Understanding emission profiles and health effects of biofuels

Krystal Pollitt, PhD
Mining Diesel Emissions Conference, October 9, 2014

What are Biofuels?

Biodiesel
Renewable Diesel
Greener Diesel

Renewable feedstocks used for all three fuel groups are the same.
Biofuel Feedstocks

<table>
<thead>
<tr>
<th>Saturated Fat</th>
<th>Mono-saturated Fat</th>
<th>Unsaturated Fat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coconut</td>
<td>Canola</td>
<td>Sunflower</td>
</tr>
<tr>
<td>Palm</td>
<td>Olive</td>
<td>Soy</td>
</tr>
<tr>
<td>Animal Lard</td>
<td>Corn</td>
<td>Fish</td>
</tr>
</tbody>
</table>

Feedstocks are Comprised of Triglycerides

Triglyceride
Biofuel Production Methods

**TRANSESTERIFICATION**

Renewable Feedstock → Alcohol + Catalyst → Biodiesel + Glycerol

Hydrogen Gas + Catalyst → Renewable Diesel + Propane + CO + CO₂ + H₂O

**HYDROGENATION**

Transesterification to Produce Biodiesel

Triglyceride + Alcohol + Glycerol → 3 Methyl Esters

Catalyst
Transesterification Methyl Ester Products

Saturated Fat  Mono-saturated Fat  Unsaturated Fat

The degree of saturation of the original feedstocks is the same as in the final biodiesel product.

Physical Properties

Lower Gel Point
Storage and operability issues at cold temperatures

Oxidative Properties
Poor Oxidative Stability
Requires an oxidant stabiliser to avoid rancidification and polymerisation problems
Biodiesel is Compositional Different

Traditional Diesel, Renewable Diesel

<table>
<thead>
<tr>
<th>Paraffins</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
</tr>
<tr>
<td>H-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-O</td>
</tr>
<tr>
<td>Full saturated carbon chain.</td>
</tr>
</tbody>
</table>

Biodiesel

<table>
<thead>
<tr>
<th>Methyl Esters</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-O</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>Oxygen content modifies emissions profile</td>
</tr>
</tbody>
</table>

What are Biofuels?

<table>
<thead>
<tr>
<th>Biodiesel (Transesterification)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Renewable Diesel (Hydrogenation)</td>
</tr>
<tr>
<td>Greener Diesel</td>
</tr>
</tbody>
</table>

Renewable feedstocks used for all three fuel groups are the same.

BUT the production processes differ.
### Biodiesel Emission Profile

**Regulated Pollutants**

- NOx

**Unregulated Pollutants**

- Increased particle number concentration (d < 50 nm)
- Increased carbonyl concentrations (formaldehyde, acrolein), attributable feedstocks with enhanced oxidation

### Renewable Diesel Emission Profile

Decreases in regulated pollutant emission across varying renewable biodiesel blends of Neste Oil’s NExBTL fuel.

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>R10</th>
<th>R50</th>
<th>R100</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM mass</td>
<td>0</td>
<td>-5%</td>
<td>-28%</td>
</tr>
<tr>
<td>NOx</td>
<td>0</td>
<td>-6%</td>
<td>-10%</td>
</tr>
<tr>
<td>Total Hydrocarbons</td>
<td>-33%</td>
<td>-48%</td>
<td>-48%</td>
</tr>
<tr>
<td>CO</td>
<td>-11%</td>
<td>-22%</td>
<td>-28%</td>
</tr>
</tbody>
</table>
**Toxicological Study Assessment**

**Exposure Type**
- Lab Engine Operation
- Real World

**Model**
- Human
- Animal
- Cell Culture
- Acellular

**Health Outcomes**
- Respiratory, Cardiovascular, Cancer and Mutagenicity,
  Reproductive Health, Neurotoxicity

**Biofuel Studies**
- Able to focus on specific pollutants
- Representative of a Whole Pollution Mixture

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**Biofuel Toxicological Study Assessment**

**Exposure Type**
- Lab Controlled, Filter Extracts

**Model**
- Animal

**Outcomes**
- Cardiovascular
- Respiratory
- Lung Cell Culture
  - Cytotoxicity
  - Inflammation
  - Oxidative Stress
  - Genotoxicity
- Nasal
- Bronchial
- Alveolar
Cellular Response to Diesel and Biofuels

DieSEL, Biofuel Pollutants

Airway Epithelial Cells

Cellular Response to Diesel and Biofuels

Diesel, Biofuel Pollutants

Airway Epithelial Cells

Oxidative Stress
Pollutant Induced Generation of Reactive Oxygen Species
Cellular Response to Diesel and Biofuels

OXIDATIVE STRESS
Pollutant Induced
Generation of Reactive
Oxygen Species

Inflammation
Protein Production

Airway Epithelial Cells

Diesel, Biofuel Pollutants

$\text{H}_2\text{O}_2$, $\cdot\text{OH}$, $\text{O}_2^•$ 

TNF$\alpha$, IL-6, IL-8

Cell Death
Loss of Viability

Protein Production

Inflammation

Diesel, Biofuel Pollutants

$\text{H}_2\text{O}_2$, $\cdot\text{OH}$, $\text{O}_2^•$ 

TNF$\alpha$, IL-6, IL-8

Cell Death
Loss of Viability

Protein Production

Inflammation
Time Scale of Cellular Responses

The magnitude of a cellular response is dependent on the exposure concentration and duration.

- **OXIDATIVE STRESS**
  - Pollutant Induced
  - Generation of Reactive Oxygen Species

- **Inflammation**
  - Protein Production

- **Cell Death**
  - Loss of Viability

Response

Hours After Exposure

Biofuel Toxicity Assessment Using Lung Cells

- **Fuel Type**
  - Chemical Composition
  - Consumption Rate
  - Temperature
  - Density

- **Engine Operation**
  - Torque
  - Speed

- **Aftertreatment**
  - DPF
  - DOC

- **Filter Sample**

- **Wash Particles Off Filter**

- **Lung Cells**
## Lung Cells Studies

<table>
<thead>
<tr>
<th>Study Cells</th>
<th>Engine Operation</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Mouse Macrophage Mouse Macrophage</td>
<td>Light, Euro II</td>
<td>X X ULSD = Rapeseed B100 = HVO R100</td>
</tr>
<tr>
<td>2 Mouse Macrophage</td>
<td>Light, Euro IV</td>
<td>x</td>
</tr>
<tr>
<td>3 Mouse Macrophage</td>
<td>Heavy, Euro II</td>
<td>X</td>
</tr>
<tr>
<td>4 Human Bronchial</td>
<td>Light, Euro IV</td>
<td>X X ULSD &lt; Rapeseed B50</td>
</tr>
<tr>
<td>5 Human Bronchial</td>
<td>Heavy</td>
<td>X ULSD &lt; Soy B100</td>
</tr>
<tr>
<td>6 Rat Alveolar</td>
<td>Heavy</td>
<td>X ULSD = Soy B20</td>
</tr>
</tbody>
</table>

Exposure Concentration = 0-500 ug/mL
Incubation Period = 24h

(1) Jalava et al 2010; (2) Jalava et al 2012; (3) Kooter et 2011;

## Biofuel Toxicity Assessment Using Animals

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Aftertreatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Composition</td>
<td>DPF</td>
</tr>
<tr>
<td>Consumption Rate</td>
<td>DOC</td>
</tr>
<tr>
<td>Temperature</td>
<td>-</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
</tr>
</tbody>
</table>

Engine Operation
- Torque
- Speed

Engine
### Biofuel Toxicity Assessment Using Animals

#### Inhalation, Soy B100, 500 µg m⁻³

<table>
<thead>
<tr>
<th>Study</th>
<th>Inhalation Method</th>
<th>Exposure Duration</th>
<th>Exposure Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heavy Duty Engine</td>
<td>6h/day, 65 days</td>
<td>Chronic Exposure</td>
</tr>
<tr>
<td>2</td>
<td>Generator</td>
<td>4h/day, 20 days</td>
<td>Subchronic Exposure</td>
</tr>
<tr>
<td>3</td>
<td>Generator</td>
<td>1 hour</td>
<td>Acute Exposure</td>
</tr>
</tbody>
</table>

- **Chronic Exposure**: Modest chronic respiratory inflammation compared to filtered air.
- **Subchronic Exposure**: Increased tissue damage, oxidative stress, inflammation in lungs and liver compared to diesel.
- **Acute Exposure**: Promoted cardiovascular alteration & increased respiratory and systemic inflammation compared to diesel.

(1) Finch et al 2002; (2) Shvedova et al 2013; (3) Brito et al 2010
Biofuel Toxicity Assessment Using Animals

**Corn B100**

**Acute Exposure**

- **1 instillation, 18 µg**

**Post-Exposure Follow-up**

- **1 day**: Diesel and Biodiesel particles can be seen in the airway.
- **7 days**: Increased inflammation by biodiesel compared to diesel.
- **28 days**: Enhanced lung damage and persistent inflammation for biodiesel compared to diesel.

(4) Yanamala et al 2013

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Summary of Biofuel Toxicity Studies

**Mixed results from acute toxicity testing with lung cell studies...**

- A range of fuels have been tested at various blends and exposure concentrations. The divergence in engine type, after-treatment controls and drive cycle present challenges in comparing the emission profiles reported across studies.

**Agreement across animal studies...**

- All published animal studies consistently describe adverse cardiovascular and respiratory physiologic responses induced by biodiesel exposure.

**Lack of human biofuel health studies...**

- No studies for human exposure to biofuel have been published to date.

**Renewable diesel...**

- Exposure to renewable diesel exhaust have not been comprehensively evaluated. Given the similarities in fuel composition, the toxicity of renewable diesel emissions is not expected to differ from traditional diesel.
**Recommendations**

**What is a biofuel?**
- **Consistency in biofuel terminology** is necessary to specify the renewable feedstock the fuel is being derived from and the production process. A distinction must be clearly stated in regulations between biodiesels and renewable diesels.

**It is not only the particles...**
- Most toxicity studies conducted to date have focused on the particulate fraction of biofuels exhaust pollutants. More work is needed to characterise the toxicity of the **gaseous emissions**.

**Align industry and lab engine operation...**
- It is necessary for the **mining industry to specify the appropriate combination of engine-related parameters** to the research community. Without testing comparable engine technologies and test cycles, toxicity study results are challenging.

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**Thank you.**

[Logo of Ontario Mining Association]

[Logo of Lung Association]

kpolliett@umass.edu
## Biodiesel is Compositional Different

<table>
<thead>
<tr>
<th>Property</th>
<th>Ultra-Low Sulphur Diesel</th>
<th>Biodiesel</th>
<th>Renewable Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Content (%wt)</td>
<td>87</td>
<td>76</td>
<td>85</td>
</tr>
<tr>
<td>Hydrogen Content (%wt)</td>
<td>13</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td>Oxygen Content (%wt)</td>
<td>0</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>0.85</td>
<td>0.88</td>
<td>0.78</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>40-45</td>
<td>45-55</td>
<td>70-90</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>60-80</td>
<td>100-170</td>
<td>99</td>
</tr>
<tr>
<td>Viscosity (mm² sec⁻¹ at 40°C)</td>
<td>2-3</td>
<td>4-5</td>
<td>3-4</td>
</tr>
<tr>
<td>Energy Content (MJ/kg)</td>
<td>43</td>
<td>39</td>
<td>44</td>
</tr>
<tr>
<td>Storage stability</td>
<td>Good</td>
<td>Very Challenging</td>
<td>Good</td>
</tr>
</tbody>
</table>
Natural Resource Canada
Diesel fuel substitute made from renewable materials such as plant oils, waste cooking oil, other oils (i.e. tall, fish, algae), animal fats and potentially from cellulosic feedstock consisting of agriculture and forest biomass.

NO COMMENT ON PRODUCTION PROCESS.

Biodiesel

Renewable Fuels Regulations (SOR/2010-189)
A liquid fuel comprised of at least one mono-alkyl ester produced from one or more renewable fuel feedstocks in reaction with an alcohol reactant.
This fuel may contain substances, other than the mono-alkyl esters that are not produced from renewable fuel feedstocks, where the combined volume of which substances accounts for <1.5% of the volume of the fuel.

Biodiesel, Renewable Diesel
Natural Resource Canada
Diesel fuel substitute made from renewable materials such as plant oils, waste cooking oil, other oils (i.e. tall, fish, algae), animal fats and potentially from cellulosic feedstock consisting of agriculture and forest biomass.

NO COMMENT ON PRODUCTION PROCESS.

Greener Diesel = Biodiesel, Renewable Diesel

Ontario Ministry of the Environment (REGULATION 97/14)
Any diesel fuel that is made in whole or in part from renewable or recurring feedstocks.
This alternative fuel type may be derived from renewable feedstocks including soy, tallow, yellow grease, canola and algae.

NO COMMENT ON PRODUCTION PROCESS.
Toxicological Study Assessment

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<td>Representative of a Whole Pollution Mixture</td>
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<tr>
<th>Model</th>
<th>Human</th>
<th>Animal</th>
<th>Cell Culture</th>
<th>Acellular</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acute Exposure</td>
<td>Acute/Chronic Exposure</td>
<td>Screening for specific response, cytotoxic effects, dose-response</td>
<td>Screening</td>
</tr>
<tr>
<td></td>
<td>Limited to non-invasive sampling</td>
<td>More Invasive sample collection</td>
<td>Dosimetry</td>
<td>Dosimetry</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dosimetry</td>
<td>Extrapolation to humans</td>
<td>Extrapolation to humans</td>
</tr>
</tbody>
</table>

Biofuel Toxicity Assessment Using Humans

Umea University, Sweden
Diesel Particle Size Distribution

Normalised Concentration, \( \frac{1}{C} \frac{dC}{d \log D_p} \)

- Ultrafine PM \(_{0.1}\)
- Fine PM \(_{2.5}\)
- Coarse PM \(_{2.5-10}\)

Diameter (µm)

Number
Mass

Diesel Particle Lung Deposition

Percentage Regional Deposition in the Lung

- Oral and Nasal Cavity
- Trachea and Bronch
- Alveoli
- Total

Diameter (µm)
Chemical Complexity of Diesel Particles

Relative contributions to PM$_{2.5}$ (%)

El Haddad 2009 Atmos. Environ. 43:6190.
Chemical Complexity of Diesel Particles

Temperature = 2 °C

Increased Gelling

Methyl Ester Physical Properties
Direct Biofuel Exposure of Lung Cells

Alveolar Lung Cells

Diesel Biodiesel B99

Inflammatory Gene Expression

Length of Exposure (minutes)

Hawley et al 2014 Tox Sci 141(2)