Project 039 Naphthalene Removal Assessment

Massachusetts Institute of Technology

Project Lead Investigator

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- P.I.(s): Prof. Steven Barrett & Dr. Raymond Speth
- FAA Award Number: 13-C-AJFE-MIT, Amendment Nos. 026 and 034
- Period of Performance: July 8, 2016 to Aug. 31, 2018 (With the exception of funding and cost share information, this report covers the period from October 1st, 2016 to September 30th, 2017)
- Task(s):
    1. Preliminary screening of refinery processes for naphthalene removal
    2. Kinetic model of PAD formation with fuel-composition effects
    3. Calculation of process requirements and fuel composition effects for selected refining processes

Project Funding Level

Project Funding Level: $490,000 FAA funding and $490,000 matching funds. Sources of match are approximately $129,000 from MIT, plus 3rd party in-kind contributions of $361,000 from Oliver Wyman Group.

Investigation Team

Prof. Steven Barrett (MIT) serves as principal investigator for the A39 project as head for the Laboratory for Aviation and the Environment. Prof. Barrett coordinates both internal research efforts and maintains communication between investigators in the various MIT research teams mentioned below.

Dr. Raymond Speth (MIT) serves as co-principal investigator for the A39 project. Dr. Speth directly advises student research in the Laboratory for Aviation and the Environment focused on assessment of naphthalene removal refinery options, climate and air quality modelling, and fuel alteration life-cycle analysis. Dr. Speth also coordinates communication with FAA counterparts.

Prof. William Green (MIT) serves as a co-investigator for the A39 project as a head of the Green Research Group. Prof. Green advises student work in the Green Research Group focused on computer-aided chemical kinetic modeling of PAH formation.

Mr. Randall Field (MIT) is the Executive Director of the MIT Energy Initiative, and a co-investigator of the A39 project. Drawing upon his experiences as a business consulting director at Aspen Technology Inc., Mr. Randall provides mentorship to student researchers in selection and assessment of naphthalene removal refining option, and process engineering at-large.

Mr. Drew Weibel (MIT) is a graduate student researcher in the Laboratory for Aviation and the Environment. Mr. Weibel is responsible for conducting selection and assessment of naphthalene removal refining options, calculation of refinery process requirements and fuel composition effects from selected processes, relating PAH formation to aircraft PM emissions, estimating capital and operating costs of naphthalene removal, air quality and climate modelling, and an integrated cost-benefit analysis.

Mr. Max Liu (MIT) is a Ph.D. candidate researcher in the Green Research Group. Mr. Liu is responsible for development and analysis of a chemical kinetic model of PAH formation with fuel-composition effects and supporting development of a relationship between PAH formation and aircraft PM emissions.

Project Overview

Aircraft emissions impact the environment by perturbing the climate and reducing air quality, which leads to adverse health impacts, including increased risk of premature mortality. As a result, understanding how different fuel components can influence pollutant emissions, as well as the resulting impacts and damages to human health and the environment, is of importance to leading future research aims and policy. Recent emissions measurements have shown that removal of naphthalenes, while keeping total aromatic content unchanged, can dramatically reduce emissions of particulate matter (Brem et al., 2015, Moore et al., 2015). The objective of this research is to determine the benefits, costs, and feasibility of removing naphthalenes from jet fuel, in regards to the refiner, the public, air quality, and the environment. Specific goals of this research include:

- Assessment and selection of candidate refining processes for the removal of naphthalenes from conventional jet fuel, including details of required technology, steady-state public cost, and changing life-cycle emissions impacts at the refinery.
- Development of a chemical kinetics model to better understand the link between fuel aromatic composition resulting PM emissions due to jet fuel combustion.
- Assessment of the intrinsic climate and air quality impacts associated with naphthalene reduction and/or removal from jet fuel.
- Development of a succinct life-cycle analysis of the relative costs of removing naphthalene from jet fuel and the associated benefits due to avoided premature mortalities and climate damages for a range of possible scenarios.

Task #1: Preliminary Screening of Naphthalene Removal Refining Processes

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Objective(s)

Naphthalene is present in varying levels in straight-run crude oil distillation cuts used to produce jet fuel, and is currently not targeted for removal in treatments used to meet industry standard fuel specifications. As a result, reducing the naphthalenic content in jet fuel entails the introduction of an additional refinery treatment process. The objective of this task is to identify suitable refinery processes that can be used to remove or convert naphthalenes. Once identified, data for key refining process parameters will be collected to inform future cost estimation of applying the selected processes for jet fuel naphthalene removal.

Research Approach

Introduction

Refining processes, and chemical processes at large, are focused on subjecting chemical species to various environments to allow for conversion, combination, separation, etc., in order to produce useful, increased value products. When considering removal of a chemical component from a mixture, say naphthalenic species from a kerosene feed, a process designer must consider unique properties shared by the chemical component that allow for its conversion, combination, separation, etc. without affecting the underlying mixture.

While naphthalenes are not currently targeted for removal to meet industry standards, there are several mature refining technologies that, once tuned, can complete this reduction/removal with high efficiency. In AY 2016/2017, we will select suitable, readily accessible refining technologies for the removal of naphthalenes from the U.S. jet fuel pool. Our focus is on technologies currently used in industry, in order to provide possible policies that could be implemented in the near term.

Methods

In order to select a number of refining processes for the large-scale removal of naphthalenes from the U.S jet fuel pool, we will complete a literature review of current technologies, qualitative evaluation of those technologies in terms of their applicability of naphthalene removal, the scope of economic and process data available, and the level of naphthalene removal achievable. Particular attention will be given to preserving non-naphthalenic aromatics, since reducing the amount of these components would limit the capacity to blend paraffinic alternative jet fuels while still meeting minimum requirements for aromatics.

In order to evaluate each candidate process, we will leverage existing literature to estimate the utility (process fuel, electricity, hydrogen, etc.) requirements for each process, the effect on the composition of the resulting jet fuel, and the capital costs of new refinery equipment required. We will include the effects of any pre-processing that may be required. We will then compare processes side-by-side in order to demonstrate the trade-offs associated with naphthalene removal at the refinery.

As a by-product of analyzing a range of different refining pathways, we will be able to assess the tradeoffs associated with different levels of naphthalene removal. Combined with later work in development of a relationship between jet fuel composition and PAH formation, we will be able to assess the level of severity in which naphthalene's should be removed, in order to optimize costs and benefits.

Results

AY 2016/2017 Task 1 was concluded with the selection of extractive distillation and selective hydro-treating as candidate refinery processes for the large-scale removal of naphthalenes from the U.S. jet fuel pool.

Naphthalenes are unsaturated, double ring aromatic species which may contain alkylated or impurity groups. They are most readily removed via conversion to mono-aromatic or saturated species – via hydrogen addition or carbon removal – or separated on the basis of polarity. A desired refinery process would remove naphthalenic species with high efficiency, not affect the remaining aromatic content, produce minimal changes to other fuel properties, and produce limited emissions and economic impact; removal of other impurities (sulfur, nitrogen, etc.) is an added bonus. A list of potential refining processes is listed below (Gary et al., 2007). Description of each process, and associated pros and cons can be found in the AY 2016/2017 deliverable 1 presentation.

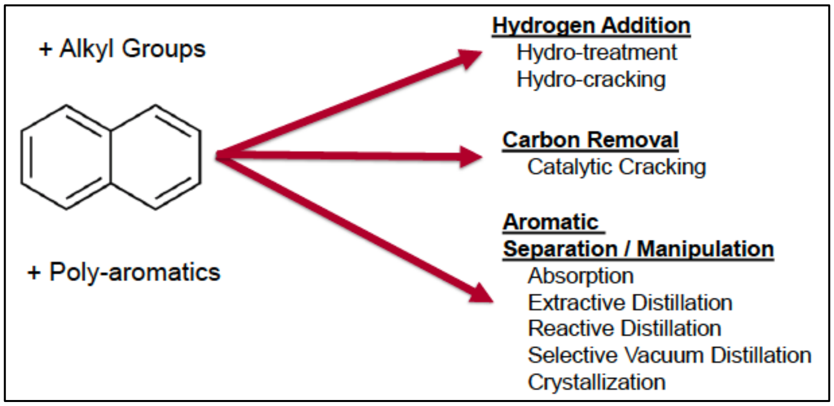

Figure 1

As noted in Figure 1, there are three families of processes pertinent to the removal of naphthalenes; conversion by hydrogen addition (saturation), conversion by carbon removal (cracking), or aromatic separation. Hydrogen addition and aromatic separation are often used as finishing processes, and can operate under mild conditions. Carbon removal, on the other hand, is often associated with molecular cracking, has the potential to radically convert the feed, is associated with the production of olefins, and often cannot break apart stable aromatic rings. As a result, only hydro-conversion and aromatic separation processes were considered.

Hydro-conversion processes are a family of refining units that react a petroleum feed with gaseous hydrogen at elevated temperatures and pressures in order to saturate – and in severe processes, crack – hydrocarbon molecules. Hydro-treating is a mild hydro-conversion finishing process used to remove impurities and saturate olefin and aromatic species. Selective hydro-treating for the conversion of naphthalenes is a viable process candidate because the second ring of naphthalenic species will tend to be fully saturated prior to the saturation of mono-aromatic species. Due to the relative selectivity of fuel components, we also expect desulfurization and di-nitrogenation to occur. As a result, with a robust catalyst selection and finely tuned process parameters, we expect a selective hydro-treating process could reduce/remove naphthalenes by converting them to mono-aromatics with little change to the overall aromatic content and other fuel characteristics, and with reasonable hydrogen requirements (Fahim, 2010).

Separation processes provided a separation of mixture components about some defining species characteristic, such as weight, size, polarity, etc. Extractive distillation provides a separation of petroleum components based on polarity, by introducing a heavy, high-boiling point polar solvent to the feed. Highly polar component (including all aromatic and impurity containing species), will bind to the solvent and be separated from other species based on weight. The solvent is then separated using by simple distillation. Finally, mono-aromatic and naphthalene species can be roughly separated in a second distillation step, the prior cut being returned to the feed. Extractive distillation, while less common for feed mixture separations, was identified as a second candidate for naphthalene removal from the U.S. jet fuel pool (Meyers, 2004).

After selection of extractive distillation and selective hydro-treating as candidate refining processes for the removal/reduction of naphthalene from the U.S. jet fuel pool, further details were collected on each process to define their offsite needs and fuel composition impacts. A table of relevant process requirements and fuel effects is given below.

Table 1

Process Name	**Hydro-Treatment**	**Extractive Distillation**
Description	Naphthalenes are hydrogenated to mono-aromatic and cyclo-paraffinic components.	All aromatics are separated via a polar solvent. Mono-aromatics are separated from naphthalenes via distillation and blended back into the jet fuel product
Process Type	Conversion (H_2 addition)	Aromatic Separation
Existing Uses	Desulfurization, impurity removal, aromatic hydrogenation	Separation of polar feed components, BTX separation
Removal of Naphthalenes	Assumed 95% efficient	Assumed 95% efficient
Effect on Mono-Aromatics	Limited (<10%) hydrogenation	Fully separated; fraction returned to product can be controlled
Impurity Removal	S, N removal to <50 ppm	Small removal of S, N impurities
Supporting Processes Req'd	Hydrogen production, Sulfur gas removal, sulfur post-treatment, steam generation and cooling facilities	Naphthalene / mono-aromatic post distillation, steam generation and cooling facilities
Process Innovation Req'd	Minimal required. Very similar to existing units	Efficient solvent with impurity (S,N) resiliency

Milestone(s)

This work was completed in February 2017, and is described in the deliverable 1 presentation provided to the FAA on February 28th, 2017.

Major Accomplishments

During this period, two refining processes – selective hydro-treating and extractive distillation – were chosen as suitable candidates for large-scale naphthalene removal from the U.S. jet fuel pool. A summary of this work is contained in the deliverable 1 presentation provided to the FAA on February 28th, 2017.

Publications

None

Outreach Efforts

None

Awards

None

Student Involvement

Drew Weibel, Master's student in the Laboratory for Aviation and the Environment is working directly with Prof. Steven Barrett and Dr. Raymond Speth to conduct the research objectives of Task 1. Mr. Weibel is a 2nd year graduate student, and will serve on the research team through the remainder of the A39 project timeline.

Plans for Next Period

The work completed in Task 1 has informed the calculation of process requirements and fuel composition effects for hydro-treating and extractive distillation systems in AY 2016/2017 Task 3, as describe below. In AY 2017/2018, an economic model for the cost of naphthalene removal via selective hydro-treating and extractive distillation will be assembled and tested to determine the societal net present value of such a policy change. This "cost" will ultimately be applied to a Cost-Benefit Analysis in order to assess the realized benefits of naphthalene removal.

Task #2: Kinetic Model of PAH formation with fuel-composition effects

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Objective(s)

The formation of black carbon (soot) from hydrocarbon fuels can be considered as taking place in two stages. First, fuel components and combustion intermediates react to form polycyclic aromatic hydrocarbons (PAHs). Large PAHs then act as soot nuclei, which grow as they absorb both PAH and other species, coagulate through collisions with other soot particles, carbonize, and partially oxidize (Richter and Howard, 2000). The details of fuel composition mainly affect the first step of this process, the formation of PAHs. In this project, we will use the Reaction Mechanism Generator (RMG) to develop a detailed chemical kinetic mechanism for jet fuel combustion that includes the formation of PAH (Gao et al., 2016).

The objective of AY2016/2017 Task 2 is to update the RMG algorithm in order to handle aromatic species, and to include aromatic reactions up to three-ring species, which will be used as identifiers for soot precursors in later models. The updates to RMG will also undergo preliminary validation using experimental results from shock-tube pyrolysis and co-pyrolysis studies.

Research Approach

Introduction

RMG (http://rmg.mit.edu) is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react. This tool provides a powerful method to identify reaction mechanisms computationally, and ensure full coverage of pertinent species and reactions based on the current literature. RMG has previously been used to analyze various fuels including JP-10 and di-isopropyl ketone combustion and pyrolysis (Gao et al., 2015; Allen et al., 2014).

In AY 2016/2017, we will add updates to the RMG algorithm in order to accurately handle aromatic species, and to include aromatic reactions up to three-ring species, which will be used as identifiers for soot precursors in later models.

Method

Previously, RMG was unable to robustly represent aromatic structures. The algorithm depended primarily on representation using Kekulé structures, which resulted in incorrectly treating them like aliphatic species. In order to correctly represent aromatic species, RMG was updated to generate the Clar structure representation of PAHs. As result, aromatic species are more clearly differentiated from aliphatic species, and the number of different representations has been reduced in many cases. An example of the reduced representations for a phenanthrene radical is shown below.

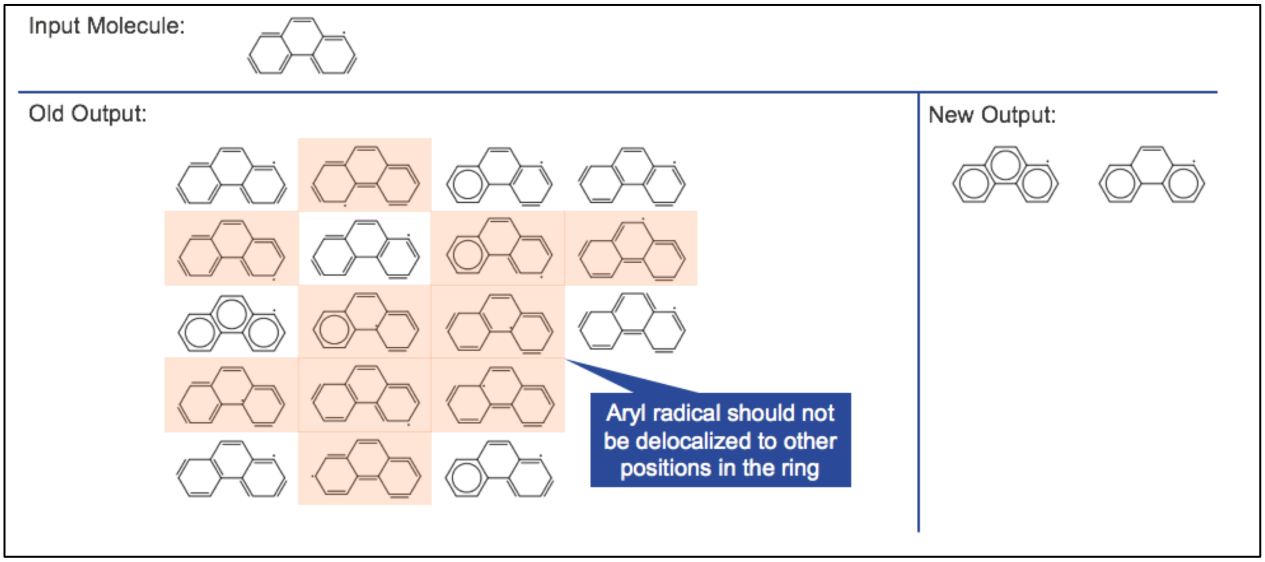

Figure 2

Other changes were made to further improve reaction rate predictions. An algorithmically challenging task of allowing aromatic bond types was completed after implementing a custom kekulization algorithm. This allows rate rules for aromatic species to be specified separately from those for aliphatic species. Also, ring perception was implemented for rate rules to allow separation of rates for linear versus cyclic species.

In order to validate updates described previously, the RMG model was tested against experimental shock-tube pyrolysis data (Lifshitz et al., 2009). Additional co-pyrolysis models were also generated, although without experimental comparisons.

Results

The improvements described above successfully enabled RMG to handle aromatic species. Prior to the updates, program crashes were inevitable when modeling any aromatic system. To support the algorithm changes, new literature data for aromatic thermochemistry and kinetics were also added to the database.

For preliminary validation, a model was generated for pyrolysis of 1-iodonaphthalene and acetylene for comparison to shock-tube data. The model predictions for the major products, acenaphthalene and naphthalene matched well with the experimental data (see figure shown below). The RMG model predicted a higher yield of 1-ethynyl naphthalene than the literature model, although none was observed in the experiment. The RMG model also predicted smaller side products such as vinylacetylene and 1,3-butadiene, which were not reported in the experiment, although the authors do note that small molecule products from acetylene reactions were assumed to be negligible.

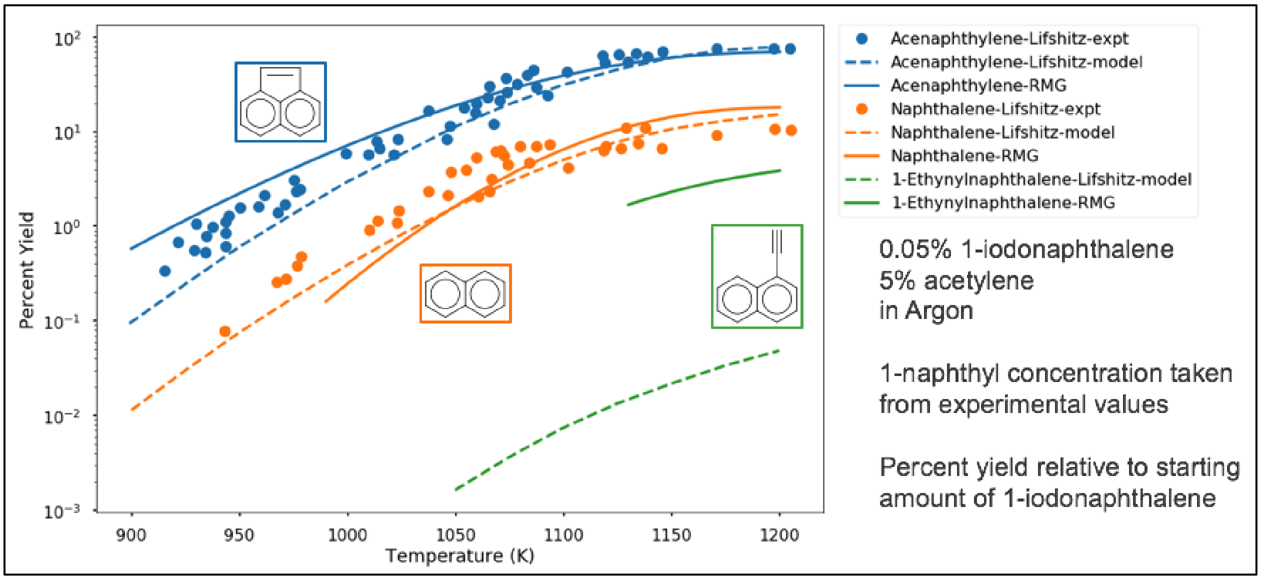

Figure 3

Co-pyrolysis models for equimolar naphthalene or tetralin with acetylene were also generated to get an initial view at whether RMG could capture the differences in reactivity. For naphthalene and acetylene, RMG predicted the major products to be acenaphthalene and hydrogen, which was initially surprising, since other PAHs such as anthracene or phenanthrene were also expected. However, these observations were corroborated by Parker et al. (2015), who also saw that acenaphthalene was the main product in contrast with generally accepted HACA mechanism for PAH growth. The model for tetralin and acetylene displayed markedly different behavior, as expected. Major products were hydrogen, naphthalene, methane, and ethene. No three ring aromatics were formed, possibly because of the overall higher hydrogen/carbon ratio.

Overall, these modeling results are very promising, and show that RMG is now much better at modeling aromatics.

Milestone(s)

This work was completed in June 2017, and is contained in the deliverable 2 presentation provided on Jun 30th, 2017.

Major Accomplishments

During this period, the RMG algorithm was successfully updated to handle aromatic species and kinetics data was added for aromatic species. These updates also underwent preliminary validation when compared to experimental shock-tube pyrolysis data. A summary of this work is contained in the deliverable 2 presentation provided to the FAA on June 30th, 2017.

Publications

Presentations

Going Bigger: Capturing PAH Chemistry in RMG *May 23, 2017*
Mengjie Liu, Kehang Han, William H. Green
Overview of RMG developments to improve thermochemistry estimation for polycyclic species and general handling of aromaticity for kinetics. International Conference on Chemical Kinetics.
Presentation, manuscript in preparation. FAA support was acknowledged.

Outreach Efforts

None

Awards

None

Student Involvement

Mengjie (Max) Liu, PhD student in the Green Research Group in MIT's Department of Chemical Engineering completed the majority of the updates to the RMG. Mengjie will be continuing work to further validate and refine the RMG models, as well as provide comparison of the kinetic model to LFP/PIMS experimental data during AY 2017/2018.

Plans for Next Period

During the next period, the work completed in Task 2 will be used to inform development of a relationships between fuel naphthalene content and aviation PM emissions. The updated RMG code is now capable of development of reaction mechanisms with aromatic species up to three rings. A reaction mechanism will be constructed to represent aviation jet fuel, and the intermediate and product species of combustion. This reaction mechanisms will then be tested in simple combustion structure models to estimate the relative production of PM precursors (three-ring aromatics) per each reactant species. As a result, the relative production of PM from naphthalenes versus mono-aromatic, cyclo-paraffinic, and paraffinic will be assessed.

Task #3: Calculation of Process Requirements and Fuel Composition Effects for Selected Refining Processes

Massachusetts Institute of Technology

Objective(s)

In AY2016/2017 Task 1, selective hydro-treating and extractive distillation were selected as candidate refinery process for large-scale reduction or removal of naphthalene from the U.S. jet fuel pool. In addition, data was collected regarding the offsite (or the supporting process) requirements and fuel composition effects of each process.

The objective of AY2016/2017 Task 3 is to continue quantitative analysis of both processes in order to develop simplified estimation models of process requirements and fuel composition effects. The result of this task will be the cost estimation for individual selective hydro-treating and extractive distillation refinery units, modelled as brown-field additions to existing refinery operations.

Research Approach

Methods

Based on the collection of process parameters as part of AY2016/2017 Task 1, utility requirements and capital cost data were collected for distillate hydro treating, extractive distillation, and their supporting processes. The supporting processes of selective hydro-treating are steam methane reforming for hydrogen production, amine separation for hydrogen sulfide separation from off-gasses, and the Claus process for sulfur recovery. Because these supporting processes are often connected to several units at a refinery, they are costed based on both the size of the modelled refinery and the capacity of the modelled hydro-treatment unit. The sole supporting process for extractive distillation is post-distillation.

In order to calculate the net present value of an added refinery finishing process for the reduction/removal of naphthalene from jet fuel, the methods described by Gary et al., 2007 are adopted. Fixed capital investment was estimated from the desired process capacities and the collected cost data. Operating cost was calculated as a function of the fixed costs, and as a function of the utility requirements and estimated utility costs (shown in the figure below) Catalyst/Solvent and process water utility costs are assumed constant (Gary et al. 2007, Peters et al., 2003). Historical and predicted natural gas and electricity prices, by U.S. census region, are taken from the U.S. Energy Information Administration. Using an auto-regressive – moving average (ARMA) model, calibrated to the predicted trend and historical price variations, natural gas and electricity prices are estimated stochastically. The net present value is then calculated using a Discounted Cash Flow Rate of Return (DCFRoR) model over the lifetime of the process unit. A discount factor of 2.74%, based on the 20 year constant maturity rate, is used for the estimated cost to society.

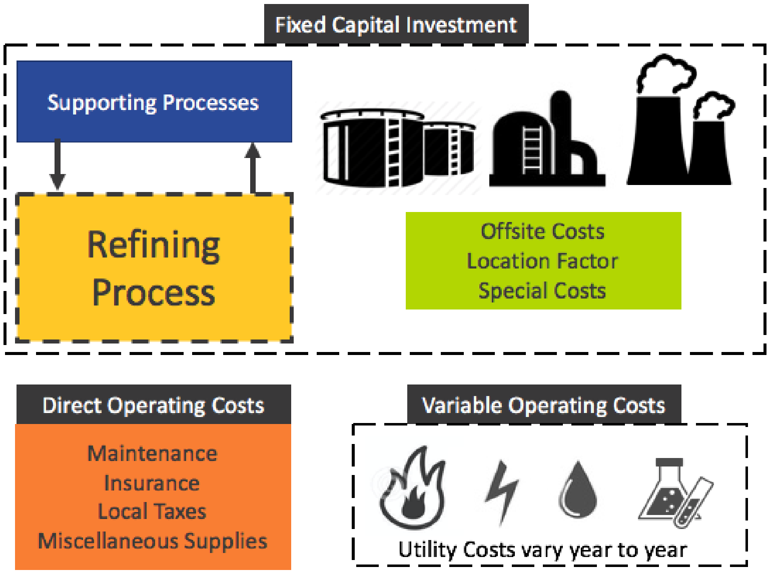

Figure 4

Results

The model successfully estimates the cost of the reduction or removal of naphthalene from U.S. jet fuel pool via operation of an additional finishing process (either selective hydro-treating or extractive distillation) at U.S. refineries. Preliminary cost data is presented in the deliverable 3 presentation provided to the FAA on August 31st, 2017.

Milestone(s)

This work was completed in August 2017, and is contained in the deliverable 3 presentation provided on August 31st, 2017.

Major Accomplishments

During this period, a simplified model was created for the purpose of cost estimation of individual selective hydro-treating and extractive distillation process units. This included effects on fuel composition, utility requirements, and estimated costs over the lifetime of the unit. Results collected from the discounted cash flow model are presented as the net present value of the unit over its life-time. A summary of this work is contained in the deliverable 3 presentation provided to the FAA on August 31st, 2017.

Publications

None

Outreach Efforts

None

Awards

None

Student Involvement

Drew Weibel, Master's student in the Laboratory for Aviation and the Environment is working directly with Prof. Steven Barrett and Dr. Ray Speth to conduct the research objectives of Task 3. Mr. Weibel is a 2nd year graduate student, and will serve on the research team through the remainder of the A39 project timeline.

Plans for Next Period

During the AY2017/2018 period, the process unit cost estimation model will be expanded to stochastically estimate the cost of removal across all U.S. refineries. This net present value estimate will be used as the "cost" the overarching cost-benefit analysis carried out in order to assess the societal benefits realized by possible naphthalene-free or –reduced jet fuel policy.

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