Naphthalene Removal Assessment

Project 39

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April 18 - 19, 2017
Alexandria, VA

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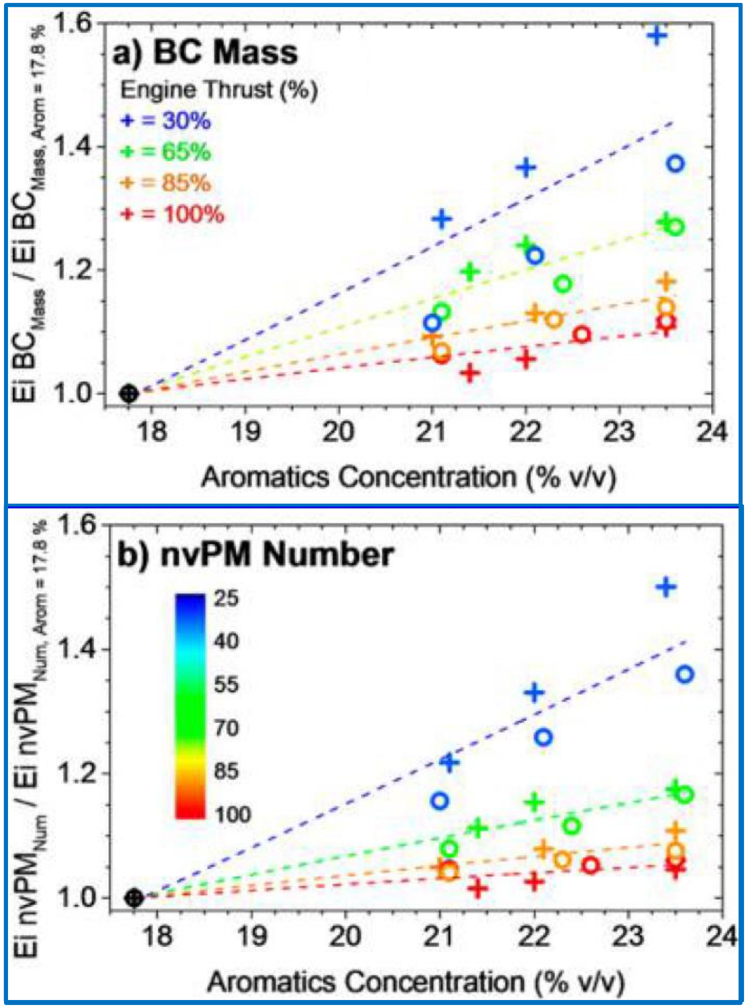
Motivation

- Naphthalene in jet fuel identified as disproportionate contributor to soot emissions[2,3]
- Aromatics reduction is a "common" process in refining / petrochemicals
  - Several refinery / petrochemical processes convert / remove aromatics from specialized feedstocks and fuels
  - Used to meet current gasoline / jet fuel / diesel aromatic specifications
- A cost-benefit analysis of jet fuel naphthalene removal is worthy of further investigation



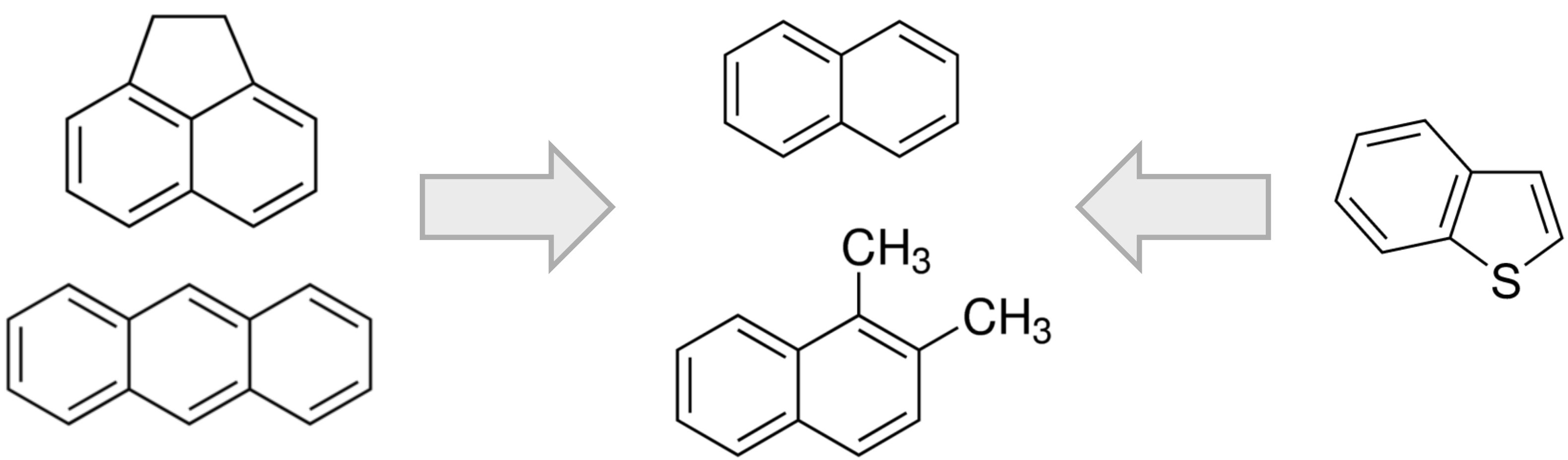
Key [2]

O :Jet A w/ Naphthalene-Depleted Aromatic Additive

+ :Jet A w/ Aromatic Additive

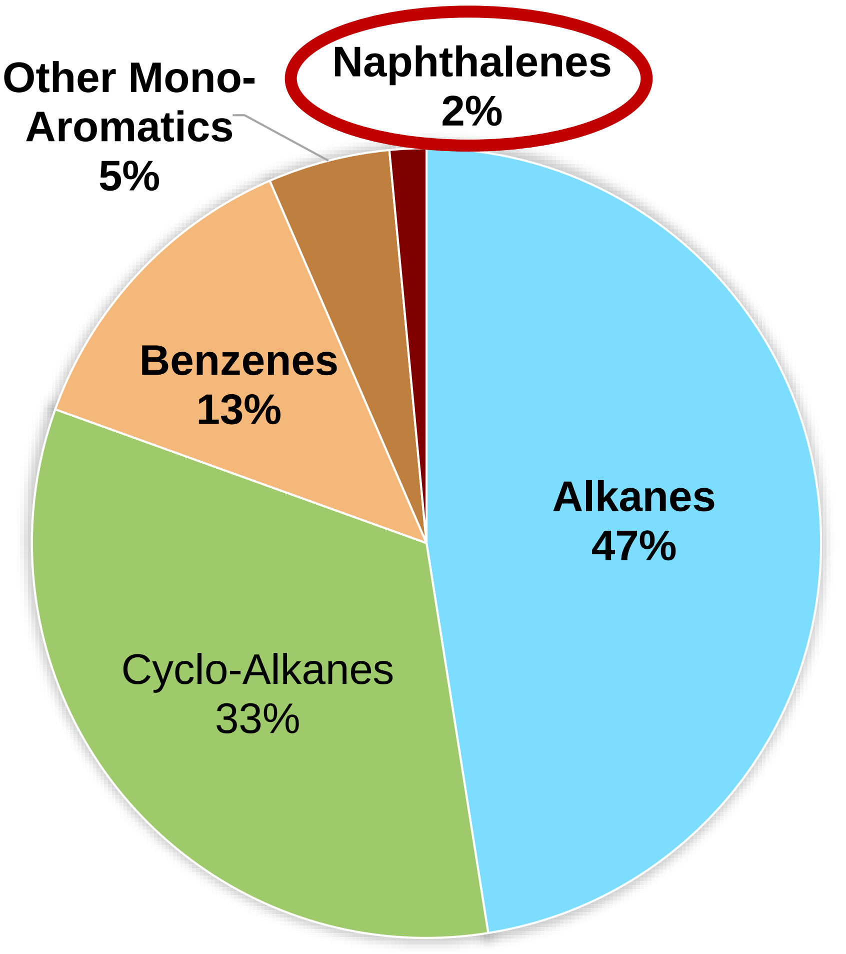
What are considered Naphthalenes?

- Consist of multi-ring aromatic compounds, may contain sulfur
- Range of species detected by fuel test (D1840)
  - Naphthalene & alkylated derivatives
  - Larger polyaromatic compounds
  - Sulfur-substituted compounds (e.g. thiophenes)



ASTM Jet Fuel Specification[4]

ASTM D1655
- Max Aromatic Content
  - 25 vol%
- Max Naphthalene Content:
  - 3 vol%



Typical Jet Fuel Composition[5]

Research Objectives

- **Determine societal costs/benefits of naphthalene removal**

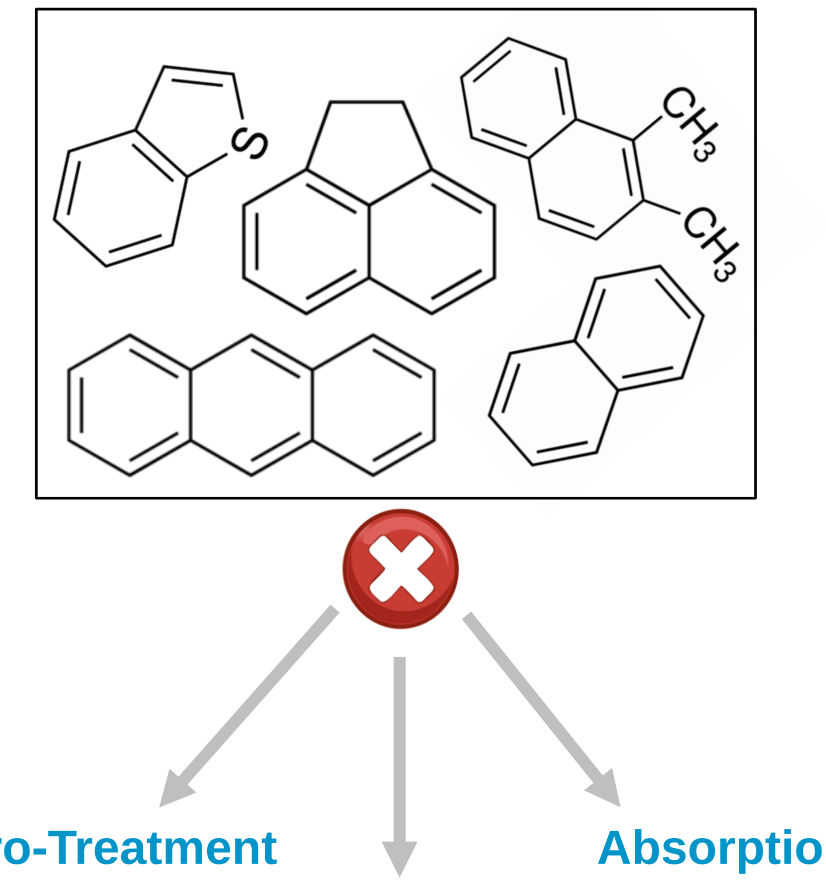
- Quantify the costs of naphthalene removal
  - Cost to the refiner in order to compare processing methods
  - Cost to society to determine net present value (NPV)

- Computational estimation of d(nvPM)/d(Naphthalene)
  - Consider changes in other combustion emissions (esp. S_{OX})

- Quantify the environmental costs/benefits of nvPM reduction
  - Climate costs/benefits based on temperature change
  - Air quality costs/benefits based on premature mortalities avoided

Cost of Naphthalene Removal

- Quantitative economic analysis of most promising processes
  - Determination of CapEx, OpEx from simplified process models, industry heuristics, and expert insight
  - Discounted cash flow (DCF) model from the refiners point of view
- Life-cycle analysis of utilities/emissions at the refinery



Process 1: Hydro-treatment

- Refining process used for sulfur, nitrogen, and metal removal, and saturation of aromatics and olefins
- Feedstock is reacted, at mild temperatures (~360° C) and pressures (50–100 bar), with high-purity hydrogen

Relative Activity of Reaction Families
(Most Active → Least Active)

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Sulfur Removal + Olefin Saturation
Halogen + Oxygen Removal
Nitrogen Removal + Aromatic Saturation

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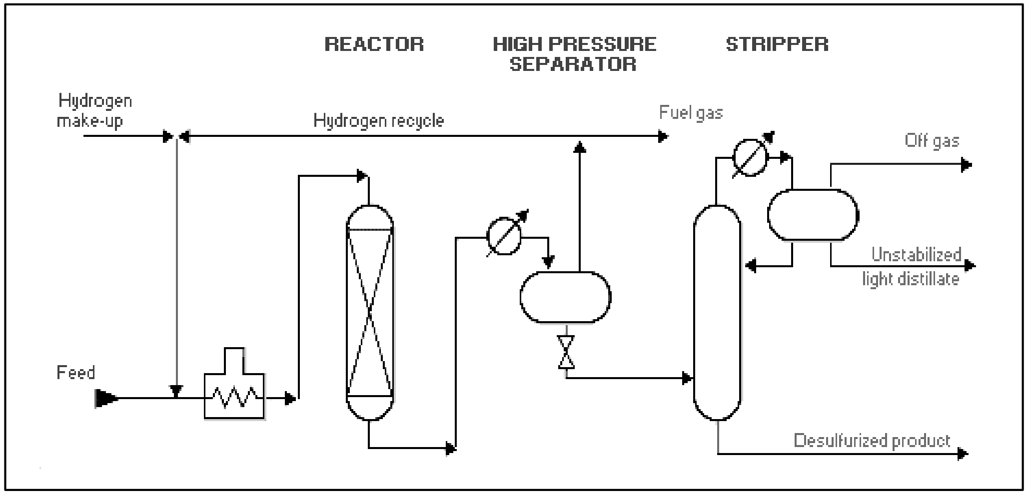
Hydrogen Consumption: 100 – 400 scfb[7]



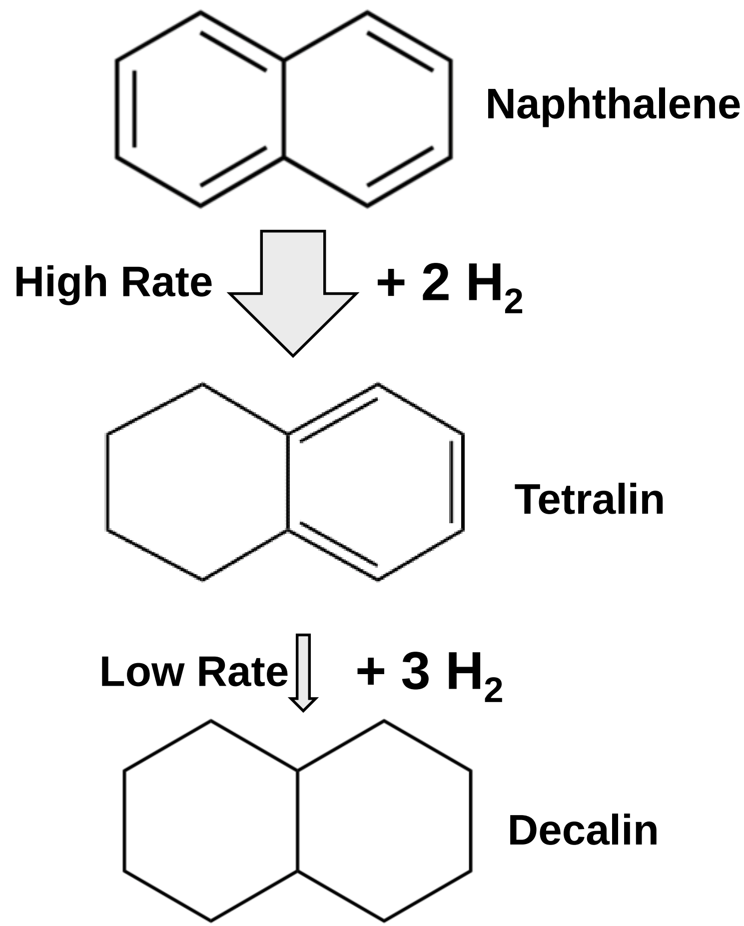
Process 1: Hydro-treatment

Pros:

- Di- & Tri- aromatic conversion with small overall aromatic change (vol%)
- Removal of impurities
- This process is currently utilized in the industry for aromatic saturation

Cons:

- Large hydrogen requirement
- Energy intensive
- Tetralin's impact on PAH formation is unclear



Process 2: Extractive Distillation

- Refining process by which the desired extract is separated from the feed via solution with a polar solvent
- Aromatic extract first separated from feed, then mono-aromatics and naphthalene's are separated via distillation

Relative Solubility of Components
(Most Active → Least Active)
==============================
Aromatics (Mono → Di)
S, N, O, Halogen impurities
Naphthenes / Cycloalkanes
Alkanes

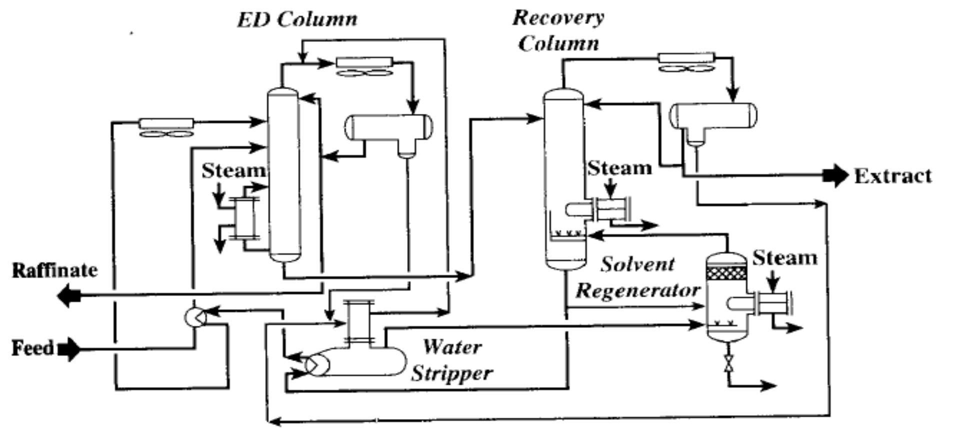


FIGURE 2.2.5 Shell Sulfolane process: extractive distillation.

Process 2: Extractive Distillation

Pros:

- Aromatics are fully removed from stream, in contrast to conversion
- Control of aromatic constituents returned to final jet fuel stream
- Current applications of this technology are similar to naphthalene removal
  - Aromatics removal from low aromatic (~25%) reformate / pygas
  - New processes have higher feedstock versatility (impurities, etc.)
- Potentially low environmental impact

Cons:

- Relatively high energy distillation required
- Specialized solvent required to handle fuel sulfur content
- Alternative use needed for separated naphthalene

Estimation of d(nvPM)/d(Naphthalene)

- Development of jet fuel reaction mechanism
- Prepare data for relative rates of reaction of alkanes, cycloalkanes, mono-aromatics, and naphthalenes towards soot precursors.

- Combustion modelling of soot precursor growth in simple configurations
- Comparison over range of P, T, Φ experienced in the combustor

- Relate results to jet engine soot measurement campaigns (APEX, ACCESS, etc.)

Climate Costs/Benefits

- Climate radiative balance will be both positively and negatively impacted by jet fuel naphthalene removal

Radiative Source	Climate Impact	Description
Refinery Emissions	Warming	Increased CO_2, light end emissions from hydrogen production / utilities
Reduced nvPM	Cooling	Reduced soot emissions from jet engine tailpipe
Reduced Sulfates*	Warming	Reduced fuel sulfur content from refining
Contrail Effects	Mixed	Increased hydrogen fuel content Decreased soot particulate size

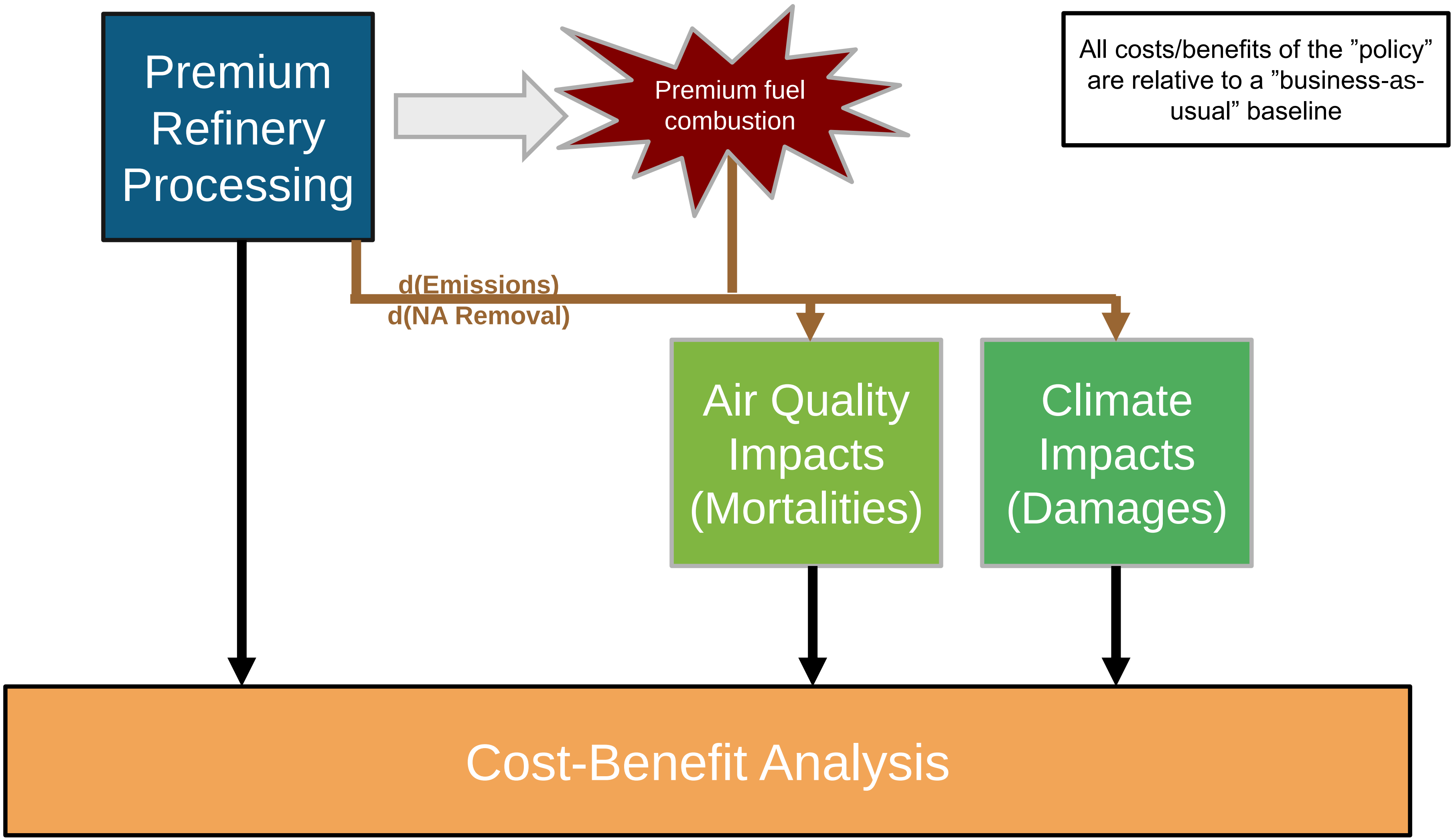
- ***Dependent on refining process used**

- APMT-I Climate used to estimate NPV of climate impacts
  - Radiative imbalance → temperature change → NPV of damages

Air Quality Costs/Benefits

- Non-volatile particulate matter emissions lead population $PM_{2.5}$ exposure, morbidity, and premature mortalities
- Reduction of naphthalenes will reduce aircraft nvPM & (possibly) sulfate emissions, and impact regional and global $PM_{2.5}$ exposure
- In order to characterize the impacts of naphthalene on air quality:
  - GEOS-Chem adjoint sensitivities for U.S. (U.S emissions → U.S. impacts)
  - GEOS-Chem forward runs available for specific scenarios

Cost / Benefit Analysis



Treatment of Uncertainty

- Stochastic techno-economic analysis to determine minimum selling price probability distributions via the three selected refining pathways
- Stochastic cost/benefit analysis using streamlined Monte Carlo simulations
- Preserves uncertainty in the input parameter distributions as uncertainty in the output quantities (minimum selling price and $\pm$NPV)
- Framework also utilized in analyses of alternative fuels

Next Steps

- Deterministic and stochastic quantification of the minimum selling price of premium, naphthalene depleted, jet fuel via the three specified refining pathways

- Combustion modelling
  - Construction of fuel-sensitive jet fuel reaction mechanisms
  - Simple combustion modelling of reaction mechanisms to determine relative rates components move towards soot
  - Correlation to jet engine conditions via emission campaign data

- Climate and air quality modelling of reduced nvPM impacts

Summary

- Naphthalenes identified as key precursors of non-volatile particulate matter emissions
- Aromatics removal is a “common” process in the modern refinery
- Hydro-treatment, extractive distillation, and adsorption shown to be promising processing methods to remove naphthalenes from jet fuel
- Existing tools (RMG, combustion models, APMT-I, GEOS-Chem, etc.) will be used to estimate reduced nvPM emissions and environmental impacts
- Cost/benefit analysis used to determine the effect on society of production of premium, naphthalene depleted, jet fuel and the ensuing changes in climate and air quality impacts.

Acknowledgements

- Warren Gillette for his FAA project management
- Randall Field, Matt Pearlson, Mark Staples, James Hileman, and George Huff for technical guidance

Participants

- Prof. Steven Barrett, Dr. Raymond Speth, Prof. William Green
- Drew Weibel, Mengjie Liu

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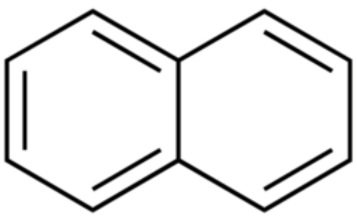
Potential Naphthalene Removal Processes

+ Alkyl Groups



+ Poly-aromatics

Hydrogen Addition

Hydro-treatment

Hydro-cracking

Carbon Removal

Catalytic Cracking

Aromatic Separation / Manipulation

Absorption

Extractive Distillation

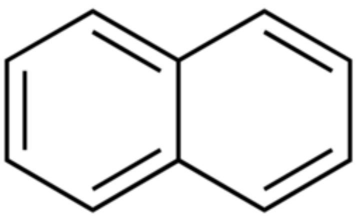
Reactive Distillation

Selective Vacuum Distillation

Crystallization

Potential Naphthalene Removal Processes

\+ Alkyl Groups



\+ Poly-aromatics

<u>Hydrogen Addition</u>

- **Hydro-treatment**
- ~~Hydro-cracking~~

<u>Carbon Removal</u>

- ~~Catalytic Cracking~~

<u>Aromatic Separation / Manipulation</u>

- **Absorption**
- **Extractive Distillation**
- ~~Reactive Distillation~~
- ~~Selective Vacuum Distillation~~
- ~~Crystallization~~

Adsorption

- Refining process in which removal of aromatic extract from mother liquor is controlled by relative adsorption rates on an adsorbent bed
- Two common process methods
  - Single-use pads: Generally used for impurity removal in liquid / gaseous streams. Appropriate for impurities in medium to low “ppm” quantities
  - Simulated Moving Bed Adsorption: Continually regenerative adsorbent process. Used for separation of streams with varying affinity to adsorbent.
    - » Appropriate for naphthalne removal
- **Naphthalenes must be used elsewhere in the refinery**

Adsorption

- Pros:
  - Naphthalene removal with small aromatics% change
  - Control of which aromatics are returned to the jet fuel product stream
  - Relatively low energy input, operating cost
  - Low environmental impact

- Cons:
  - Only demonstrated in specific applications
  - Adsorbent pad life restrictions may require pre-treating process
  - High capital investment required for specialized systems