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

Washington State University, University of Washington

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University Participants

Washington State University

- P.I.(s): Manuel Garcia-Perez
- FAA Award Number: 13CAJFEWaSU-004
- Period of Performance: March 1st, 2015to February 29, 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 blends and evaluation of the effect of five most important oxygenated compounds identified on the fuel properties of AJFs.
    4. Literature review to identify characterization strategies for the fast identification and quantification of the residual oxygenated compounds in AJFs
    5. Final Report

University of Washington

- P.I.(s): John Kramlich, Philip Malte
- FAA Award Number: 13CAJFE-UW-003
- Period of Performance: March 1st, 2015 to February 29, 2016
    6. AJF sample collection
    7. Determination of lean blow out limit, NOx and sooting threshold
    8. Final Report

Project Funding Level

Washington State University: Amount of funding from the FAA ($ 49,998), Matching funds ($ 55,000), Source: State Funds (from Dr. Cavalieri's 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

Washington State University:

Yinglei Han (PhD student): Development of analytical techniques for the identification and quantification of oxygenated compounds in jet fuels

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

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

University of Washington:

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

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 three 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). Currently, (4) Alcohol to Jet (ATJ | Gevo) (Johnston 2013, GEVO 2012) is under consideration and is expected to be balloted in 2014 (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 or positively 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.

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 14 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.

Mr. Brice Dally (R&D Manager Virent) very kindly shipped 200 mL of the following AJFs for analysis: (14) Synthetic kerosene (SK) and (15) Synthetic Aromatic Kerosene (SAK)

Milestone(s)
All the samples were received at WSU

Major Accomplishments
All the samples were received and are being studied at this time.

Publications
None

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
WSU researchers will identify 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). The content of carbonyl groups will be determined with 2,4 dinitrophenylhydrazine according with the ASTM E411-12 standard. The HPLC and GC/MS for the identification and quantification of residual oxygenated compounds in AJFs and the spectrophotometer needed to determine the content of carbonyl groups are available at LJ Smith Analytical Lab.

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). We are currently purchasing the standards to quantify the content of these compounds. 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). We are currently purchasing the standards to quantify these compounds. 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). A few days ago we purchased a calorimetric bomb and a tensiometer to part of our growing Jet Fuel characterization lab. These instruments will be used in the analysis of the AJFs studied in this project.

Publications
None

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 found in alternative Jet Fuels on their fuel properties.

Research Approach: The WSU researchers were initially planning to purchase 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 heating baths and the Cannon-Fenske viscometers needed for this study were purchased with funds requested from this project. 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).

We recently purchased a tensiometer (with matching funds from Biological Systems Engineering) and a calorimetric bomb (with funds from the FAA and matching funds from Biological Systems Engineering) that will be soon used to characterize the fuel properties of the fuels. These two instruments will be part of our fuel characterization lab.

We do not have installations to conduct the JFTOT procedure in our labs so were planning to assess the effect of oxygenated compounds on the thermal stability of the surrogate jet fuel blends following the method described by Dunn (2005) and Garcia-Perez et al. (2010). We encountered some problems with the implementation of this method in our DSCs, so we are now developing a new method to study jet fuel thermal stability in our lab.

We are planning to study the effect of oxygenated compounds on the growth of two microorganisms typically found in jet fuels (pseudomona aeruginosa and cladosporium resinae). The studies will be carried out over 3 to 4 months in two-phase systems containing the surrogate fuels and water following the methods described by Neihof and Bailey (1978).

Three liters of surrogate blends of o-cresol and phytol and three liters of commercial jet fuel were delivered to the University of Washington team for combustion tests. The surrogate blends contained 1 and 5 wt. % of the oxygenated compounds (o-cresol and phytol).

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). The instruments to measure surface tension and calorific value in our labs.

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
None

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 will determine 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 will be determined 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 will be 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 variation of 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, and the data are being interpreted by chemical kinetic models to identify the reasons for the variation in emissions.

Publications
None.

Outreach Efforts
Presentation at ASCENT workshops

Awards
None.

Student Involvement
Arshiya Hoseyni is operating 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 the residual oxygenated compounds in AJFs
Washington State University

Objective(s)
Literature review on methods for the identification and quantification of oxygenated compounds in alternative jet fuels.

Research Approach
The team at Washington State University will conduct a literature review on potential fast methods (or sensors) to identify the presence of the undesirable oxygenated compounds identified in the previous tasks. The goal of this review is to contribute to develop in the future on-line real time system for the identification of these compounds in AJs.

Milestone(s)
We just started this task.

Major Accomplishments
We just started to work on this task.

Publications
None.

Outreach Efforts
None

Awards
None

Student Involvement

This task will be conducted by the MSc student Anamaria Paiva.

Plans for Next Period

Task 1. AJF samples Collection
Washington State University and University of Washington

This task has been completed.

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

The nature of the oxygenated compounds in all the jet fuel received was identified. In the next period we will work on the quantification of each of the oxygenated compounds.

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

We have completed the preparation of surrogate blends with three oxygenated compounds and have determined selected fuel properties of these blends (viscosity, flash point, carbonyl content, total acid number, water content, water equilibrium). In the next period we will continue studying the effect of these oxygenated compounds on other properties (surface tension, calorific value, density, microbial growth and thermal stability).

Three four liter samples of the surrogate jet fuels will be shipped to the Air Force Laboratory for thermal oxidative stability analysis (JFTOT) analysis.

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

All of the samples received will be tested for soot point (Meker burner), and the NOx data will be completed (stirred reactor). Surrogate fuels to test chemical kinetic hypotheses will be selected, as will samples which are higher in oxygenates than normal to help data interpretation. The goal is to understand how the various oxygenate groups, at various concentrations influence behavior.

Task 5. Literature review to identify characterization strategies for the fast identification and quantification of the residual oxygenated compounds in AJFs
Washington State University

In the next period we plan to complete the literature review on potential methods to identify and characterize oxygenated compounds in AJFs.

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