U.S. Department of Transportation
Federal Aviation Administration

FINAL PROJECT REPORT

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PART I - PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Washington State University	2. FAA Program Centers of Excellence	3. FAA Award Number 13-C-AJFEW-WaSU, 31B
Office of Research Support and Operations, Lighty 280, PO Box 641060, Pullman, Washington	4. Award Period From 10/1/2015 To 9/31/2017	5. Cumulative Award Amount 130,958

6. Project Title

Effect of Residual Oxygenated Functional Groups on the Behavior of Alternative Jet Fuel Properties (Project 31B)

, PART II - SUMMARY OF COMPLETED PROJECT (For Public Use)

The goal of this project is to identification of the nature and the content of the oxygenated compounds present in alternative jet fuels and to develop methods for the fast identification of these oxygenated compounds. 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) were studied. 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 oxygenated compounds measured was in all the cases very low and comparable with the amount found in commercial jet fuels. Phenols are the most common trace oxygenated compounds found in aviation fuels.A new method based on the identification of extracted phenolic compounds by UV-fluorescence was developed. This method is much faster to identify the presence of phenols but does not allow to quantify them and still requires SPE of phenols. In order to avoid the extraction step, fluorescence quenching with Rhodamine-B in jet fuel was studied. Rhodamine-B shows fluorescence quenching in the presence of phenols. A new method is proposed for the fast identification of phenols in jet fuels at operational field conditions.

PART III - TECHNICAL INFORMATION (For Program Management Uses)

1. **ITEM** (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (X)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators		X			
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					

2. Principal Investigator/Project Director Name (Typed) Manuel Garcia-Perez	3. Principal Investigator / Project Director Signature	4. Date 4/29/18

FAA Form 9550-5 (03-03) Supersedes Previous Edition

PART III- TECHNICAL INFORMATION

a) Abstracts of Thesis

Author: Anamaria Paiva, MSc Thesis, April 2016

Title: Characterization of Alternative Jet Fuels and Effect of Residual Oxygenated Functional Groups on their Properties.

Abstract: Concerns with CO_2 emissions by the aviation industry have increased in the last decades as the global warming have induced record levels of temperature and this sector is likely to expand in the following years, contributing more to climate change. The use of alternative fuels is a promising alternative to help address this issue. In this thesis we study the properties of alternative jet fuels are measured as a way to better understand their performance and to identify ways to improve their quality. In the first chapter, a general introduction provides an overview of the feedstocks and technologies currently used to produce alternative jet fuels. In the second chapter, the chemical composition and fuel properties of twelve alternative jet fuels (Two from Gevo, FT coal, FT methane, HEFA Tallow and two HEFA Camelina, Amyris Renewable Diesel, ReadiJet, Kior and Virent SK and SAK) and three commercial jet fuels (Jet-A, JP5 and JP8) were investigated. Our results confirm that the alternative jet fuels studied today cover a wide range of composition and fuel properties. Overall the fuels analyzed comply with most of ASTM requirements and offer opportunities to develop specialized jet fuel. In chapter three, the presence of oxygenated compounds in these fuels was investigated and surrogate blends of three common oxygenated molecules in the fuels (Phenol; 2-methylphenol; Ethanol-2-methoxyethoxy) were prepared with Jet A commercial fuel, at five different concentrations: 0.01, 0.1, 1, 2 and 5 % wt. Our results indicate that none of the oxygenated compounds, in the concentration

range studied, affect surface tension, viscosity or flash point. The higher heating value showed a slight decline with the increment on surrogate concentration, achieving 1.19% reduction for the highest concentration on Phenol surrogate, 1.22% reduction on Methyl phenol 5% surrogate and a maximum reduction on Ethanol-2-methoxyethoxy 5% surrogate, achieving a value of 1.46 %. Water solubility at 0 ºC increased with the content of oxygenated compound in the fuel.

Author: Kalidas Mainali, MSc thesis, 2018
Title: Identification and Quantification of Trace Oxygenated Compounds in Alternative Jet Fuels

In modern society, air transport is a part of everyday life. The study of alternative jet fuel is motivated by the need to reduce the environmental impact of the aviation industry. The final step in all the pathways for the production of alternative jet fuels is the removal of oxygen via hydro-treatment. If not properly conducted, some trace oxygenated compounds may remain in the fuel. Thus, a major challenge of using biofuels in a commercial aircraft is ensuring low levels of oxygenated compounds which are known to be responsible for fuel reduced thermal stability. A number of methods available in the literature for the isolation and characterization of oxygenated compounds in jet fuel are reviewed. Most of the methods reported are based on the concentration of trace oxygenated compounds in a polar adsorbent by solid phase extraction (SPE) followed by the solubilization in methanol and the quantification of targeted polar compounds by GC/MS. Phenols are the most common trace oxygenated compounds found in aviation fuels. Our results, using phenolic model compounds added to jet fuel confirm that the SPE removal and GC/MS quantification steps are done quantitatively. A new method based on the identification of extracted phenolic compounds by UV-fluorescence was developed. This method is much faster to identify the presence of phenols but does not allow to quantify them and still requires SPE of phenols. In order to avoid the extraction step, fluorescence quenching with Rhodamine-B in jet fuel was studied. Rhodamine-B in Jet fuel shows fluorescence quenching in the presence of phenols. A new experimental approach based on Rhodamine-B fluorescence quenching is proposed for the fast identification of phenols in jet fuels at operational field conditions.

b) Publication Citation:

1. Pires APP, Han Y, Kramlich J, Garcia-Perez M: Chemical Composition and Fuel properties of Alternative Jet Fuels. BioResources, 2018, Vol. 13, No 2, 2632-2657
2. Mainalis K, Garcia-Perez M: Identification and Quantification of Trace Oxygenated Compounds in Alternative Jet Fuels: Fluorescence Quenching Methods for Fast detection of Phenolic Compounds in Operational Field conditions. In Preparation. Paper to be submitted to Energy and Fuels, 2018

c) Data on Scientific Collaborators

Investigative Team

Manuel Garcia-Perez, PI, Washington State University, Project lead Fuel Characterization

Philip Malte, Co-PI, University of Washington, Experimental supervision and data interpretation

John Kramlich, C-PI, University of Washington: project management, experimental supervision and data interpretation

Arshiya Hoseyni, Graduate research assistant, University of Washington: Determination of the combustion properties of the oxygenated fuels: lean blowout, NOx emissions, and soot point

Anamaria Paiva, Graduate research assistant, Washington State University, primary responsible for fuel properties quantification

Yinglei Han, Graduate research assistant, Washington State University, primary responsible for fuel chemical characterization

Kalidas Mainali, Graduate research assistant, Washington State University, primary responsible for the development of methods for the fast quantification of trace oxygenated compounds using UV fluorescence and UV fluorescence quenching

ASCENT
AVIATION SUSTAINABILITY CENTER
FAA CENTER OF EXCELLENCE FOR ALTERNATIVE JET FUELS & ENVIRONMENT

Project 31B Methods for the Fast Quantification of Oxygenated Compounds in Alternative Jet Fuels

Washington State University

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University Participants

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- P.I.(s): Manuel Garcia-Perez
- FAA Award Number: 13CAJFEWaSU-004 and 008
- Period of Performance Reported: October 1st, 2015, to August 31st, 2017
- This report covers two separate period: October 1st, 2015 to March 1st, 2016 (First year project) and July 1st, 2016 to August 31st, 2017. This project was not funded between March 1st and July 1st, 2016.
- Task(s):
    1. AJF sample collection
    2. Identification of the nature and quantity of residual oxygenated compounds in selected AJFs under ASTM consideration
    3. Preparation of surrogate blend and evaluation of the effect of five most important oxygenated compoinds indentified on the fuel properties of AJFs
    4. Determination of lean blow out limit, NOx and sooting threshold
    5. Literature review to identify characterization strategies for the fast identification and quantification of the residual oxygenated compounds in AJFs
    6. Improving the method for quantification of independent oxygenated compounds in AJFs
    7. Development of methods for the fast quantification of oxygenated compounds in jet fuels

Project Funding Level

Washington State University: Funds from the FAA ($ 100,961), Matching funds ($ 106,130), Source: State Funds to support one graduate student (from Dr. Wolcott's state funded program), departmental funds to purchase analytical equipment and Dr. Garcia-Perez's salary.

University of Washington: Amount of funding from the FAA ($ 29,997), Matching funds ($30,002), Source: State funds from salaries of Profs. Kramlich and Malte

Investigation Team

Arshiya Hoseyni (PhD student): Determination of the combustion properties of the oxygenated fuels: lean blowout, NOx emissions, and soot point

Anamaria Paiva (MSc student): Analysis of chemical composition and fuel properties of alternative jet fuels

Yinglei Han (PhD student): Improving the methods for quantification of independent oxygenated compounds in AJFs

Mainali Kalidas (MSc student): Literature review and development of methods for the fast quantification of oxygenated compounds in jet fuels

Manuel Garcia-Perez (Associate Professor): Principal Investigator, project management and reporting

Philip Malte (Professor): Experimental supervision and data interpretation

John Kramlich (Professor): Principal Investigator, project management, experimental supervision and data interpretation

Project Overview

By 2050 the International Air Transportation Association (IATA) aims to reduce the net CO_2 production by 50 % compared with the 2005 levels (Hileman et al. 2013). The large scale production of alternative jet fuels could achieve this goal while improving national energy security, and helping to stabilize fuel costs for the aviation industry. The goal of the Federal Aviation Administration (FAA) is to contribute to catalyze the production of 1 billion gallons of "drop in fuels" by 2018. Today there are four technologies approved by ASTM (ASTM D7566) to produce AJFs (Brown 2013): (1) Hydro-processed Ester and Fatty Acid (HEFA) (Pealson 2011, 2013, Malina 2012, Seber et al. 2014), (2) Fischer Tropsch (FT) (Malina 2012, Henrich 2007, 2009, Spath et al. 2005, Wright 2008, Swanson et al. 2010, Marano and Ciferno 2001), and (3) Direct Sugars to Hydrocarbons (DSHC | Amyris) (Total-Amarys, 2012) (http://www.astmnewsroom.org/default.aspx?pageid=3463) and (4) Alcohol to Jet (ATJ | Gevo) (Johnston 2013, GEVO 2012) (http://www.iata.org/pressroom/facts_figures/fact_sheets/pages/alt-fuels.aspx). Another four additional pathways are under various stages of the ASTM evaluation process: (5) Hydrotreated depolymerized cellulosic jet (HDCJ | UOP, Kior) (Wildschut et al. 2009, French et al. 2010, Ringer et al. 2006, Jones et al. 2009, Elliott 2010), (6) Synthesized Kerosene containing aromatics (SKA | UOP), (7) Synthetic Kerosene and Synthetic Aromatic Kerosene (SK&SAK | Virent), and (8) Catalytic hydro-thermolysis (CH | ARA (ARA 2011).

Each of the fuels that will be produced by these alternative pathways must undergo rigorous testing to meet ASTM International specifications (ASTM D4054-09, D7566-14a) (Appadoo 2009). Of particular interest, the presence of residual oxygenated functional groups in alternative jet fuels (AJF) could negatively impact some of the properties of AJFs (Balster et al. 2006). Most of the pathways currently studied to produce AJF rely on a final de-oxygenation step via hydrotreatment. Under certain circumstances (catalyst deactivation, changes in the composition of the feedstock, operational problems), the de-oxygenation efficiency might decrease and some residual oxygenated compounds will remain in the product fuel (Christrensen et al. 2011). Although it is possible that some fuels with low contents of oxygen residual oxygen could pass existing ASTM standards, others will not. The difference in the behavior of fuels with residual oxygenated compounds can be related to the content and nature of these molecules. The identification of undesirable oxygenated functional groups and their acceptable limits is critical to the aviation industry to develop new standards and assist the AJF producers to develop strategies to avoid the formation of undesirable compounds.

The chemical Composition and fuel properties of nine alternative jet fuels (names AJF1-9) and three commercial jet fuels (named as CJF1, 2 and 3) are were analyzed. The fuels were characterized by solid phase extraction-Gas Chromatography, mass spectroscopy (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 were also measured for all the fuels. 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 ASTM requirements and offer opportunities to develop specialized products.

Our experimental results also confirmed that SPE followed by methanol extraction of phenolic compounds can quantitatively separate and recover the oxygenated polar species from the fuel. Synchronous fluorescence spectroscopy was used because of its simplicity and high sensitivity to phenols. The method was successfully used to quantify the content of phenolic compounds in solid phase extracted jet fuels. The response of UV-Fluorescence to different phenolic species was studied. Although in general the UV-fluorescence response of phenols in jet fuel is linear, differences in response were observed when phenolic standards were prepared by simply blending with methanol and after SPE of jet fuels. The differences in response can be explained by the presence of phenols quenching molecules in jet fuels. Fluorescence quenching was explored for the direct analysis of phenols in jet fuels. These studies were conducted using Rhodamine B (Rh-B) as quencher. The strong binding ability of phenols on Rh-B explain the quenching effect observed in our experimental results. These results allowed us to propose a fast method for identifying the presence of large quantities of phenolic compounds in jet fuels at field operational conditions.

Tasks

Task 1. AJF samples Collection

Leading University: Washington State University and University of Washington

Objective(s): Collect the samples that will be studied in this project

Research Approach: In total 10 samples were received at WSU.

Profs. Kramlich and Malte shipped WSU 200 mls of the following AJFs: (1) Gevo, (2) FT coal, (3) FT methane, (4) HEFA Tallow and (5) HEFA Camelina (6) JP5 (7) JP8.

Dr. Tim Edwards from the Air Force Research Laboratory (AFRL) shipped WSU 200 mls of the following AJFs: (8) Gevo (9) Amyris Renewable Diesel, (10) ReadiJet (ARA Jet), (11) HEFA Camelina and (12) HDCJ from Kior and (13) 10 gallons of Shell Commercial jet fuel.

Milestone(s)

All the samples were received at WSU. Table 1 shows the nomenclature used for each of these jet fuels.

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

Major Accomplishments

All the samples were received.

Publications

Pires APP, Han Y, Kramlich J, Garcia-Perez M: Chemical Composition and Fuel Properties of Alternative Jet Fuels. *Bioresources*, **2018**, 13 (2), 2632-2657

Outreach Efforts

Presentation at ASCENT workshops

Awards

None

Student Involvement

A PhD student Yinglei Han travelled to the University of Washington to collect the samples.

Task 2. Identification of the nature and quality of residual oxygenated compounds in selected AJFs under ASTM consideration

Washington State University

Objective(s)

Identification of the nature and the content of the oxygenated compounds present in the AJF received from UW and from the AFRL.

Research Approach

The content of the main macro fractions quantified in each of the jet fuels studied is shown in table 2.

Table 2. Overall content of the fractions (wt. % of total quantified oil).

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

WSU researchers identified the oxygenated compounds present in the AJF received from UW and from the AFRL using the SEP-HPLC-GC/MS method proposed by Balster et al (2006) (See Table 3)

Table 3. Oxygenated molecules identified on alternative jet fuels and quantified. N/S = the molecule was found but no standard was available for quantification. Concentration unit: mg/g.

	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	-	-	-	-	-

The analysis of the trace oxygenated compounds in commercial jet fuels is shown in Table 3.

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 content of carbonyl groups and total acid were quantified at WSU. The results are shown in table 7 and 8.

Table 7. Carbonyl content of fuels. 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 7 fuels.

	CO (μg/g)	σ (μg/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	-

Table 8. Total acid number results.

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

Milestone(s)
The nature of the oxygenated compounds in the AJF received has been identified using the SEP-HPLC-GC/MS method proposed by Balster et al (2006). The content of carbonyl groups and total acid number of all the oils received have been quantified.

Major Accomplishments
The nature of the oxygenated compounds in each of the AJFs have been identified by the method proposed by Balster et al (2006). The overall content of carbonyl compounds and the total acid number of all the AJFs received have been measured. Complementary to the work of this project and as part of the MSc thesis of Anamaria Paiva we have also studied other fuel properties (Overall composition by GC/MS, water content, clouding point by DSC, Flash point, equilibrium water and kinematic viscosity).

Publications

Pires APP, Han Y, Kramlich J, Garcia-Perez M: Chemical Composition and Fuel Properties of Alternative Jet Fuels. *Bioresources*, **2018**, 13 (2), 2632-2657

Outreach Efforts
Presentations at ASCENT workshops.

Awards
None

Student Involvement
Two graduate students (Yinglei Han and Anamaria Paiva) worked on this task.

Task 3. Preparation of surrogate blends and evaluation of the effect of the five most important oxygenated compounds identified on the fuel properties of AJFs

Washington State University

Objective(s): Identification of the effect of oxygenated compounds found in alternative Jet Fuels on their fuel properties.

Research Approach: The WSU researchers were initially planning to purchase chemical standards of the five oxygenated compounds most commonly identified in AJFs. However, due to the limited amount of commercial jet fuel available to prepare surrogate blends we decided to reduce our study to three of the oxygenated molecules identified in the previous task (Phytol, 2-methyl Phenol, Ethanol, 2-methoxy-ethoxy). We prepared blends containing 0, 0.01, 0.1, 1.0, 2.0 and 5.0 wt. % of these oxygenated compounds with the commercial jet fuel received from the Air Force Research Lab.

The effect of the three oxygenated compounds chosen on selected fuel properties of a conventional jet fuel were measured. The water solubility characteristics (equilibrium water) was measured following a method described elsewhere (Lam et al. 2014). The water content of the AJFs was determined with a Coulometric Karl Fischer Titrator available at our Analytical Lab. The TAN number (an indicator of acidity) was measured following the method described elsewhere (Christensen et al. 2011) using a potentiometric titrator (Wu et al. 2014) also available at LJ Smith Analytical Lab. The Flash point was determined by the Pensky-Martens Closed Cup Tester following the ASTM D93-13e1 standard. The kinematic viscosity was measured following by ASTM D445 standard. The cloud point of the blends were measured by differential scanning calorimetry (DSC) using the method described elsewhere (Heino et al. 1987, Zabarnick and Widmor 2001, Widmor et al. 2003).

Milestone(s)

Surrogate blends of three oxygenated compounds were prepared and several fuel properties of these blends were studied (carbonyl content, total acid, viscosity, water content, flash point, surface tension, calorific value).

Major Accomplishments

The effect of three oxygenated molecules found on AJFs (Phytol, 2-methyl Phenol and Ethanol, 2-methoxy-ethoxy) on selected fuel properties of surrogate blends of commercial jet fuels was studied.

Publications

Paiva A: Characterization of Alternative Jet Fuels and Effect of Residual Oxygenated Functional Groups on their properties. MSc thesis, Washington State University, April 2016

Outreach Efforts

Presentations at ASCENT workshops.

Awards

None

Student Involvement

Two graduate students (Yinglei Han and Anamaria Paiva) worked on this task.

Task 4. Determination of lean blow out limit, NOx and sooting threshold

University of Washington

Objective(s)

To identify the effect of oxygenated molecules found in Alternative Jet Fuel on te lean blow out limit, NOx and sooting threshold of commercial jet fuels.

Research Approach

The surrogate blends prepared at Washington State University were delivered to the University of Washington for further testing. The UW team determined for each of the three identified oxygenated compounds the lean blow out limit, the NOx emission at 1900 K, and the sooting threshold. The blowout and NOx data are obtained in a stirred reactor, while the sooting threshold is obtained in a laminar premixed burner (Meker). The lean blow out and NOx emissions are being measured in the jet stirred reactor at the UW Combustion Lab. The UW group has performed extensive testing on JP8, hydroprocessed biofuels, Fischer-Tropsch fuels, and chemically pure surrogate compounds. These results were compared with the UW group's extensive database on conventional and alternative aviation fuels.

Milestone(s)

Testing for lean blowout and NOx emissions on several of the baseline fuels and surrogates has been completed.

Major Accomplishments

Blowout data suggest that the oxygen content within expected ranges does not significantly change the lean blowout point. Testing with higher oxygen contents is planned to show where the threshold does exist. Variations in NOx emissions were noted.

Publications

None.

Outreach Efforts

Presentation at ASCENT workshops

Awards

None.

Student Involvement

Arshiya Hoseyni is conducting all the experimental combustion work, consisting of lean blowout tests, NOx emissions tests, and soot threshold measurements. She is interpreting the data as part of her PhD dissertation.

Task 5. Literature review to identify characterization strategies for the fast identification and quantification of trace oxygenated compounds on AJFs

Leading University: Washington State University

Objective(s)

To conduct a literature review on the methods for the quantification of oxygenated compounds in alternative jet fuels.

Research Approach

We concluded a literature review on methods for the quantification of oxygenated compounds in alternative jet fuels. The main goal of this task was to review the methods available for the quantification of total functional groups (acids, carbonyl, phenols) and the methods for the quantification of independent compounds in alternative jet fuels. We also reviewed methods that can be potentially used for the quantification of targeted oxygenated compounds in organic matrices.

Milestone(s)

The literature review completed.

Major Accomplishments

The literature review on the methods for the quantification of oxygenated compounds was completed.

Publications

None

Outreach Efforts

None

Awards

None

Student Involvement

A MSc student (Mainali Kalidas) conducted this literature review.

Plans for Next Period

Task completed.

Task 6 Improving the method for quantification of independent oxygenated compounds in AJFs

Washington State University

Objective(s)

Validation of Balster's method (Balster et al 2006) for the quantification of oxygenated compounds in AJFs.

Research Approach

In the first year of this project we quantified the content of individual oxygenated compounds by the method described by Balster et al. (2006). 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 to polar species. The samples collected from SPE were then analyzed by GC/MS. Both internal and external standards were used for the analysis. Both methods were validated. with new standards. The scheme of the tasks conducted are shown in Figure 1.

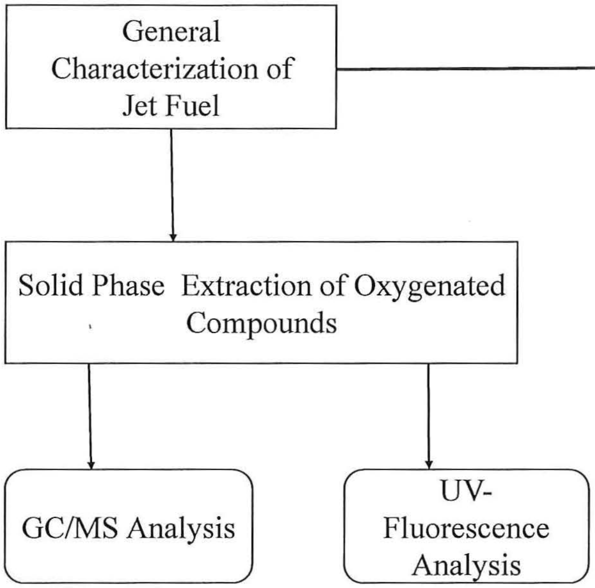

Figure 1. Strategy followed to develop a method for the fast detection of trace oxygenated compounds in jet fuels.

Milestone(s)

We conducted several tests varying jet fuel/methanol ratios, with jet fuels doped with several phenols.

Major Accomplishments

This task was completed early this year.

Publications

Mainali K: Identification and Quantification of Trace Oxygenated Compounds in Alternative Jet Fuels. MSc thesis, June 2018

Outreach Efforts

None

Awards

None

Student Involvement

Two graduate students (Yinglei Han and Kalidas Mainali) worked in this task.

Plans for Next Period

This task was completed early this year.

Task 7 Development of Methods for the Fast Quantification of Oxygenated Compounds in Jet Fuels

Washington State University

Objective(s)

Develop a method for the fast quantification of oxygenated functional groups in alternative jet fuels

Research Approach

The third task consists on studies to develop methods for the fast quantification of oxygenated functional groups in alternative jet fuels (E411 2012, Christiensen et al. 2011). The goal is to develop fast detection kids that can be used on field conditions. We focused on the development of kids for the analysis of total phenols by UV-Fluorescence spectroscopic that can be easily miniaturized (Kauffman 1998, Qian et al 2008, Galuszka et al 2013, Novakova and Vickova 2009, Saito et al 2002, Tobiszewski et al 2009).

Figure 2 and 3 show the UV fluorescence response when phenolic compounds were added to alternative jet fuels.

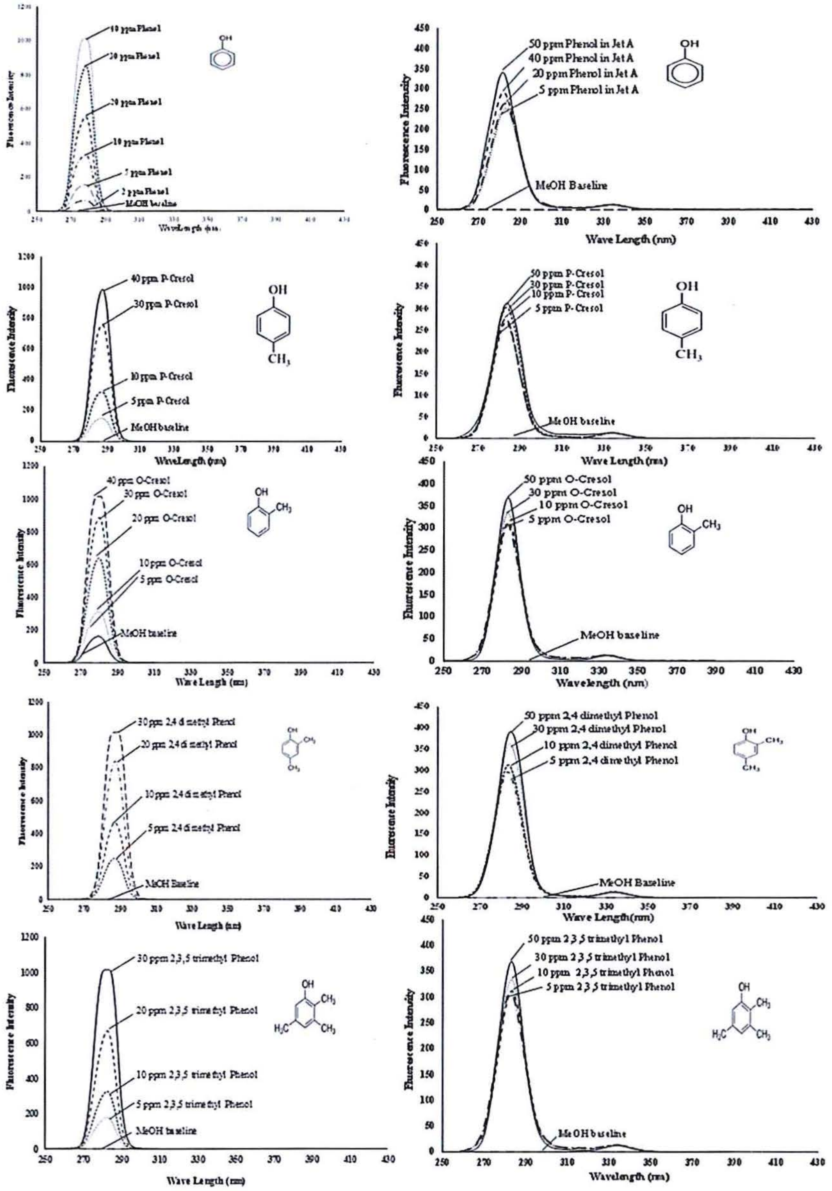

Figure 2. Synchronous fluorescence spectra of different phenolic compounds in methanol as follows: **a)** Phenols in MeOH, **b**) Phenol in MEOH after SPE of doped Jet A

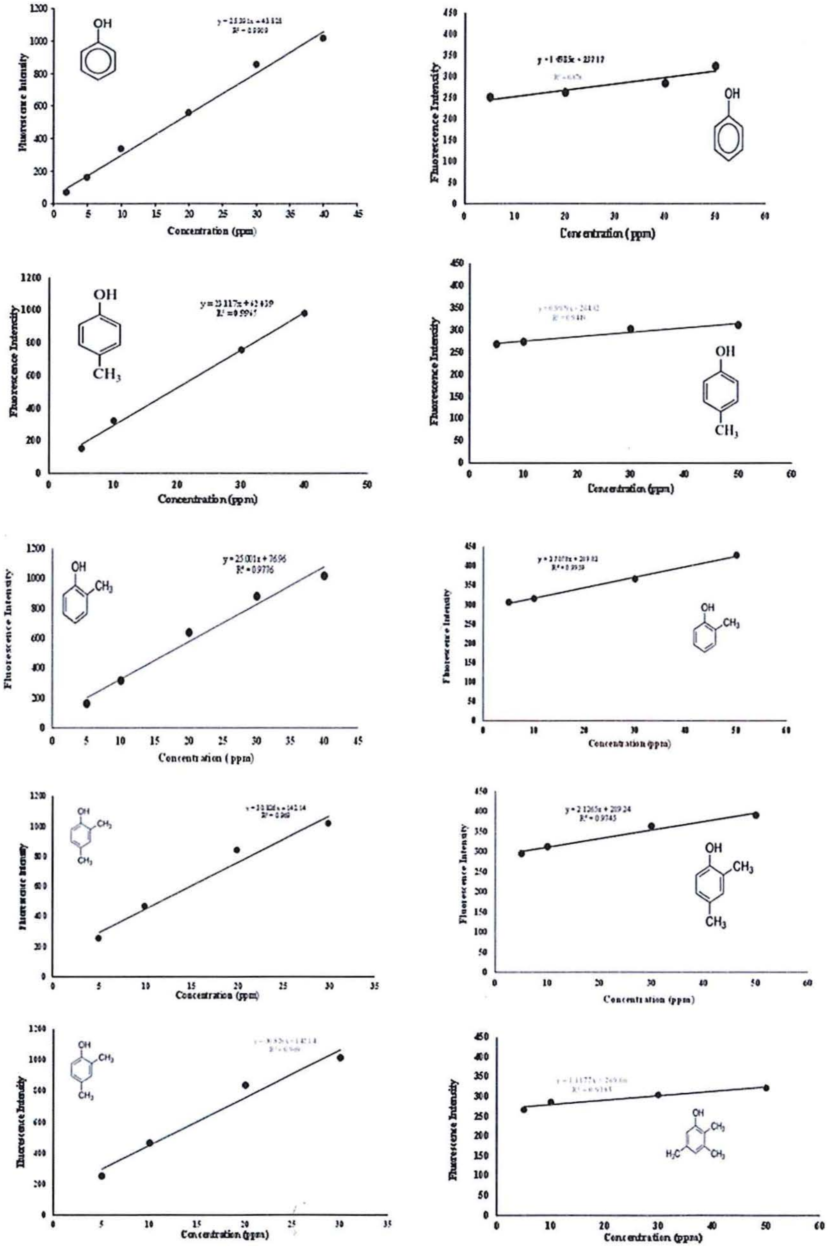

Figure 3: A general method of quantification by fluorescence intensity of respective oxygenated compounds as follows: **a)** Phenols in MeOH **b**) Phenols in MEOH after SPE of doped Jet A

Figure 3 shows the general proposed method of quantification for different oxygenated molecules. It is due to simplification of spectra signal and low concentration: the fluorescence intensity is directly proportional to respective concentration. By knowing the fluorescence intensity, it is possible to quantify each phenolic compounds in jet A. However, it is due to difference in fluorescence intensity of each oxygenated molecules, it was not possible to use calibration curve for quantification. In some spectra, the weaker overlapping bands were also observed in the range 310-350 due to π-π transitions and interferences. This information concludes that the jet fuel is already concentrated with phenolic compounds. It is due to extra sensitiveness of instruments, even the phenolic concentration was observed at sub-ppm level.

So we decided to study the use of fluorescence quenching for the identification of trace oxygenated compounds in jet fuels. Rhodamine B dye was chosen because of its surface binding ability for polar compounds. Rhodamine B emits very strong pinkish fluorescence. If phenol is present, the fluorescence of Rhodamine B quenches. Depending on the chemical nature of dye and its interaction with different phenolic compounds, two types of quenching may occur: Collisional and static quenching. In the case of collisional quenching, the quencher must diffuse to the fluorophore during the life time of the excited state. On this process, the intrinsic physical and chemical properties of both the species remain unchanged through this interaction. In contrast, in static quenching, hydrophobic and electrostatic interactions lead to formation of a non-fluorescent ground state complex between the fluorophore and the quencher which forms new compound with new properties. Figure 4 shows a schematic representation of Rh-B fluorescence quenching in the presence of phenols.

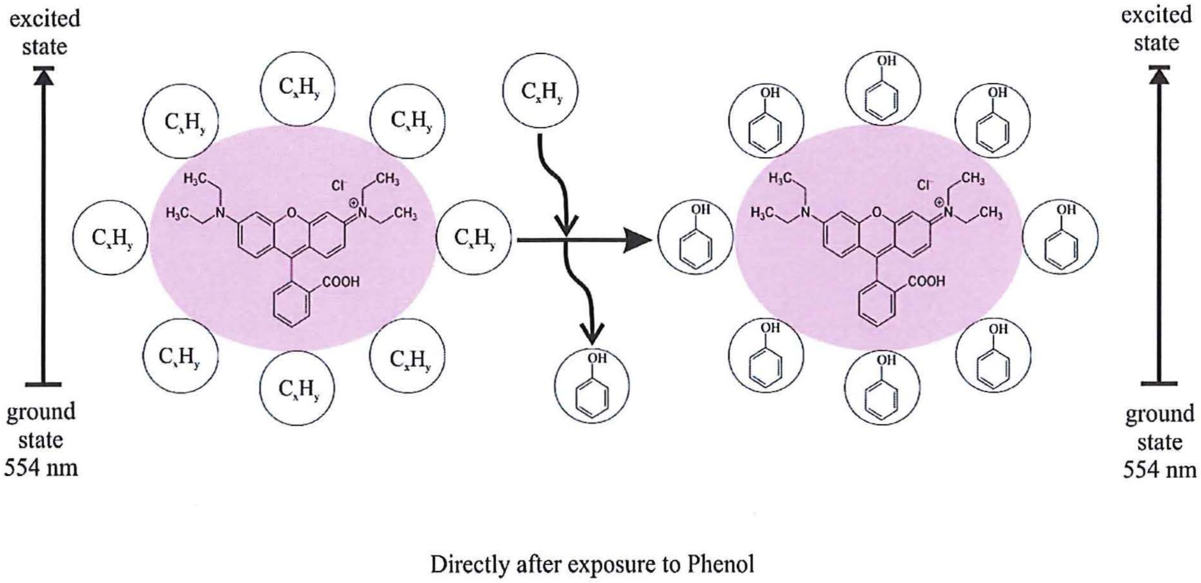

Figure 4 Schematic showing the quenching of Rh-B fluorescence by phenolic concentration

Figure 5 shows the general procedure proposed for fast identification of trace phenols in jet fuel.

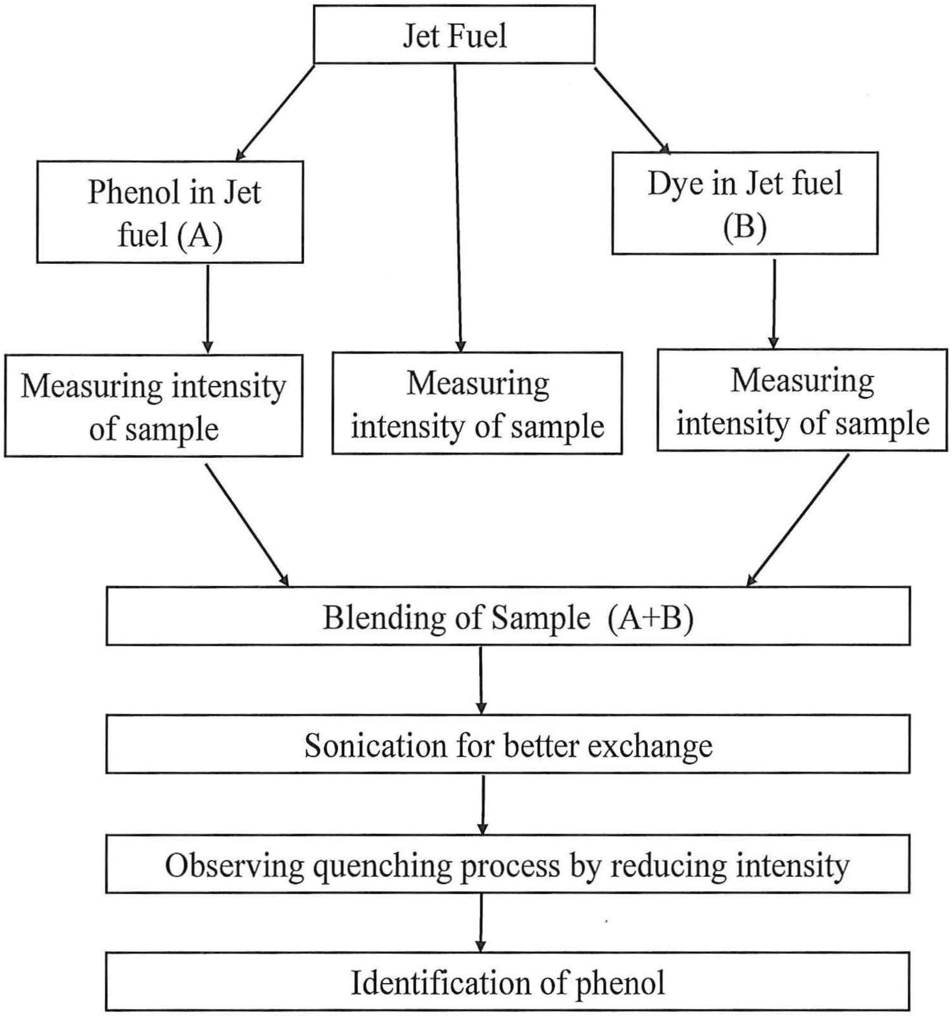

Figure 5: General procedure for fast identification phenols in jet fuel.

Figure 6 shows the effect the presence of phenols has on the UV fluorescence of Rh-B. Clearly when small quantities of phenols are present the fluorescence of Rh-B is quenched.

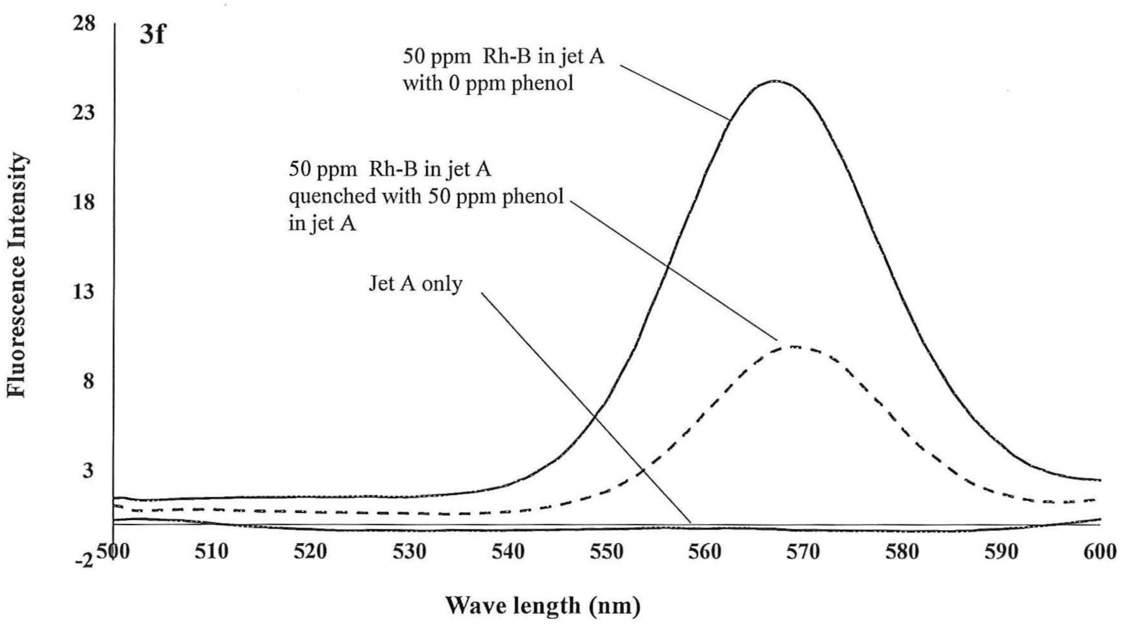

Figure 6. Fluorescence quenching studies of phenol in the presence of Rhodamine-B **(**Effect quenching of 50 ppm phenol in dye).

Milestone(s)

This task completed

Major Accomplishments

A new method for the identification of trace phenolic compounds in jet fuel was proposed.

Publications

We are currently writing a peer review manuscript with our results.

Mainali K: Garcia-Perez M: Identification and Quantification of Trace Oxygenated Compounds in Alternative Jet Fuels: Fluorescence Quenching Method for Fast Detection of Phenolic Compounds in Operational Field Conditions. Paper submitted to Fuel.

Outreach Efforts

None

Awards

None

Student Involvement

This task was conducted by our MSc student Mainali Kalidas.

Plans for Next Period

This task was completed.

References:

Appadoo R: Insights into Jet Fuel Specifications. February 11, 2009, ICAO Alternative Fuels Workshop.

ARA: "Drop-in" Jet and Diesel Fuels from Renewable Oils. Presnetation 11 May 2011 (www.ara.com/fuels)

ASTM D4054-09: Standard Practice for Qualification and Approval of New Aviation Turbine Fuels and Fuel Additives.

ASTM D7566-14a: Standard Specification for Aviation Turbine Fuel containing Synthesized Hydrocarbons.

ASTM D3241-14: Thermal Oxidation Stability of Aviation Turbine Fuels.

ASTM E411-12: Trace Quantities of Carbonyl Compounds with 2,4 Dinitrophenylhydrazine.

Balster LM, Zabarnick S, Striebich RC, Shafer LM, West Z: Analysis of Polar Species in Jet Fuel and Determination of their Role in Auto-oxidative Deposit Formation. Energy & Fuels 2006, 20, 2564-2571

Brown N: FAA Alternative Jet Fuel Activities. Overview. Presented to: CLEEN Consorptium, November 20, 2013

Christensen ED, Chupka GM, Luecke J, Surthwaite T, Alleman TL, Iisa K, Franz JA, Elliott DC, McCormick RL: Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions. Energy Fuels 2011, 25, 5462-5471

Dunn RO: Effect of antioxidants on the oxidative stability of methyl soryate (biodiesel). Fuel Processing Technology 86 (2005) 1071-1085

E411, ASTM. 2012. "Standard Test Method for Trace Quantities of Carbonyl Compounds with 2 ,4-."

Kauffman RE: Rapid, Potable Voltammetric Techniques for Performing Antiocidant, Total Acid Number (TAN) and Total Base Number (TBN) Measurements. *Lubrication Engineering* 54.1 (1998), 39

French RJ, Hrdlicka J, Baldwin R: Mild Hydrotreating of Biomass Pyrolysis Oils to Produce a Suitable Refinery Feedstock. Environmental Progress & Sustainable Energy (Vol. 29, No. 2) pp. 142

Henrich E: The status of FZK concept of biomass gasification. 2nd European Summer School on Renewable Motor Fuels. Warsaw, Poland 29-31, August 2007

Henrich E, Dahmen N, Dinjus E: Cost estimate for biosynfuel production via biosyncrude gasification. Biofuels, Bioproducts & Biorefining.3: 28-41 (2009)

Heino EL: Determination of cloud point for petroleum middle distillates by differential scanning calorimetry. Thermochemical Acta. Volume 114, Issue 1, 1987, 125-130/

Hileman JI, De la Rosa-Blanco E, Bonnefoy PA, Carter NA: The carbón dioxide challenge facing aviation. *Progress in Aerospace Sciences*. Volume 63, Nov. 2013, 84-95

Johnston G: Presentation: Alcohol to Jet (ATJ) Gevo, 2013

Galuszka A, Migaszewski Z, Namiesnik J: The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. TrAC *Trends in Analytical Chemisytry*, Vol. 50, 2013, 78-84

Garcia-Perez M, Adams TT, Goodrum JW, Das KC, Geller DP: DSC studied to evaluate the impact of bio-oil on cold flow properties and oxidation stability of bio-diesel. *Bioresource Technology* 101 (2010) 6219-6224

Gevo: Gevo Overview: Isobutanol to ATJ: Berlin Air Show, September 2012

Qian K, Edwards KE, Deschert GJ, Jaffe SB, Green LA, Olmstead WN: Measuremnt of Total Acid Number (TAN) and TAN Boiling Point Distribution in Petroleum Products by electrospray Ionization Mass Spectrimetry. *Analytical Chem*. 2008, 80 (3), pp. 849-855

Malina R: HEFA and F-T jet fuel cost analyses. Laboratory for Aviation and the Environment. MIT, Nov 27, 2012

Neihof RA, Bailey CA: Biocidal Properties of Anti-Icing Additives for Aircraft Fuels. Applied and Environmental Microbiology. April 1978, 35, 4, 698-703

Novakova L, Vickova H: A review of current trends and advances in modern bio-analytical methods: Chromatography and sample preparation. *Analytical Chimica Acta*. Vol. 656, Issues 1-2, December 2009, pages 8-35

Ringer M, Putsche V, Scahil J: Large-Scale Pyrolysis Oil production: A technology Assessment and Economic Analysis. Technical Report. NREL/TP-510-37779, Nov. 2006

Saito Y, Kawazoe M, Imaizumi M, Morishima Y, Nakao K, Hayashida M, Jinno K: Miniaturized Sample Preparation and Separation Methods for Environmental and Drug Analyses. *Analytical Sciences*. Vol. 18 (2002) No 1, pp. 7-17

Seber G, Malina R, Pearlson MN, Olcay H, Hileman JI, Barret SRH: Environmental and Economic Assessment of Producing hydroprocessed jet and diesel fuel from waste oil and tallow. Biomass and Bioenergy 67 (2014) 108-118

Spath P, Aden A, Eggeman M, Ringer B, Wallace B, Jechura J: Biomass to Hydrogen Production detailed Design and Economic Utilizing the Battelle Columbus Laboratory Indirectly Heated Gasifier. Technical Report NREL/TP-510-37408

Swanson RM, Platon A, Satrio J, Brown RC: Techno-economic analysis of biomass to liquid production based on gasification. Fuel, 89 (2010) 511-519.

Tobiszewski M, Mechlinska A, Zygmut B, Namiesnik J: Green analytical in sample preparation for determination of trace organic pollutants. TrAC *Trends in Analytical Chemistry*, Vol. 28, 8, 2009, 943-951

Total-Amyris: Breaking the Barrier with Breakthorugh Jet Fuel Solutions. Presentation at the Renewable Aviation Fuel Join Development Program. Berlin Airshow-September 2012

Widmor N, Ervin JS, Zabarnick S, Vangness M: Studies of Jet Fuel Freezing by Differential Scanning Calorimetry and Cold-Stage Microscopy. Transactions of the ASME, Vol. 125, January 2003, 34-39

Wildschut J, Arentz J, Rasrendra CB, Venderbosch RH, Heeres HJ: Catalytic hydrotreatment of Fast Pyrolysis Oil: Model Studies on Reaction Pathways for the Carbohydrate Fraction. Environmental Progress & Sustainable energy (Volume 28, No3) p. 450

Wright MM, Brown RC: Distributed processing of biomass to bio-oil for subsequent production of Fischer-Tropsch liquids. Biofuels, Bioporducts & Biorefining. 2:229-238 (2008)

Wu L, Hu X, Mourant D, Wang Y, Kelly C, Garcia-Perez M, He M, Li C-Z: Quantification of strong and weak acidities in bio-oil via non-aqueous potentiometric titration. Fuel, Vol. 115, 2014, pp 652-657

Zabarnick S, Widmor N: Studies of Jet Fuel Freezing by Differential Scanning Calorimetry. Energy & Fuels 2011, 15, 1447-1453