Air Quality Considerations for Biofuels: Potential Air Emissions from a Cellulosic Biorefinery Producing Renewable Diesel Blendstock

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Support DOE’s Bioenergy Sustainability Program: NREL’s sustainability analysis program aims to better understand air emissions from the biofuel supply chain, applicable regulations and implications for cost, operations and sustainability

- **Ultimate aim:** to develop tools and analyses that can assess air pollutant emissions and potential health consequences from the cellulosic biofuel supply chain at high spatial, temporal and chemical resolution and can compare results to those from incumbent systems.

Address research gaps

1. Lack of information linking DOE’s advanced designs of different biofuel supply chain facilities and processes that enable comparison of estimated emissions to applicable regulatory limits.

2. Lack of quantification of life cycle (supply chain) ozone and PM-potential precursor emissions from different cellulosic biofuel pathways based on DOE advanced designs.

3. Lack of spatially, temporally, and chemically resolved life cycle inventories of air pollutant emissions to enable
   a. Examination of source-level emission reduction opportunities
   b. Comparison to existing inventories (e.g., EPA’s National Emissions Inventory)
   c. Estimation of air quality and health impacts from large-scale cellulosic biofuel production and use using high resolution air quality models.
Approach

For each life cycle stage, based on inventory

- Approach
  - Spatially,
  - temporally,
  - and chemically explicit inventory
- Air quality modeling
- Exposure assessment
- Health impact assessment and externalities estimation

For life cycle impact evaluation, considering all stages and net effects

Life Cycle Stages

- Feedstock Production
- Logistics
- Conversion
- Distribution
- End Use

Indicators

Best Practices

Trends and Tradeoffs

Baselines and Targets

Indicator Values

Feedstock Production

Logistics

Conversion

Distribution

End Use
Progress to Date

For each life cycle stage, based on inventory

- Best Practices
- Trends and Tradeoffs
- Baselines and Targets
- Indicator Values
- Indicators

For life cycle impact evaluation, considering all stages and net effects

- Spatially, temporally, and chemically explicit inventory
- Air quality modeling
- Exposure assessment
- Health impact assessment and externalities estimation

Life Cycle Stages

- Feedstock Production
- Logistics
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- Distribution
- End Use

FY12-14

FY14-15 (regulations, PTE, controls)
Sugars-to-Hydrocarbons (HC) Biorefinery Air Emissions

Draft – not for distribution, quotation or citation
Objectives of the Analysis

• Understand potential air emission impacts of hydrocarbon biofuel production
  - Identify air pollutants likely to be generated from a sugars-to-hydrocarbon (HC) biorefinery via biological conversion of cellulosic sugars to diesel blendstock per a design case developed by NREL
  - Examine federal air regulations potentially applicable to the sugars-to-HC biorefinery
  - Estimate potential-to-emit of air pollutant emissions for all emission sources at the biorefinery
• Provide feedback to the biorefinery design team to incorporate emission controls to meet applicable air regulations and further reduce emissions if needed
Overview of Sugars-to-HC Conversion Process

A100 FEEDSTOCK HANDLING
Corn stover/ Switchgrass/ wood waste

A200 PRETREATMENT & CONDITIONING

A300 ENZYMATIC HYDROLYSIS, CONDITIONING, BIOCONVERSION

A400 CELLULASE ENZYME PRODUCTION

A500 PRODUCT RECOVERY & UPGRADING

A600 WASTE WATER TREATMENT

A700 STORAGE

A800 BOILER, COMBUSTOR, TURBO-GENERATOR

Renewable Diesel Blendstock (RDB)

Design Case for the Sugars-to-HC Biorefinery

• **Capacity and Yield**
  - 2,205 dry ton biomass/day
  - RDB yield: 43 gallons/dry ton
  - 31.3 million gallons of RDB/year

• **Design Goals**
  - Feasibility-level analysis (proof of concept)
  - Meet cost target (an intermediate DOE cost goal of $5/gallon gasoline equivalent by 2017)

• **Limitations**
  - Lack of detailed specifications necessary for an accurate estimation of air pollutant emissions
  - Some control strategies could be included by vendors but not included in design
  - Process not optimized to minimize air pollutant emissions
## Air Pollutants Likely Emitted by Area

<table>
<thead>
<tr>
<th>Plant Area</th>
<th>Equipment/Operations</th>
<th>Air Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area 100: Feed handling</strong></td>
<td>Dust collection systems</td>
<td>PM, PM(<em>{10}), PM(</em>{2.5})</td>
</tr>
<tr>
<td><strong>Area 200: Pretreatment and conditioning</strong></td>
<td>Pre-steamers and Pretreatment Reactors</td>
<td>VOC, HAP, SO(_2), H(_2)SO(_4) mist</td>
</tr>
<tr>
<td></td>
<td>Flash tank</td>
<td>VOC, HAP, SO(_2), H(_2)SO(_4) mist</td>
</tr>
<tr>
<td></td>
<td>Ammonia addition tank</td>
<td>NH(_3)</td>
</tr>
<tr>
<td></td>
<td>Leaking equipment</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td><strong>Area 300: Enzymatic hydrolysis, hydrolysate conditioning, and bioconversion</strong></td>
<td>Enzymatic hydrolysis reactors</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Filter press</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Aerobic bioreactors and storage tank</td>
<td>CO(_2), VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Leaking equipment</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td><strong>Area 400: Cellulase enzyme production</strong></td>
<td>Bioreactors</td>
<td>CO(_2), VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Leaking equipment</td>
<td>VOC, HAP, SO(_2)</td>
</tr>
<tr>
<td><strong>Area 500: Product recovery and upgrading</strong></td>
<td>Pre-heater</td>
<td>PM, PM(<em>{10}), PM(</em>{2.5}), NO(_x), SO(_2), CO, CO(_2), VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Hydrotreating process</td>
<td>CO(_2), VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Leaking equipment</td>
<td>VOC, HAP</td>
</tr>
</tbody>
</table>
## Air Pollutants Likely Emitted by Area (cont’d)

<table>
<thead>
<tr>
<th>Plant Area</th>
<th>Equipment/Operations</th>
<th>Air Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 600: Wastewater treatment</td>
<td>Anaerobic digester</td>
<td>CH4, CO2, VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Aerobic digester</td>
<td>CO2, VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Leaking equipment</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td>Area 700: Storage</td>
<td>RDB product storage tank</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Sulfuric acid tank</td>
<td>H2SO4 mist, SO2</td>
</tr>
<tr>
<td></td>
<td>Ammonia storage tanks</td>
<td>NH3</td>
</tr>
<tr>
<td></td>
<td>Loading operations</td>
<td>VOC, HAP</td>
</tr>
<tr>
<td>Area 800: Combustor, boiler, and turbogenerator</td>
<td>Boiler</td>
<td>PM, PM10, PM2.5, NOx, SO2, CO, CO2, VOC, HAP</td>
</tr>
<tr>
<td>Area 900: Utilities</td>
<td>Cooling towers</td>
<td>PM, PM10, PM2.5, VOC, HAP</td>
</tr>
<tr>
<td></td>
<td>Fire pump and emergency generator</td>
<td>PM, PM10, PM2.5, NOx, SO2, CO, CO2, VOC, HAP</td>
</tr>
<tr>
<td>Truck Traffic</td>
<td>Dust from trucks hauling feedstock, raw materials, waste, and product</td>
<td>PM, PM10, PM2.5</td>
</tr>
</tbody>
</table>
Planned Control Devices Currently in the Sugars-to-HC Design Case

- **PM/PM$_{10}$/PM$_{2.5}$**
  - BAGHOUSE (Areas 100, 800) [EFFICIENCY: 99%]

- **SO$_2$**
  - FLUE GAS DESULFURIZATION (Area 800) [EFFICIENCY: 92%]

- **NO$_x$**

- **CO**

- **Lead (Pb)**

- **VOC**

- **NH$_3$**

- **H$_2$SO$_4$**

- **CO$_2$e**

- **HAP**
  - FLUE GAS DESULFURIZATION (Area 800)
    - Efficiency:
      - Hydrogen Chloride: 98%
      - Hydrogen Fluoride: 88%

There are no planned control devices for **NH$_3$, H$_2$SO$_4$, CO$_2$e, and HAP**.
# Federal Air Regulations Potentially Applicable to the Sugars-to-HC Biorefinery

<table>
<thead>
<tr>
<th>Affected Equipment</th>
<th>Federal Rule</th>
<th>Target Pollutant(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler</td>
<td>Boiler NSPS, 40 CFR 60, Subpart Db</td>
<td>SO$_2$, PM, and NO$_x$</td>
</tr>
<tr>
<td>Boiler</td>
<td>One of these Boiler NESHAP will apply: 40 CFR 63, Subpart JJJJJJ <em>or</em> Subpart DDDDD</td>
<td>HAP</td>
</tr>
<tr>
<td>Emission release points: Process vents, equipment leaks, storage tanks, wastewater, heat exchange system</td>
<td>One of these Chemical Manufacturing NESHAP will apply: 40 CFR 63, Subpart FFFFF (MON) <em>or</em> Subpart VVVVVV (CMAS)</td>
<td>HAP</td>
</tr>
<tr>
<td>Fire pump and emergency generator</td>
<td>Engine NSPS 40 CFR 60, Subpart IIII</td>
<td>PM, VOC, NO$_x$</td>
</tr>
<tr>
<td>Fire pump and emergency generator</td>
<td>Internal Combustion Engine NESHAP 40 CFR 63, Subpart ZZZZ</td>
<td>HAP</td>
</tr>
</tbody>
</table>
### Preliminary Facility-Wide Potential-to-Emit (PTE) Estimates

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>PTE (tpy)</th>
<th>Major source threshold (tpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM(filterable)</td>
<td>78</td>
<td>100</td>
</tr>
<tr>
<td>PM&lt;sub&gt;10&lt;/sub&gt;</td>
<td>32</td>
<td>100</td>
</tr>
<tr>
<td>PM&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>SO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>NO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>290</td>
<td>100</td>
</tr>
<tr>
<td>CO</td>
<td>610</td>
<td>100</td>
</tr>
<tr>
<td>VOC</td>
<td>99.8</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>&lt;1</td>
<td>100</td>
</tr>
<tr>
<td>GHG (CO&lt;sub&gt;2&lt;/sub&gt; equivalent)</td>
<td>1,200,000</td>
<td>Pending</td>
</tr>
<tr>
<td>Hazardous air pollutants (HAP) (total)</td>
<td>41</td>
<td>25</td>
</tr>
<tr>
<td>Ammonia (NH&lt;sub&gt;3&lt;/sub&gt;)</td>
<td>2.0</td>
<td>Reporting requirement</td>
</tr>
<tr>
<td>Sulfuric acid (H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;) mist</td>
<td>21.0</td>
<td>100</td>
</tr>
</tbody>
</table>

**PTE calculations take into account:**

1) regulatory requirements applicable to the Sugars-to-HC biorefinery, and  
2) planned control devices in the design case, which are assumed to be made federally enforceable in a permit.
Major Emission Sources by Pollutants

- **CO**
  - Area 800: Boiler (>90%)

- **NOx**
  - Area 800: Boiler (>90%)

- **PM**
  - Truck Traffic (>80%)

- **PM$_{10}$**
  - Truck Traffic (>40%)

- **PM$_{2.5}$**
  - Area 800: Boiler (>50%)

- **SO$_2$**
  - Area 800: Boiler (>90%)

- **VOC**
  - Area 300: Enzymatic Hydrolysis (>30%)

- **Lead (Pb)**
  - Area 800: Boiler (>90%)

- **CO$_2$e**
  - Area 800: Boiler (>80%)

- **HAP**
  - Area 800: Boiler (>60%)

- **NH$_3$**
  - Area 800: Boiler (>60%)

- **H$_2$SO$_4$**
  - Area 800: Boiler (>60%)

Area 400: Cellulase enzyme production (>90%)
Details about the Boiler

- Boiler type: TowerPak Stirling Boiler
- Efficiency: 80%
- Heat duty: 300 MMBtu/hr
- Feed inputs: Lignin, unfermented sugars, biogas from wastewater treatment
- Emission control devices:
  1) Baghouse and 2) Flue gas desulfurization
Evaluation of whether current emission controls in the design case can meet applicable federal air regulations

<table>
<thead>
<tr>
<th>Affected Sources</th>
<th>Potentially Applicable Federal Air Regulations</th>
<th>Regulatory Requirements</th>
<th>Feasible Emission Control Options to Achieve Compliance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler (Area 800)</td>
<td>1) NSPS - Standards of Performance for Industrial-Commercial-Institutional Steam Generating Units (40 CFR 60, Subpart Db)</td>
<td>Limit SO$_2$ emission rate to 0.2 lb/MMBtu of heat input or less (NSPS)</td>
<td>Flue gas desulphurization (FGD) with 92% SO$_2$ reduction efficiency is planned in the design case and is expected to meet the requirement.</td>
</tr>
<tr>
<td></td>
<td>2) NESHAP for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters (40 CFR 63, Subpart DDDDD)</td>
<td>Limit filterable PM emission rate to 0.03 lb/MMBtu of heat input or less (NSPS &amp; NESHAP)</td>
<td>A baghouse planned in the design case is expected to achieve ≥ 99% PM reduction and meet the requirement.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Limit HCl emission rate to 0.022 lb/MMBtu of heat input (NESHAP)</td>
<td>FGD planned in the design case is expected to reduce HCl by approximately 98% and is expected to meet the requirement.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Limit CO emission rate to 0.58 lb/MMBtu of steam output (NESHAP)</td>
<td>New boiler designs are expected to meet this CO emission limit. Subpart DDDDD also specifies work practice standards.</td>
</tr>
</tbody>
</table>
Evaluation of whether current emission controls in the design case can meet applicable federal air regulations

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</tr>
</thead>
<tbody>
<tr>
<td>Multiple emission release points e.g., process vents, equipment leaks, wastewater, and heat exchange system (e.g., cooling tower) (Areas 200 to 600 and Area 900)</td>
<td>NESHAP for Miscellaneous Organic Chemical Manufacturing (40 CFR 63, Subpart FFFF)</td>
<td>Reduce hazardous air pollutant (HAP) emissions by ≥ 98% from enzymatic hydrolysis, conditioning, and bioconversion (Area 300)</td>
<td>No emission control is included in the design case to reduce HAP from the fermentor vent in Area 300. Feasible control options could include one of the following: 1) venting the emissions to a) the boiler (present in design case), or b) a thermal incinerator (e.g., the pre-heater present in design case), or c) a catalytic incinerator, or d) a packed-bed wet scrubber, or e) an adsorption tower using activated carbon, 2) venting emissions through a closed vent system to a flare.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduce HAP emissions from equipment leaks (Areas 200 to 600)</td>
<td>Comply with an acceptable Leak Detection And Repair (LDAR) program.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Reduce HAP from cooling tower leaks (Area 900)</td>
<td>Comply with the work standards for cooling tower specified in Subpart FFFF.</td>
</tr>
</tbody>
</table>
Key Findings

- If no further emission controls are in place, the sugars-to-HC biorefinery would be deemed a major source under the New Source Review Program and a major source of HAP (for the purpose of Title V permitting) based on current design and our preliminary PTE estimates.

- Boiler is the single largest emitting source for CO, NOx, PM$_{2.5}$, SO$_2$, Pb, H$_2$SO$_4$, GHG, and HAP. However, emissions factors specific to the boiler used in this process, and its process fuel, are not readily available.

- There are significant uncertainties associated with many design specifications necessary for accurate estimation of air pollutant emissions.
Future Work on this Pathway

• Investigate cost and performance implications of incorporating emission control technologies into the sugars-to-HC design case to meet regulatory requirements, and considering potential to be a minor source

• Provide feedback to biorefinery design cases to ensure the designs meet applicable air pollutant regulations

• Validate emission estimates with available data
  – If/when available, collect stack testing data from newly built biorefineries and analogous unit operations
Other Work on the Project

• Quantification of air pollutant emissions associated with advanced biomass logistics systems designed by DOE national labs

• Air regulatory analysis and PTE estimation for other conversion pathways such as fast pyrolysis followed by upgrading of bio-oils to hydrocarbon fuels

• Spatially-explicit air emission inventory for large-scale biomass production under high biofuel and bioenergy penetration scenarios
Thank you!

Questions?