposits [$\mu\text{g}/\text{cm}^2$]	Swelling	SFC [$\text{g}/\text{kN}\cdot\text{s}$]	Re
Uncertainty	2.3	0.048%	7.4	22%

CHAPTER 4: ANALYSIS

4.1 Engine performance

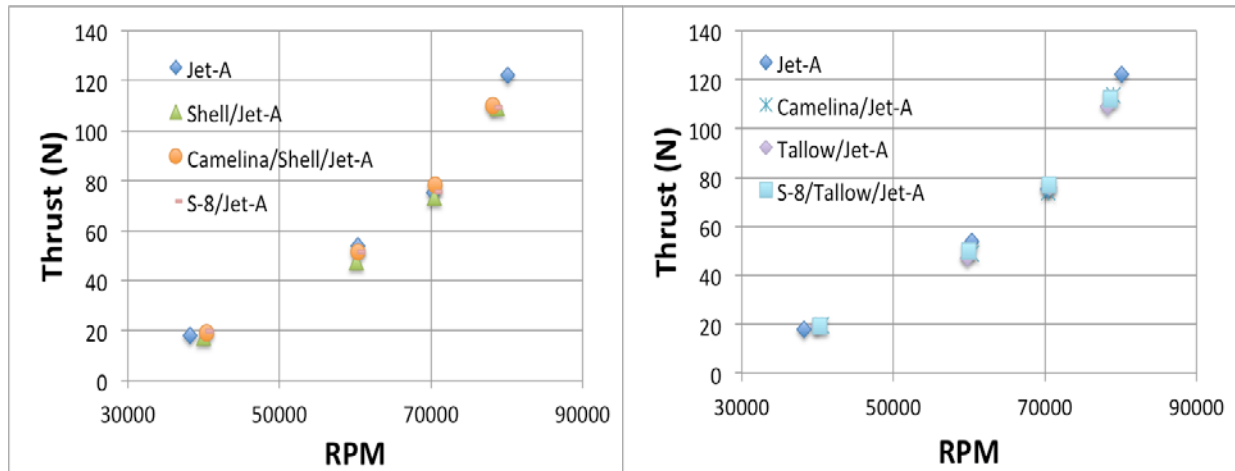
Figure 6 shows the thrust vs. RPM for the different fuels. No significant differences are found, except at the maximum throttle setting, where the Jet-A produces about 10% more thrust than renewable fuels tested, and is believed to be caused by the lower density, and subsequent lower heating value per unit volume of the renewable fuels. At full throttle, engine fuel consumption is in the order of 28 L/h. For the Jet-A, the product of the density and heating value results 34.4 MJ/L, while this value is around 33 MJ/L for the renewable fuels, and the Shell FT having the lowest value of 32.5 MJ/L. The maximum spool velocity, while using Jet-A, corroborates this effect: while running with Jet-A engine velocity reaches 80,000 RPM at full throttle, while it does not pass the 78,500 RPM with renewable fuels.

Figure 7 shows the variation of thrust specific fuel consumption for the tested fuels. Calculated values do not differ much between fuels, as reported previously by Klingshirn et al. (2011) who tested the same HEFA fuels in a T63 engine test bench at the AFRLA. However this is not true for the Shell FT, and its blends with Jet-A and UOP Tallow, particularly at idle power.



(a)

(b)



(c)

(d)

Figure 6 – SR-30 engine thrust as function of RPM for several fuels (a) Synthetic; (b) HEFA; (c) Synthetic blends; and (d) HEFA blends.

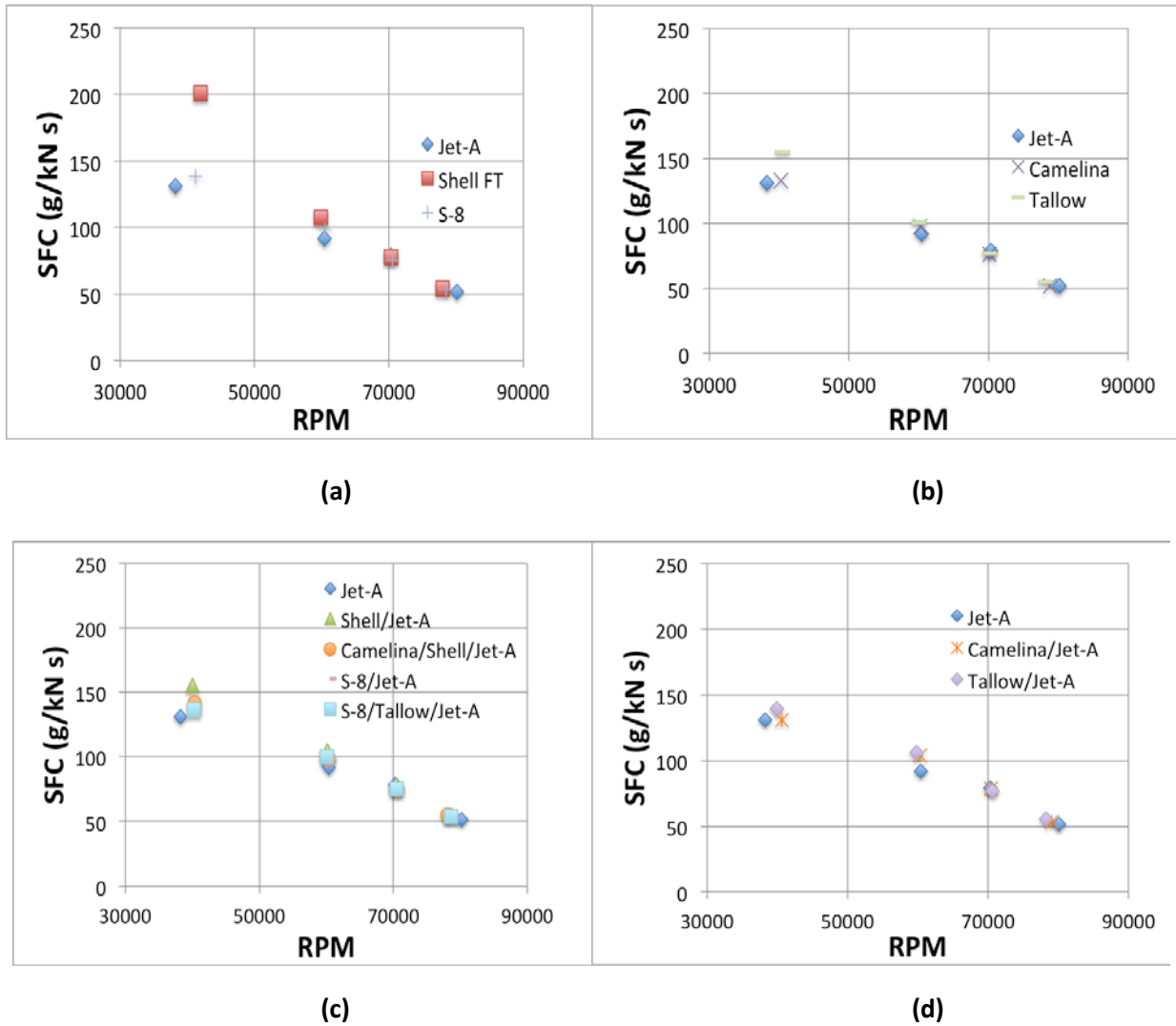


Figure 7 – SR-30 engine specific fuel consumption for several fuels (a) Synthetic; (b) HEFA; (c) Synthetic blends; and (d) HEFA blends.

Turbine inlet temperature (TIT) vs. engine RPM are plotted in fig. 8. The larger the rotational speed, the larger the TIT, as consequence of the increased fuel being burned at the combustor, but once again, there are not significant differences between the different fuels, which is not a surprise, since the SR-30 engine was designed to operate with kerosene like hydrocarbons and the tested fuels are that,

except that their source is not petroleum, as reported by Moses (2012) in his research survey about Aromatics and Distillation slope.

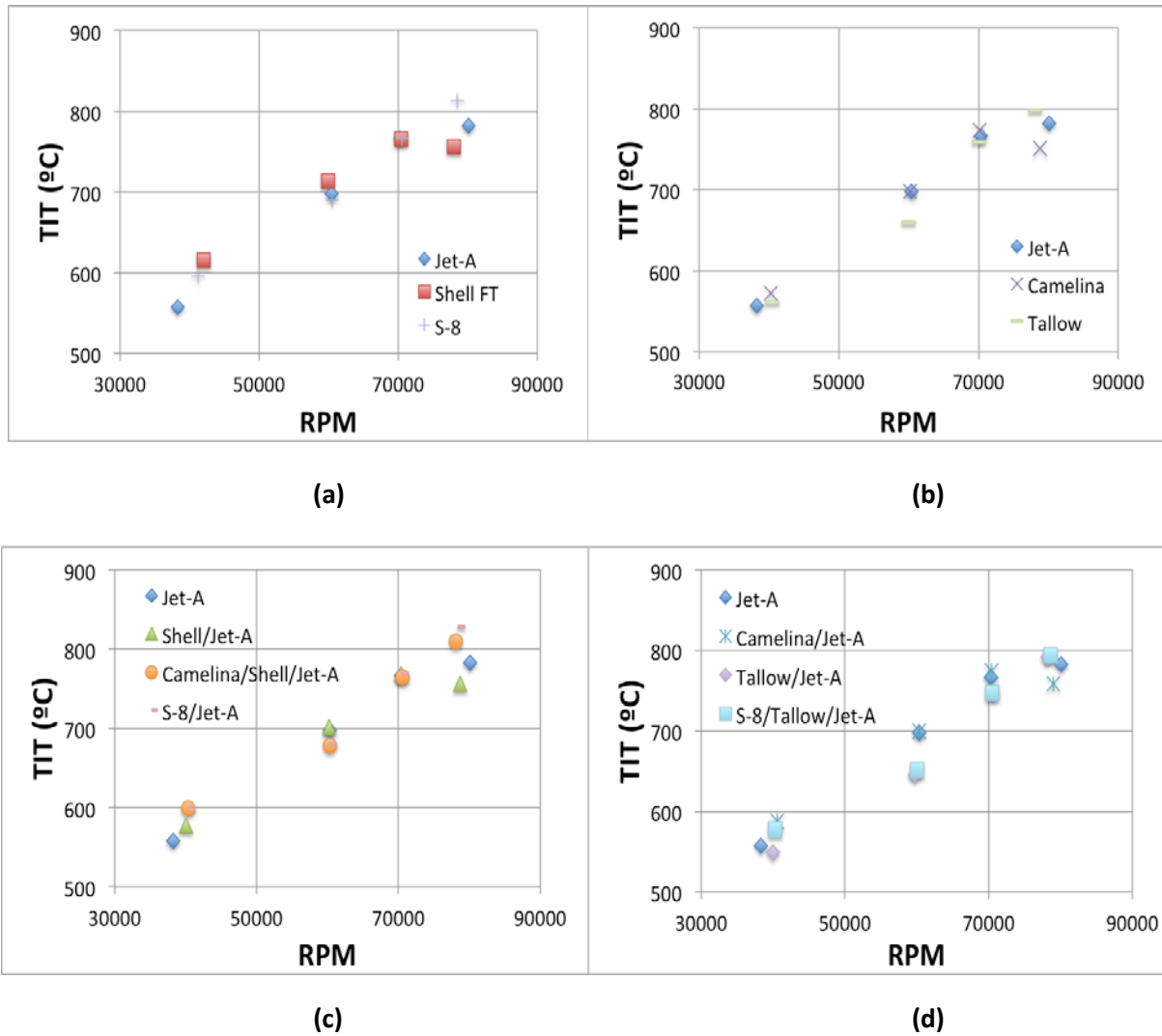


Figure 8 – SR-30 engine specific fuel consumption for several fuels (a) Synthetic; (b) HEFA; (c) Synthetic blends; and (d) HEFA blends.

4.2 Elastomer compounds compatibility

Figure 9 presents data for the mass variation of the O-ring samples after 3, 9 and 28 days immersion time in synthetic (fig. 10a), and HEFA (fig. 10b) fuels. For the case of raw fuels, it can be seen the effect of the lack of aromatic compounds, where the samples have an average loss of 0.4%, 0.8 and 1.6% after 3, 9 and 28 days of immersion, versus a mass gain of 6.1%, 8% and 10.9% after 3, 9 and 28 days, respectively for aromatics containing Jet-A. Blended fuels, on the other hand, did not show large mass variations between measurements, with a mass gain close to 2.5% after testing was completed.

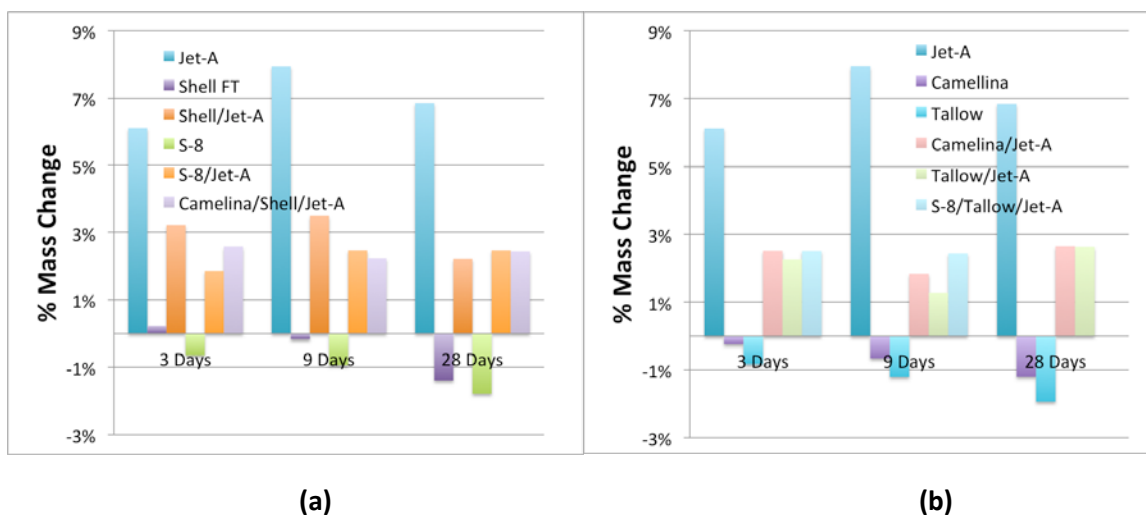


Figure 9 – O-ring mass change after immersion in fuels (a) synthetic; (b) HEFA

Volume variation for the immersed o-ring samples is shown in fig. 16 for synthetic (fig. 16a), and HEFA (fig.16b) fuel blends. For the oil derived Jet-A, aromatic species produce a swelling of 8%, 13.5% and 12% after 3, 9 and 28 days. On the other hand, raw FT and HEFA fuels experience a swelling of 1.1%

after 3 and 9 days, and only 0.3% after 28 days immersion, manifesting the impact of the lack of aromatics, and the reason why aircraft using those fuels are prone to fuel leaks. Blended fuels have a better behavior, with an average volume increase of 4.4%, 5.2% and 5.6% after 3, 9 and 28 days respectively, reasonable values for preventing leaks but still far from the effects of conventional Jet-A. Those results are in agreement with previous studies of the swelling of elastomer materials soaked up to 28 days in Sasol IPK and Syntroleum S-8 fuels, and 50% blends with Jet-A or JP-8 fuels (Moses, 2007, Graham et al., 2006) finding reduced swelling as result of the lack of aromatic compounds. Corporan et al. (2011) extended this analysis with Shell FT, UOP Camelina, Rentech FT, UOP Tallow and Dynamic HRJ fuels with an immersion time limited to 40 hours, finding an average swelling of 10%, compared to 16.6% in JP-8.

Inspection of figures 15 and 16, show an interesting trend in the mass and volume changes between days 9 and 28 for Jet-A, with a larger volume and mass variation at day 9 (8% and 13.5%) compared to day 28 (6.9% and 12%), and should be attributed to the removal effect of plasticizing compounds in O-rings by the fuels which can result in volume reductions up to 10%, as mentioned by Corporan et al. (2011). By day 9 some plasticizing compounds should be still present on the samples, while in day 28 they should be almost completely removed, and as consequence, resulting in lower mass and volume gains, as observed. This trend is not observed with the raw renewable fuels or their blends with Jet-A, and should be related to the lower concentration of aromatics.

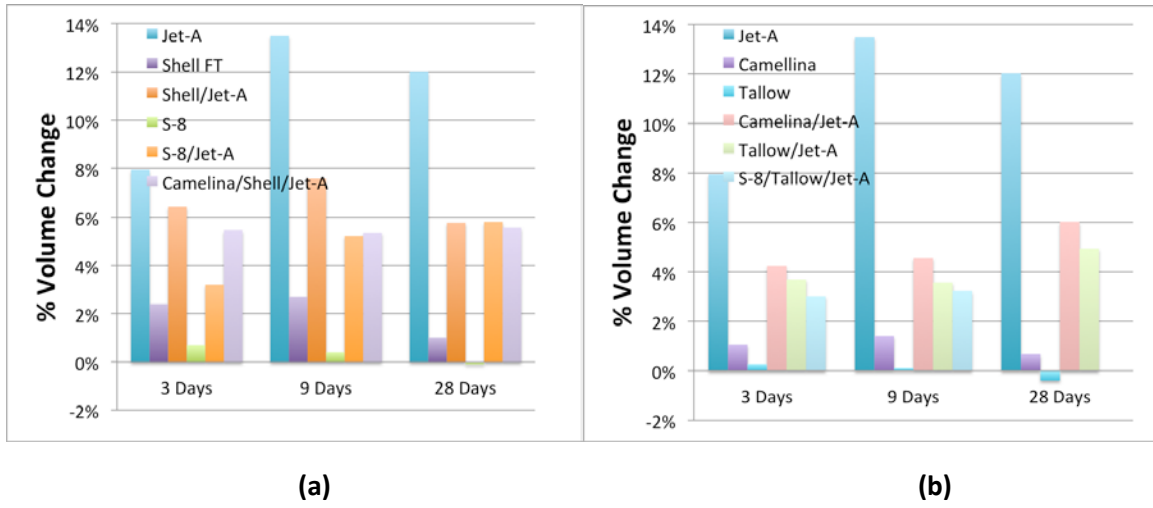


Figure 10 – O-ring volume change after immersion in fuels (a) synthetic; (b) HEFA

Figures 11 and 12 presents data for the mass and volume variation of the O-ring samples after switch loading, which is defined as the change between fuel aromatic-containing fuel to no aromatics fuel¹⁵. In a similar way to previously shown results, mass and volume measurements were taken after 3, 9 and 31 days. At the end of day 31, o-ring samples immersed in FT and HEFA fuels were switched to beakers filled with Jet-A, and samples previously immersed in Jet-A were switched to renewable fuels. Figures 14(b) and 15(b) show the quick mass (5.5% loss from day 31 to day 34) and volume (7.5% loss from day 31 to day 34) caused by the lack of aromatic compounds, and backs the current negative to certify fuels without aromatics for aircraft use. Finally, it must be mentioned how figures 17(b) and 18(b) back the affirmation about the plasticizing compounds, and the mass and volume changes difference between days 9 and 28 (31, in the present case). After the 31 day immersion, plasticizers should be completely removed from the samples, and therefore mass and volume variations for day 9 (40) are less than the ones at day 31 (62), when the o-rings have reached an equilibrium mass and volume increase.

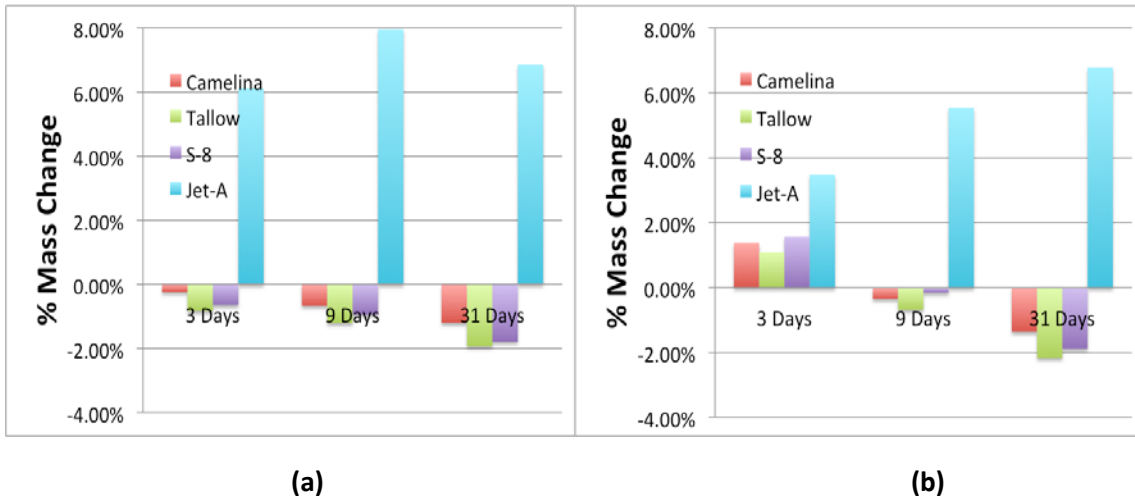


Figure 11 – O-ring mass change after (a) regular immersion and (b) switch loading

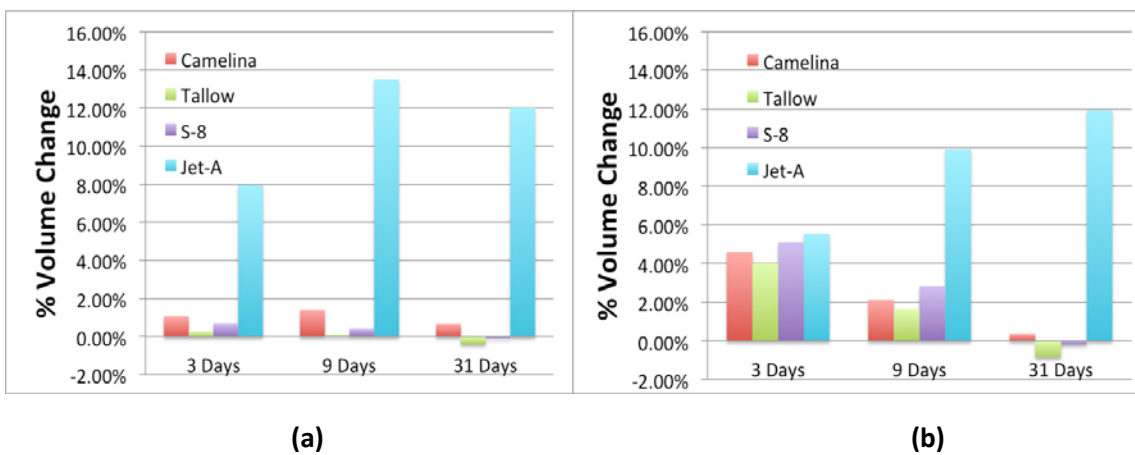


Figure 12 – O-ring volume change after (a) regular immersion and (b) switch loading

4.3 Deposits formation

Coking behavior of 2 Fischer-Tropsch (Shell FT and Syntroleum S-8) and 2 Hydrotreated Esters and Fatty Acids (UOP Camelina and Tallow) jet fuels, and their blends 50:50 in volume with Jet-A were compared against baseline Jet-A under operating conditions, and materials representative of aircraft

fuel systems. Dr. Blair’s fixed bed reactor, configured as a single tube heat exchanger was used where each fuel sample was allowed to flow through a metal tube placed inside a tube furnace set at 325 °C at 2 mL/min flow rate for 3 hours. Flow velocity, residence time, and Reynolds number within the test section for the different tests, can be seen in table 4.

Table 4 – Flow velocity, residence time and Reynolds number within test section

	Steel	Aluminum	Inconel	Titanium
Internal Diameter (mm)	1.8	1.9	1.4	2.4
Area (cm ²)	0.02	0.03	0.02	0.04
Velocity (cm/min)	82.9	70.2	130.5	45.6
Residence Time (s)	18.1	21.4	11.5	32.9
Reynolds Number	55.0	50.6	69.0	40.8

Figure 13 shows the carbon deposits for the studied fuels and three metal alloys: 316 Stainless Steel, Inconel 600 Nickel alloy, and Grade 2 Titanium. Thermal deposits, up to 36 µg/cm², are consistent with similar experiments with Jet-A under similar conditions (Venkataram and Eser, 2008). The lowest thermal deposits were obtained with the Camelina and Sytnroleum blends with Jet-A (22.7 µg/cm² in average) while the largest amounts were obtained with baseline Jet-A and its blends with Shell FT and Tallow fuels (26.3 µg/cm² in average). Blank spaces correspond to deposit measurements below the resolution of the analytical balance used to determine the weight of the tubes after thermal stressing, and for this reason deposits from aluminum tubing are not shown. Some fuels exhibit peaks in deposition when the flow rate was increased, while others maintained a flat response, as consequence of the chemical and physical factors in the laminar flow regime (Hazlett, 1991). Regarding the effects of flow rate in the deposits observed in fig. 13, fuels with low chemical reaction rates in the viscous layer adjacent to the surface may exhibit little effects of flow rate in the deposition rate, while physical factors (diffusion) limit the availability of reactants in the boundary layer (Clark and Thomas, 1988) in fuels with

higher chemical reaction rates. Despite the flow rate for the coking deposition experiments presented in this study is fixed, the difference in tube diameters, as seen in table 4 resulted in Reynolds number, and residence time variations. As result of its inner diameter, fuel stressed in Titanium tubes stayed almost three times that of Inconel, however the coking deposits were within $15 \mu\text{g}/\text{cm}^2$ while fuel stressed in Al3003 stayed an average of 21 seconds, and the deposits formed were the smallest. Therefore, it is suggested that the fuels tested are reaction rate limited, instead of diffusion limited at the transition regime. On the other hand, further experiments, varying furnace temperature and flow rate should be performed, in order to fully corroborate this finding, and provide a view from the reaction kinetics perspective.

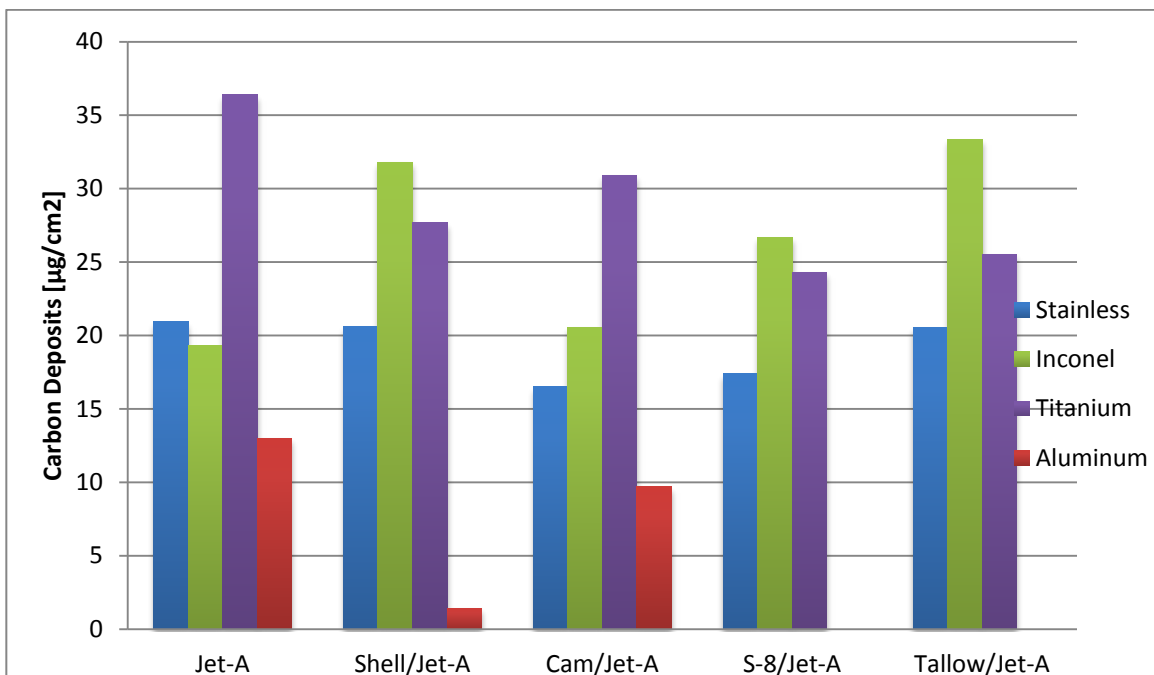


Figure 13 – Carbon deposits on different metal surfaces for Jet-A and renewable fuels

Regarding the different metal alloys tested, deposit formation was in the following order: Grade 2 Titanium > Inconel 600 > SS 316 >> Al3003. Given that flow conditions, oven set temperature, and fuels were the same for all tests, the differences between depositions, especially in the case of aluminum tubing may only be explained by the alloys surface nature (Taylor, 1968). Researchers have proposed two theories associated with the role of surface metal and deposits: When fuels get in contact with the hot metal, fuel components, such as naphthenic acids react with metals forming fuel-soluble metal naphthenates which may initiate autoxidation reactions or enhance reaction rates, while the second theory suggest that gums formed in the autoxidation process have different affinities on the surface materials, adhering to some surfaces more than others (Stavinoha et al., 1990). UV-visible absorption measurements on the stressed fuels revealed the formation of deposits precursors, as discussed in the next section of this study, for all the fuels and surfaces tested. Therefore, it is suggested that resistance of aluminum, stainless steel tubes (in a lesser proportion) to surface deposits formation, despite the creation of precursor species, is related to a lower affinity of the base metals to the deposits adhesion.

Table 5 shows the elemental composition of the metal alloys used in the experiments. In addition to their effect in improving the mechanical properties of the material, alloy metals have an effect on the deposition behavior of the tubes. In the case of the stainless steel, base iron and iron oxides are known to catalyze dehydrogenation reactions and carbon deposition (Tanabe et al, 1989), however, the surface passivation effects of chromium may reduce this catalytic action (Mohan and Eser, 2010). Inconel 600 tubes base Nickel is alloyed with chrome, manganese, iron and copper, while 3003 aluminum is alloyed with manganese, cooper and iron. Of those elements, copper is known for its

catalytic behavior and negative effects on the thermal stability of fuels (Hazlett, 1991). However, as shown in fig. 13, Inconel and Al3003 tubes present the lowest deposits, meaning that surface copper is not available for acting as deposition catalyst. An opposite effect is seen when observing the behavior of the fuels stressed in titanium tubes. Addition of Ti to stainless steel reduces susceptibility to intergranular corrosion, stabilizing the alloy (Eser et al., 2006), and suppressing carbon deposition under pyrolytic conditions (Mohan and Eser, 2010). On the other hand grade 2 titanium tubes presented higher deposits than the Inconel and aluminum tubing, therefore it is suggested that unalloyed titanium has an important catalytic effect on the fuels, contributing to the cracking of fuel bulk constituents, such as paraffins and cycloalkanes, into reactive intermediates, and a good affinity for deposits adhesion at the surface.

Table 5 – Elemental composition of alloys (ASTM)

Alloy	Elemental Composition										
	Fe	Ni	Cr	Mn	C	Mo	Si	S	Cu	O	Zn
SS 316		14	18	2.0	0.08	3	0.75	0.03			
AL3003	0.7			1.5			0.6		0.2		0.1
IN600	10	72	14	1.0	0.15		0.5	0.015	0.5		
Grade 2 Titanium	0.3				0.08					0.08	

UV-visible absorption measurements were performed in order to determine fuel composition changes as result of the thermal stressing. Figure 14a shows the absorption spectrum for an unstressed Jet-A sample, where it can be seen how it absorbs a large amount of light from 400 nm and below, and is quasi-transparent at larger wavelengths, which is typical of molecular species with a structured absorption spectrum (Parker et al., 1992).

Figure 14b shows the absorption spectra for Jet-A samples thermally stressed, where a shift towards longer excitation wavelengths is observed. This phenomenon should be attributed to a larger

concentration of aromatic compounds produced by the break up of long chain alkanes and cycloalkanes at higher temperature (Andrésen et al., 2001), as well as the formation of dissolved particulate, which act as broadband absorbers, when present in large quantities (Parker et al., 1992). Figure 15(b), shows a chromatogram of a Shell FT sample blended 50% in volume with Jet-A prior to thermal stressing (blue), and after 3 hours stressing in a 3003 aluminum tube at an oven temperature of 325°C (red).

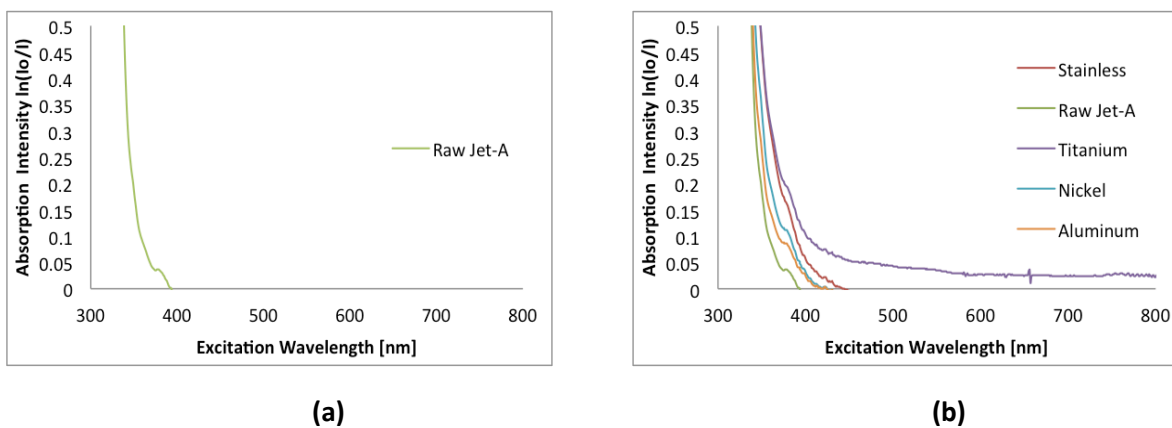


Figure 14 – UV visible absorption spectra of (a) raw Jet-A, and (b) stressed Jet-A.

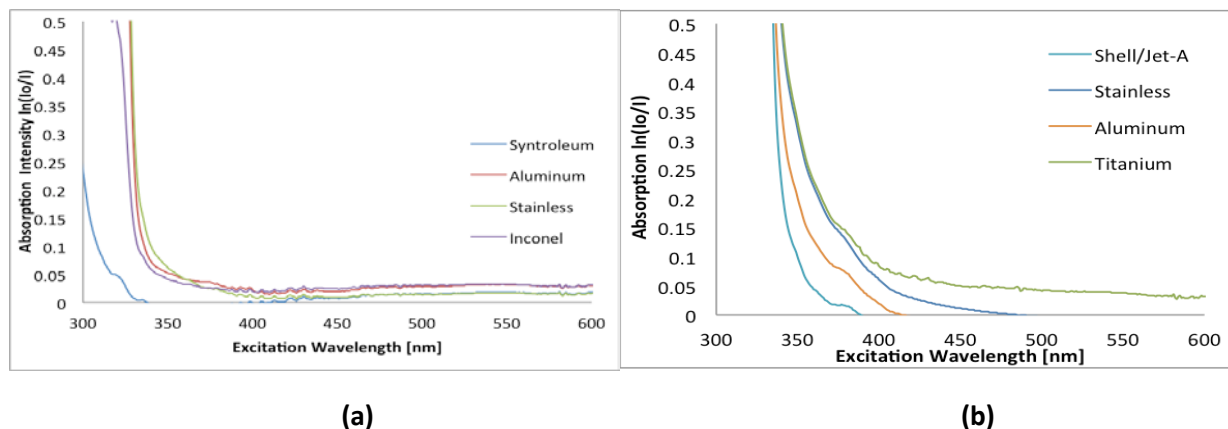


Figure 15 – UV light absorption spectra of (a) raw Syntroluem S-8, and (b) Shell FT blended with Jet-A

Analysis of jet fuel samples by gas chromatograph-mass spectrometry (GC-MS) was also performed in order to further analyze the changes in the fuel composition after thermal stressing. Figure 15, shows a chromatogram of a Shell FT sample blended 50% in volume with Jet-A prior to thermal stressing (blue), and after 3 hours stressing in a 3003 aluminum tube at an oven temperature of 325°C (red). A decrease in the relative concentration of species can be seen, suggesting the breakup of raw hydrocarbons into coking precursor compounds. Low residence time, and relatively lower temperatures, compared to the pyrolytic regime (~500 °C vs. ~300 °C of the present experiments) explain the relatively small concentration differences between raw and stressed fuels compared to those reported for Jet-A under pyrolytic conditions (Andrésen et al., 2001). It must also be noted, that the large number of compounds, and the low concentration of some individual species makes difficult the task of identifying them under GC/MS analysis (Balster et al., 2006).

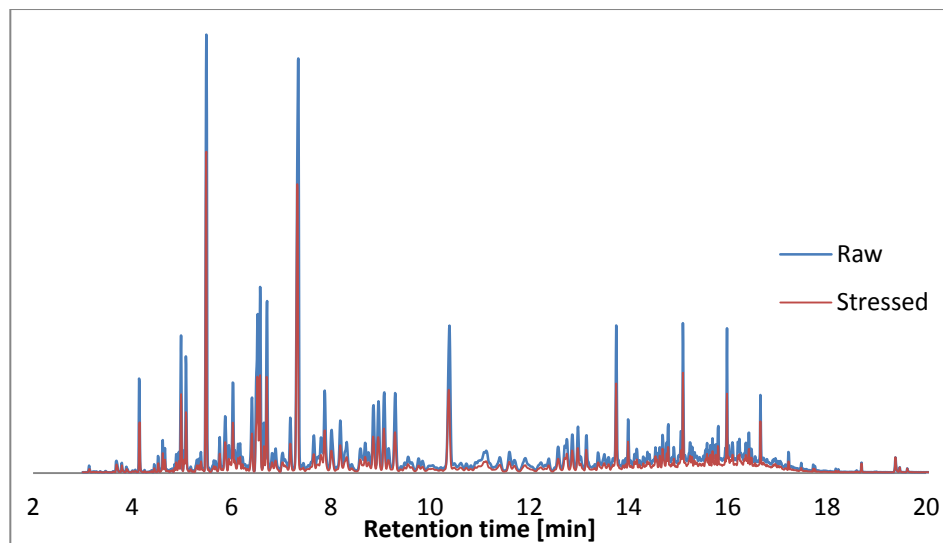


Figure 16 – Gas chromatogram of Shell FT blended with Jet-A prior to thermal stressing (blue), and after 3 hours at 325°C (red)

CHAPTER 5: CONCLUSION

5.1 Summary

Fit-for-purpose ability of alternative aviation fuels was investigated by studying the effects of the fuel properties and composition effects on elastomer materials, and micro-turbine performance. When elastomer o-rings, similar to those used in aircraft fuel systems were immersed in renewable fuels, smaller volume change or swelling was detected (lower than 2%), contrary to a 14% swelling observed for baseline Jet-A. Lower swelling may result into leaks during aircraft operation. This trend was reversed when renewable fuels were blended with aromatics containing Jet-A.

Lower energetic content per unit volume of the renewable fuels, resulted in a thrust reduction around 10% when compared to baseline Jet-A at full throttle settings, but other than this, no other significant effect on the engine combustion temperature or other parameters were found for short duration testing. However, after longer duration testing and frequent fuel switching coking deposits were formed in the fuel injectors resulting in turbine malfunction. It is this finding that led to the primary focus of this thesis - thermal stability and deposit formation for alternative fuels.

Thermal stability behavior of 4 alternative fuels developed under Fischer-Tropsch or Fatty Acids Hydrotreating, and their blends 50:50 in volume with Jet-A was compared against baseline Jet-A under operating conditions, and materials representative of aircraft fuel systems in a single tube heat exchanger with temperature set at 325 °C and 2 mL/min flow rate for 3 hours. Thermal deposits, obtained by gravimetric analysis of tubes before and after testing, were in the following order: Grade 2 Titanium > Inconel 600 > SS 316 >> Al3003, in consistency with experiments with Jet-A under similar

conditions (Venkataram and Eser, 2008) Given that flow conditions, oven set temperature, and fuels were the same for all metals, differences in deposition behavior, were the result of a lower affinity of base metal to the deposits adhesion in certain alloys, despite the creation of precursor species, as observed when analytical techniques as UV absorption and GC/MS were performed on fuel samples in order to find compositional changes after thermal stressing. UV-visible absorption showed the presence of dissolved particulate and aromatic compounds as result of the break up of longer hydrocarbon chains as due to temperature and surface catalytic effects.

5.2 Future work

Since stressed tubes were stored it is possible to expand and improve the presented study by performing thermally programmed oxidation (TPO) in order to measure with more precision the deposits. In addition techniques such as scanning electron microscopy should reveal useful information, linking the carbonaceous solids to the hydrocarbon precursors that formed them. Finally extension of the experiments at different temperature and flow rate settings should provide a better understanding in the fuel deposits kinetics.

APPENDIX A: SUMMARY OF FUEL THERMAL STABILITY EXPERIMENTS

Test Fuel	Test Metal	Date	Temperature [°C]	Test Time [h]	Carbon Deposits [µg]
Jet-A	SS316	8/24/12	325	3	357
Shell	SS316	9/19/12	325	3	...
Camelina	SS316	9/4/12	325	3	...
S-8	SS316	8/30/12	325	3	220
Tallow	SS316	9/5/12	325	3	...
Shell/Jet-A	SS316	8/31/12	325	3	514
Camelina/Jet-A	SS316	8/28/12	325	3	...
S-8/Jet-A	SS316	8/30/12	325	3	369
Tallow/Jet-A	SS316	10/2/12	325	3	0
Jet-A	Al 3003	8/27/12	325	3	58
Shell	Al 3003		325	3	25
Camelina	Al 3003		325	3	...
S-8	Al 3003		325	3	52
Tallow	Al 3003		325	3	...
Shell/Jet-A	Al 3003	9/7/12	325	3	8
Camelina/Jet-A	Al 3003	9/6/12	325	3	18
S-8/Jet-A	Al 3003		325	3	...
Tallow/Jet-A	Al 3003		325	3	64
Tallow/Jet-A	Al 3003	8/29/12	325	3	...
Jet-A	Inconel 600		325	3	...
Shell	Inconel 600		325	3	...

Test Fuel	Test Metal	Date	Temperature [°C]	Test Time [h]	Carbon Deposits [µg]
Camelina	Inconel 600		325	3	...
S-8	Inconel 600	9/11/12	325	3	...
Tallow	Inconel 600		325	3	...
Shell/Jet-A	Inconel 600		325	3	384
Camelina/Jet-A	Inconel 600	9/13/12	325	3	...
S-8/Jet-A	Inconel 600	9/13/12	325	3	143
Tallow/Jet-A	Inconel 600	9/12/12	325	3	128
Jet-A	Titanium	9/28/12	325	3	675
Shell/Jet-A	Titanium	9/28/12	325	3	83
Camelina/Jet-A	Titanium	10/1/12	325	3	828
S-8/Jet-A	Titanium	10/1/12	325	3	598
Tallow/Jet-A	Titanium	10/1/12	325	3	103

APPENDIX B: ENGINE DAMAGE

After longer-term test runs with the renewable fuels, it was noted a drop in maximum engine RPM, from ~79,000 to ~76,000 RPM. In a beginning this trend was believed to be a consequence of the lower heating value per unit volume of renewable fuels, as discussed earlier, but this tendency continued, even when the engine fuel was switched back to Jet-A. Concerns about the engine status increased, when post-processing of the engine temperature data, showed that Turbine Exit Temperature (TET) readings were anomaly high, close to 1000°C, vs. ~ 700 °C nominal values. Additional test runs were performed discarding instrumentation error, but after contacting the engine manufacturer, it was suggested the possibility of a malfunction in the fuel system, resulting in localized heat areas in the engine, thus explaining the temperature readings. This was confirmed by taking a look on the turbine from the rear, where an overheated area was located just next to the turbine exhaust temperature thermocouple, as seen in fig. 17. For safety reasons the engine was removed from its test stand and sent to the manufacturer for inspection.

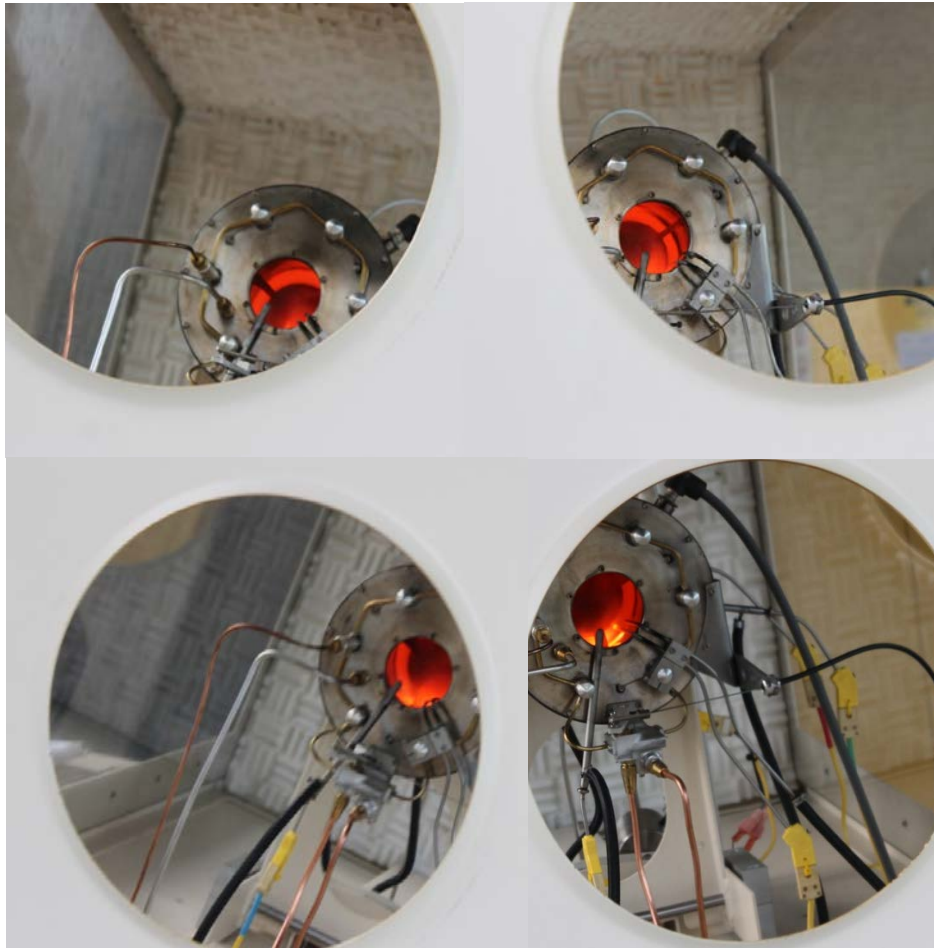


Figure 17 – Localized overheated zone (bottom right hand picture) at the turbine exhaust.

When manufacturer technical staff inspected the engine, it was found that the vane guide ring (the airfoil nozzle Inconel casting before the turbine rotor) was damaged beyond repair, as seen in fig. 18. Two of the 21 vanes were completely burned out, and a third one partially with a crack spanning from leading to trailing edge, with the biggest damage in this area. Fuel injection system inspection revealed an apparently normal spray pattern, however it results puzzling to see such a large damage in the vane guide ring, and not any at the combustor liner; an unstable flame, hot enough, as to cause the

damage seen in the nozzle vanes, should have also eroded the combustor liner, since the hot gas path includes a 180° turn towards the turbine section, as seen in fig. 19.



Figure 18 – Turbine stator damage

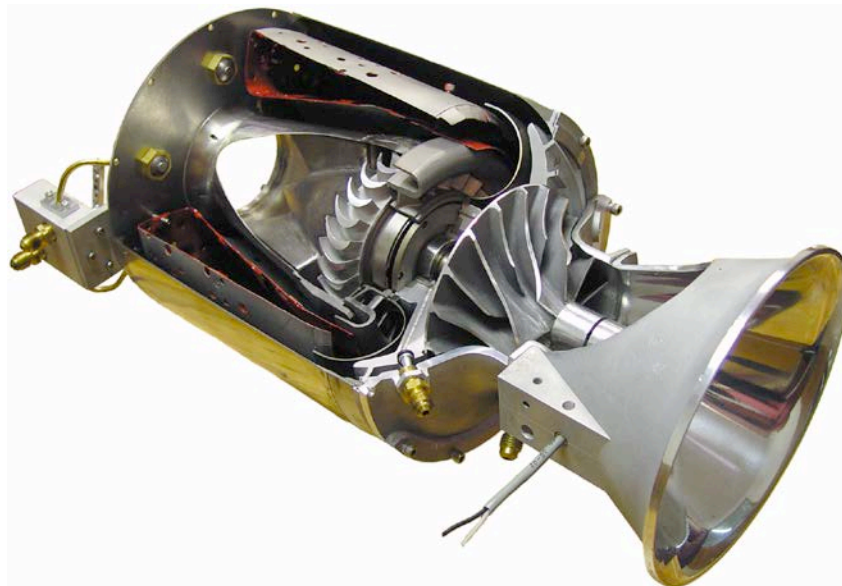


Figure 19 – SR-30 engine cutaway (courtesy of Turbine Technologies).

After the reception of the turbine from the manufacturer the unit was assembled, and test runs were made using crude-derived Jet-A, with all the temperature instruments reading nominal values. However the turbine exhaust was also inspected, finding once again a localized heated zone, in the same area where the turbine stator had failed (fig. 20). This zone was only visible at high throttle settings, and once the issue was detected, throttle was immediately set at a lower RPM in order to avoid turbine damage. Engine manufacturer was contacted, and it was recommended to disassembly the fuel injectors (fig. 21), to be re-inspected at the factory. The inspection report revealed a non-homogeneous spraying pattern, with larger size fuel droplets leaving from one of the injectors. Apparently those droplets did not burn completely in the combustor, but downstream, causing the localized heat zone, and the damage to the turbine stator. Fuel injectors were overhauled, and sent back to UCF where the turbine was reassembled. A new test run under Jet-A did not reveal the localized heat zone, however it still must be addressed the causes of this nozzle fouling, which may be related to fuel contamination, fuel thermal stability issues, or nozzle fouling during assembly.



Figure 20 – Localized overheated zone after repair (left) and before repair (right)

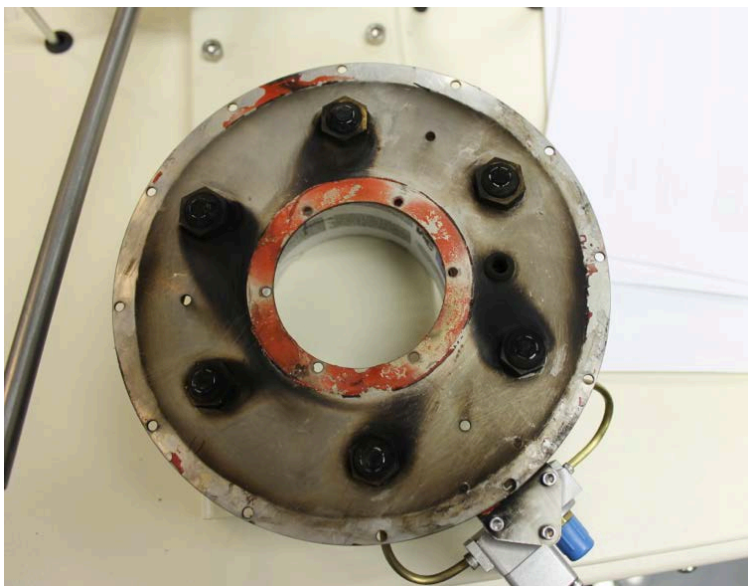


Figure 21 – SR-30 Engine fuel injectors before overhaul

APPENDIX C: ALTERNATIVE FUELS EFFECT IN AIRCRAFT RANGE AND PAYLOAD

Figure 22 shows the effect of different renewable fuels mixes in the range versus payload plot for a mid size wide-body airliner. The horizontal line at the beginning of the plot is based in structural considerations representing the maximum design payload the aircraft can safely carry. It should be noted that in this point the aircraft has no fuel, and therefore the range is 0 nm. As fuel is added, the range is increased, until the maximum aircraft weight, which is based on structural and operational limitations. At this point reducing the payload as the aircraft is fueled is the only way to increase range, until the tanks are full, with further range increases made by reducing drastically the payload, as seen in the steep slope afterwards, with a maximum range obtained at zero payload, which does not make sense from an operational point of view). Since it has been shown that range is a function of SFC, which is affected by the fuel heating value, and the fuel density, changes in those fuel properties will have a significant impact on aircraft performance. Paraffinic compounds are a major component of renewable fuels, noted by their higher hydrogen to carbon ratio, and therefore a lower density and higher heat release per unit mass as shown in table 1. Those properties should lead to an increased range at maximum payload, as seen in fig. 22, where the use of the FT and HEFA fuels results in an average increase of 2.4% in range when compared to the baseline case, value reduced to 1.2% when blended in 50/50 by volume with Jet-A. Those results agree with conclusions drawn by the Airport Cooperative Research Program (2011) regarding the improvement by around 1% in SFC for aircraft when flown with 50/50 volume blends with renewable fuels, and therefore an increased aircraft range. Reduced density has also a negative impact at the full tank configuration, resulting in a reduction in the maximum range. On the other hand, this effect is partially compensated by an increase in the payload, for the studied aircraft model, the use of raw FT and HEFA fuels resulted in a 6.4% range decrease, with a remarkable payload increase of 23.6% (3.6% range decrease for an increment of 11.8% in payload when blended

with Jet-A. As a final note, it should be stressed that the presented analysis is an oversimplified one, and does not take into account all the conditions found in actual aircraft operations, but the presented results provide helpful outline of the fuel composition effects on aircraft range and payload performance.

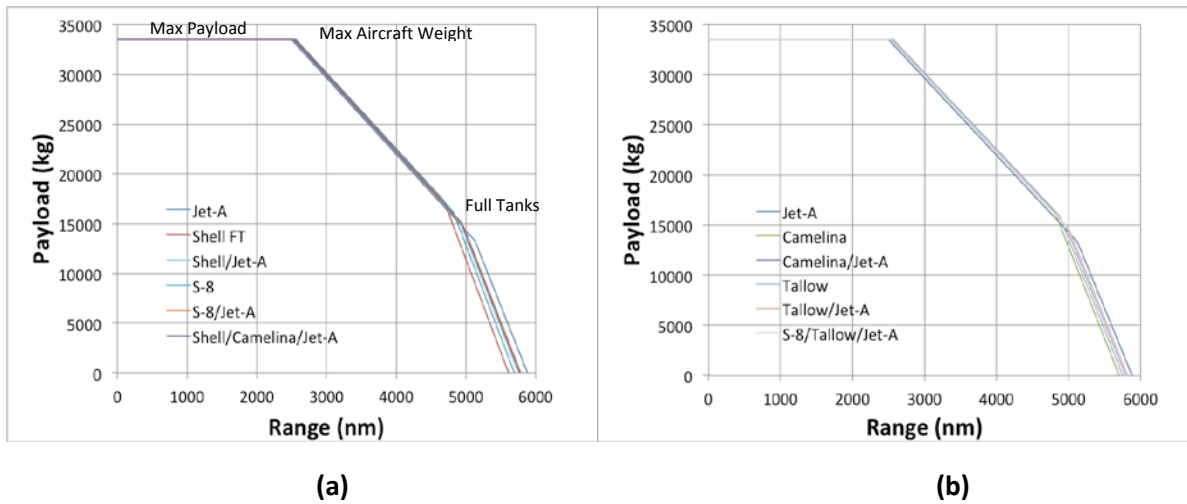


Figure 22: – Effect of fuels in aircraft payload vs. range (a) FT fuels; (b) HEFA fuels.

APPENDIX D: PUBLICATION LIST

- Arias Quintero, S., Schmitt, J., Blair R., and Kapat, J., 2013. "Alternative Microturbine Fuels Feasibility Study Through Thermal Stability, Material Compatibility and Engine Testing". ASME Turbo Expo 2013, San Antonio, TX, GT2013-95032. (Draft paper submitted).
- Arias Quintero, S., Nash, D., Blair, R., and Kapat, J., 2013. "Comparison of Thermal Stability Characteristics of Fischer-Tropsch and Hydroprocessed Renewable Jet Alternative Fuels in a Fixed Bed Reactor". ASME Turbo Expo 2013, San Antonio, TX, GT2013-95041. (Draft paper submitted).
- Arias Quintero S., Ricklick, M., and Kapat, J., 2012, "Synthetic Jet Fuels and their Impact in Aircraft Performance and Elastomer Materials" AIAA Joint Propulsion Conference, July 30-August 1, Atlanta, GA.
- Arias Quintero, S., 2012, "Synthetic Fuels and the UCF Experience." Presentation at the 6th Annual Alternative Energy NOW Conference, March 7, 2012, Lake Buena Vista, FL.

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