Understanding emission profiles and health effects of biofuels

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Mining Diesel Emissions Conference, October 9, 2014

Chemical Engineering & Applied Chemistry
UNIVERSITY OF TORONTO

UMassAmherst
Department of Public Health
Environmental Health Sciences

What are Biofuels?

Biodiesel

Renewable Diesel

Greener Diesel

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

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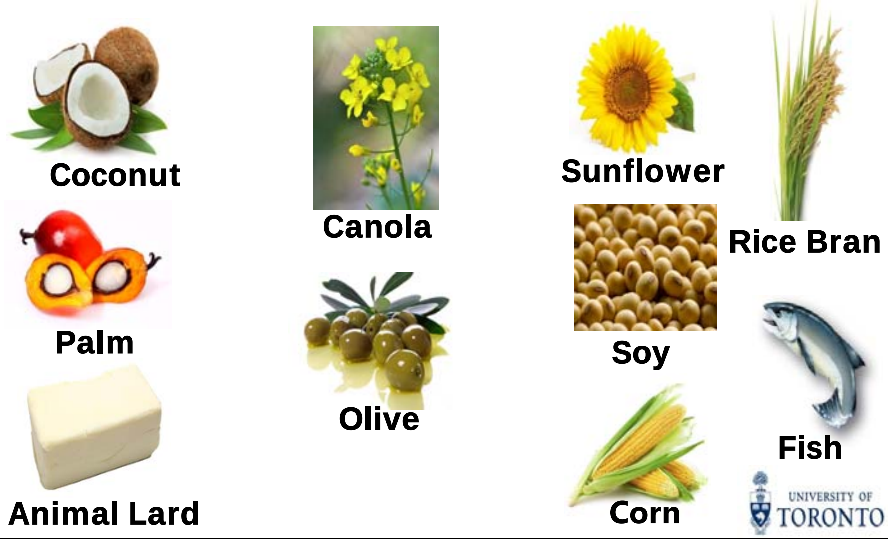
Biofuel Feedstocks

Saturated Fat | Mono-saturated Fat | Unsaturated Fat



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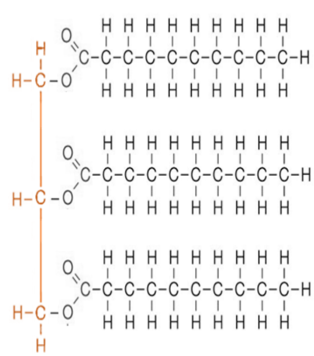
Feedstocks are Comprised of Triglycerides



Triglyceride

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Biofuel Production Methods

TRANSESTERIFICATION

Renewable Feedstock → (Alcohol, Catalyst) → **Biodiesel** + Gycerol

Renewable Feedstock → (Hydrogen Gas, Catalyst) → **Renewable Diesel** + Propane + CO + CO_2 + H_2O

HYDROGENATION

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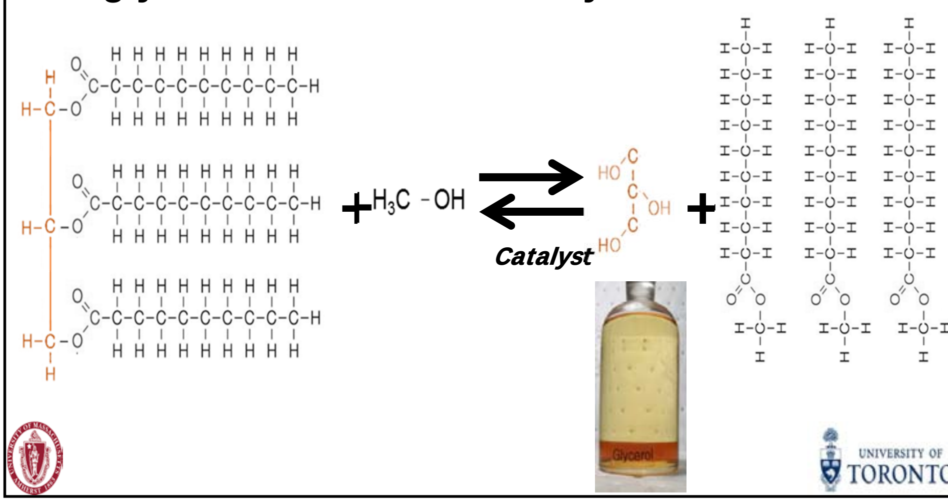
Transesterfication to Produce Biodiesel

Triglyceride **Alcohol** **Glycerol** **3 Methyl Esters**



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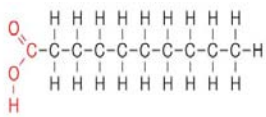
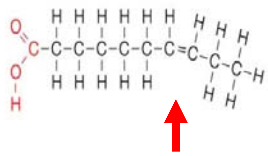
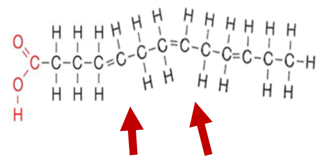
Transesterfication Methyl Ester Products

Saturated Fat | Mono-saturated Fat | Unsaturated Fat

No double bonds | **ONE double bond** | **MULTIPLE double bonds**



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

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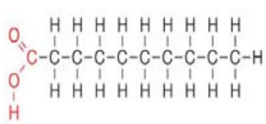
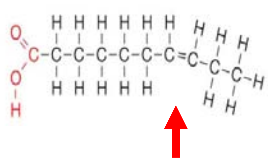
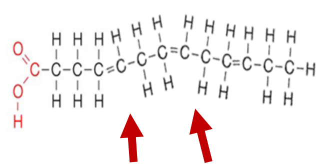
Transesterfication Methyl Ester Products

Saturated Fat | Mono-saturated Fat | Unsaturated Fat

No double bonds | **ONE double bond** | **MULTIPLE double bonds**

Lower Gel Point
Storage and operability issues at cold temperatures

$\xrightarrow{\textit{Physical Properties}}$

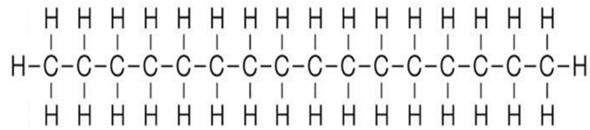
$\xrightarrow{\textit{Oxidative Properties}}$

Poor Oxidative Stability
Requires an oxidant stabiliser to avoid rancidification and polymerisation problems

Biodiesel is Compositional Different

Traditional Diesel, Renewable Diesel

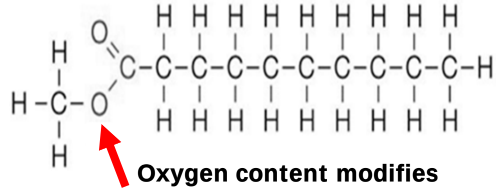
Paraffins



Full saturated carbon chain.

Biodiesel

Methyl Esters



Oxygen content modifies emissions profile

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What are Biofuels?

Biodiesel (Transesterification)

Renewable Diesel (Hydrogenation)

Greener Diesel

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

BUT the production processes differ.

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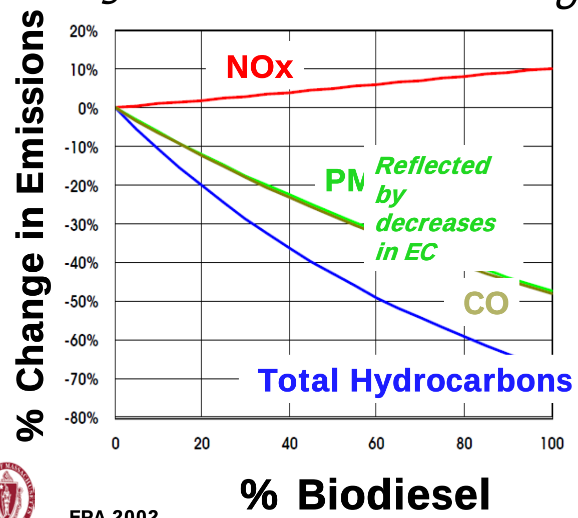
Biodiesel Emission Profile

Regulated Pollutants



EPA 2002

Unregulated Pollutants

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

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Renewable Diesel Emission Profile

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

Pollutant	R10	R50	R100
PM mass	0	-5%	-28%
NOx	0	-6%	-10%
Total Hydrocarbons	-33%	-48%	-48%
CO	-11%	-22%	-28%

University of California 2010

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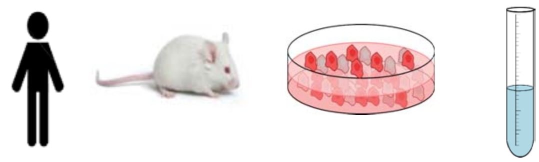
Toxicological Study Assessment

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

Able to focus on specific pollutants — *Representative of a Whole Pollution Mixture*

Biofuel Studies

Model — **Human** — **Animal** — **Cell Culture** — **Acellular**



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

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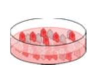
Biofuel Toxicological Study Assessment

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

Able to focus on specific pollutants

Model

Animal

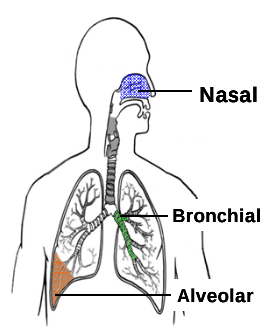


Lung Cell Culture

Outcomes

Animal:
- *Cardiovascular*
- *Respiratory*

Lung Cell Culture:
- *Cytotoxicity*
- *Inflammation*
- *Oxidative Stress*
- *Genotoxicity*



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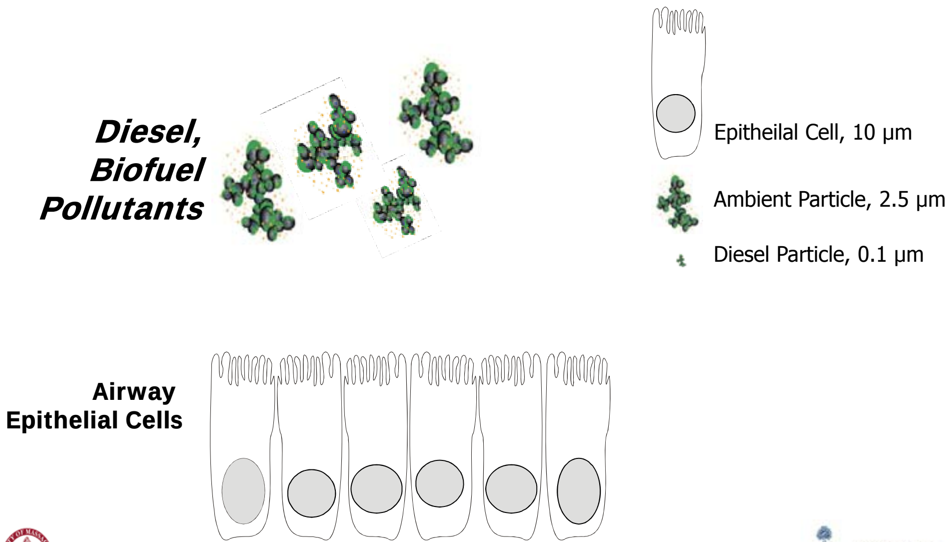
Cellular Response to Diesel and Biofuels



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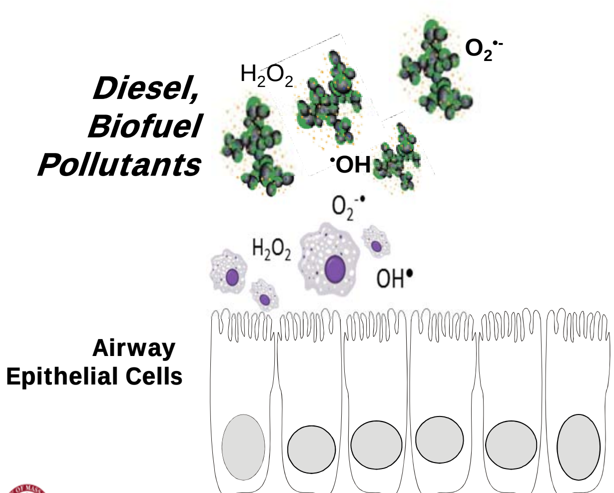
Cellular Response to Diesel and Biofuels



OXIDATIVE STRESS
Pollutant Induced Generation of Reactive Oxygen Species

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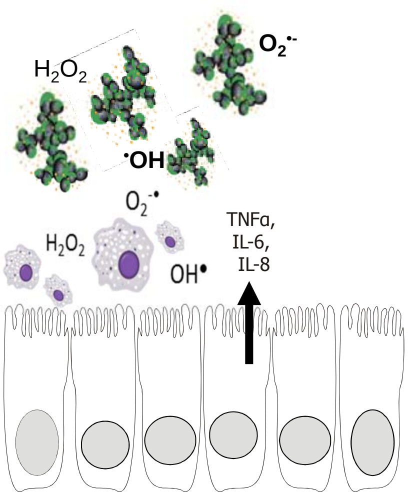
Cellular Response to Diesel and Biofuels

Diesel, Biofuel Pollutants



Airway Epithelial Cells

OXIDATIVE STRESS
Pollutant Induced Generation of Reactive Oxygen Species

Inflammation
Protein Production

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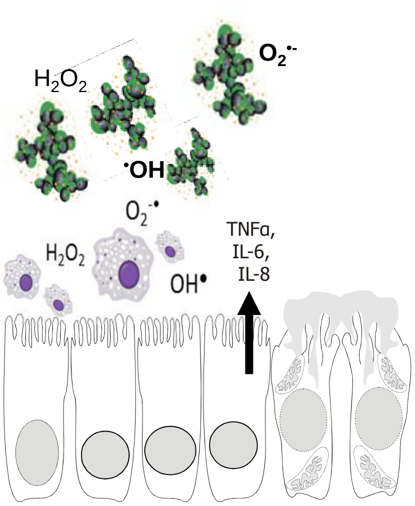
Cellular Response to Diesel and Biofuels

Diesel, Biofuel Pollutants



Airway Epithelial Cells

OXIDATIVE STRESS
Pollutant Induced Generation of Reactive Oxygen Species

Inflammation
Protein Production

Cell Death
Loss of Viability

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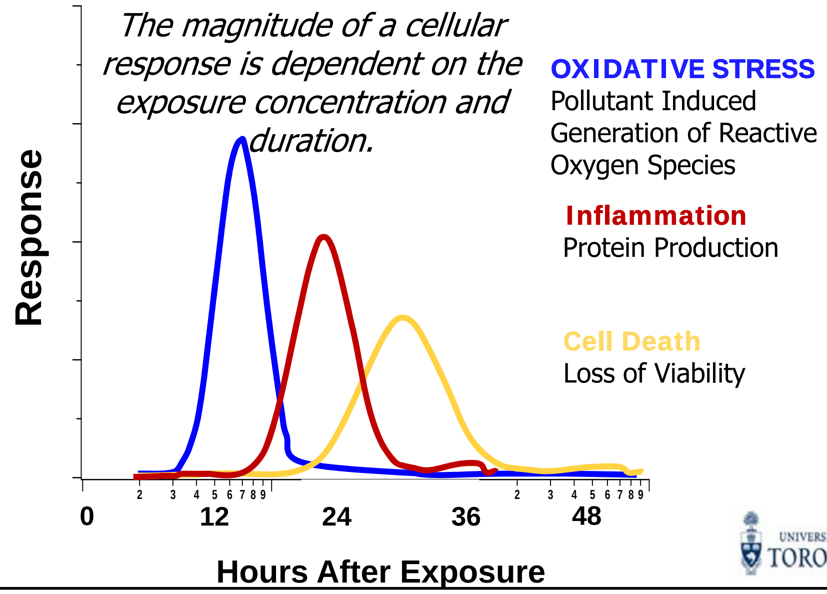
Time Scale of Cellular Responses



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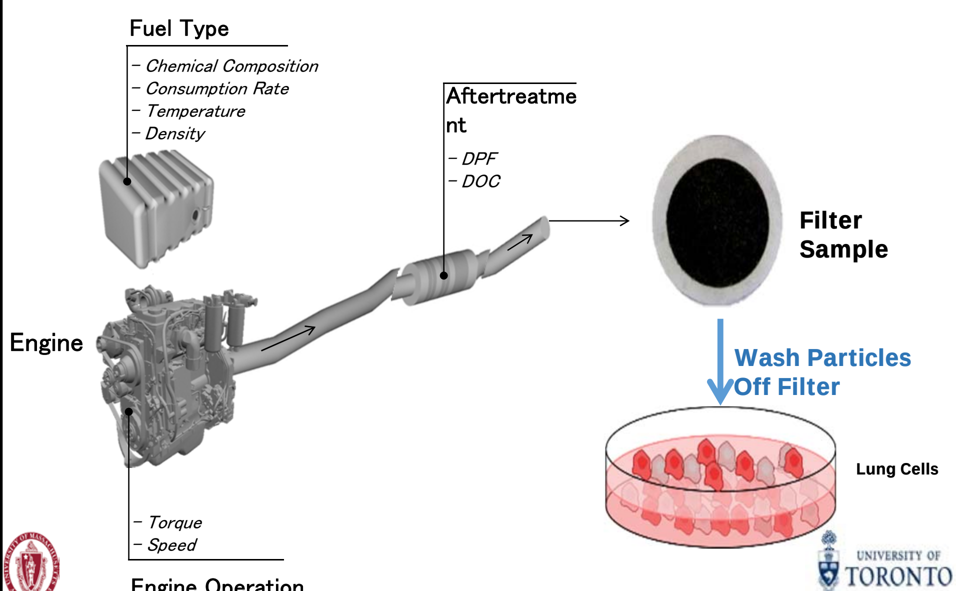
Biofuel Toxicity Assessment Using Lung Cells



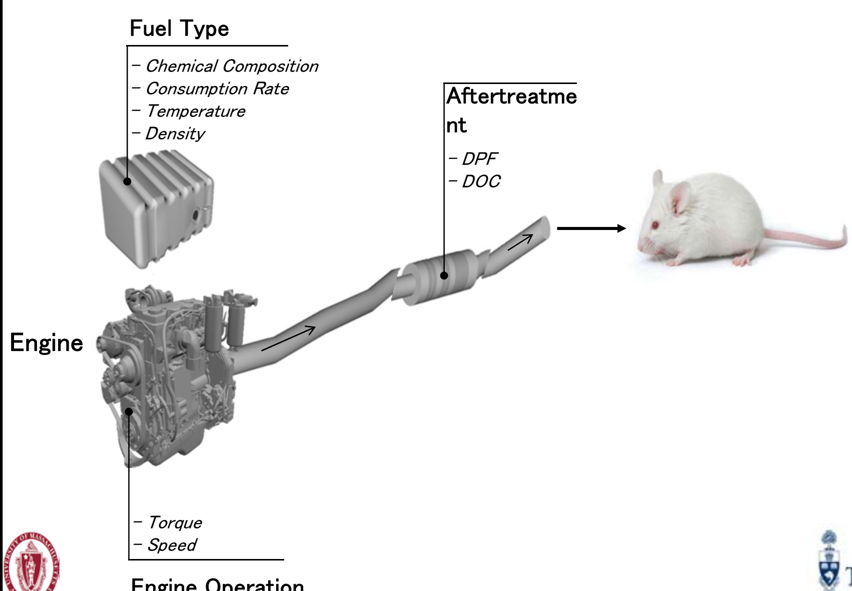
Lung Cells Studies

	Study	Cells	Engine	Oxidative Stress	Inflammation	Cell Death	Results
Organic Solvent	1	Mouse Macrophage	Light, Euro II	X		X	**ULSD = Rapeseed B100 = HVO R100**
	2	Mouse Macrophage	Light, Euro IV	X			**HVO R100 < ULSD < Rapeseed B100**
	3	Mouse Macrophage	Heavy, Euro II			X	**DF < Plant B100**
	4	Human Bronchial	Light, Euro IV		X	X	**ULSD < Rapeseed B50**
	5	Human Bronchial	Heavy		X		**ULSD < Soy B100**
						X	**ULSD = Soy B100**
Water	6	Rat Alveolar	Heavy	X			**ULSD = Soy B20**
					X		**ULSD < Soy B20**

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

(1) Jalava et al 2010; (2) Jalava et al 2012; (3) Kooter et 2011; (4) Gerlofs-Nijland et al 2013; (5) Swanson et al 2009; (6) Bhavaraju et al 2013

Biofuel Toxicity Assessment Using Animals



Biofuel Toxicity Assessment Using Animals

Biodiesel Toxicity Assessment Using Animals

Inhalation, Soy B100, 500 µg m^{-3}

Study

Chronic Exposure

1  Heavy Duty Engine → 6h/day, 65 days → Modest chronic respiratory inflammation compared to *filtered air*.

Subchronic Exposure

2  Generator → 4h/day, 20 days → Increased tissue damage, oxidative stress, inflammation in lungs and liver compared to diesel.

Acute Exposure

3  Generator → 1 hour → 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

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Biofuel Toxicity Assessment Using Animals

Corn B100

Study

Acute Exposure

4  Light Duty Engine → 1 instillation, 18 µg

Post-Exposure Follow up

- 1 day → Diesel and Biodiesel particles can be see 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.

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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.

Ontario Mining ASSOCIATION

THE LUNG ASSOCIATION™

kpollitt@umass.edu

Biodiesel is Compositional Different

Property	Ultra-Low Sulphur Diesel	Biodiesel	Renewable Diesel
Carbon Content (%wt)	87	76	85
Hydrogen Content (%wt)	13	13	15
Oxygen Content (%wt)	0	11	0
Specific Gravity	0.85	0.88	0.78
Cetane Number	40-45	45-55	70-90
Flash Point (^oC)	60-80	100-170	99
Viscosity (mm^2 sec^{-1} at 40^oC)	2-3	4-5	3-4
Energy Content Mass Basis (MJ/kg)	43	39	44
Storage stability	Good	Very Challenging	Good

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What are Biofuels?

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.

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What are Biofuels?

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.

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Toxicological Study Assessment

Exposure Type	Lab Controlled, Filter Extracts	Real World
	Able to focus on specific pollutants	*Representative of a Whole Pollution Mixture*

Model	Human	Animal	Cell Culture	Acellular
+	Acute Exposure	Acute/Chronic Exposure More Invasive sample collection	Screening for specific response, cytotoxic effects, dose-response	Screening
-	Limited to non-invasive sampling	Dosimetry Extrapolation to humans	Dosimetry Extrapolation to humans	Dosimetry Extrapolation to humans

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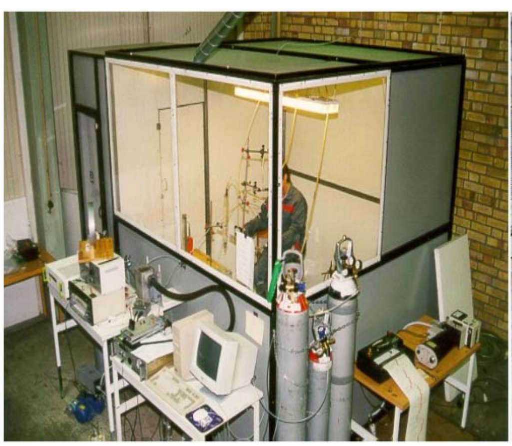
Biofuel Toxicity Assessment Using Humans



Umea University, Sweden

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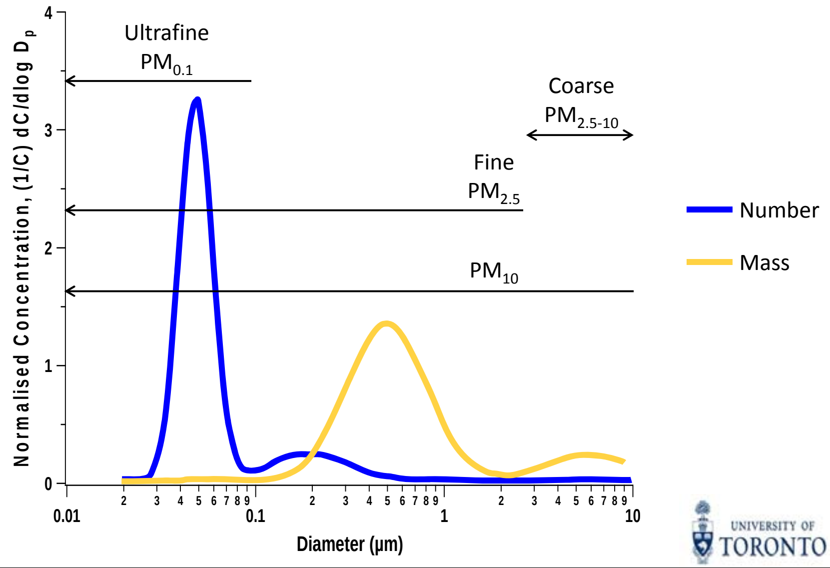
Diesel Particle Size Distribution



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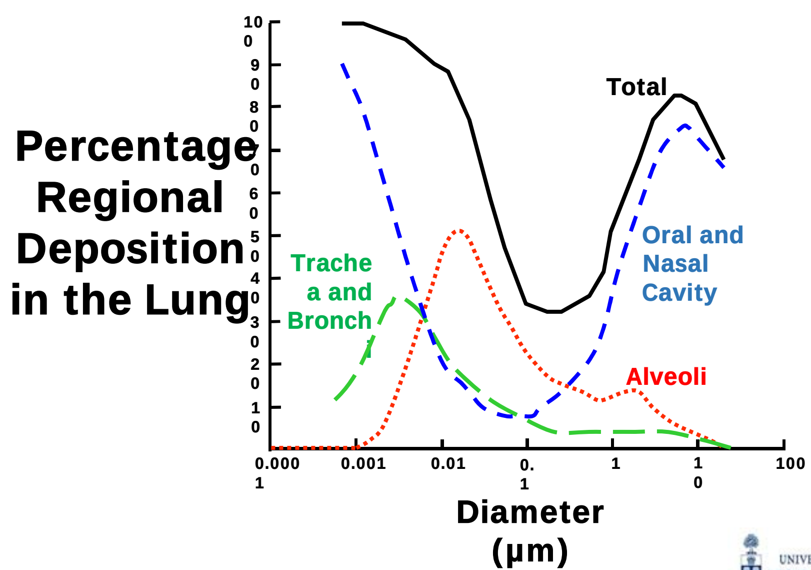
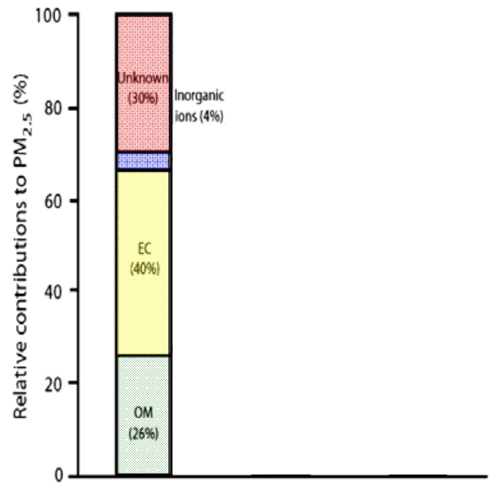
Diesel Particle Lung Deposition

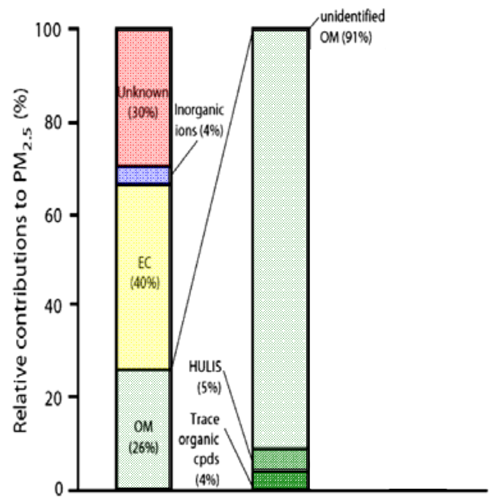


Chemical Complexity of Diesel Particles



El Haddad 2009 Atmos. Enviro. 43:6190.

Chemical Complexity of Diesel Particles



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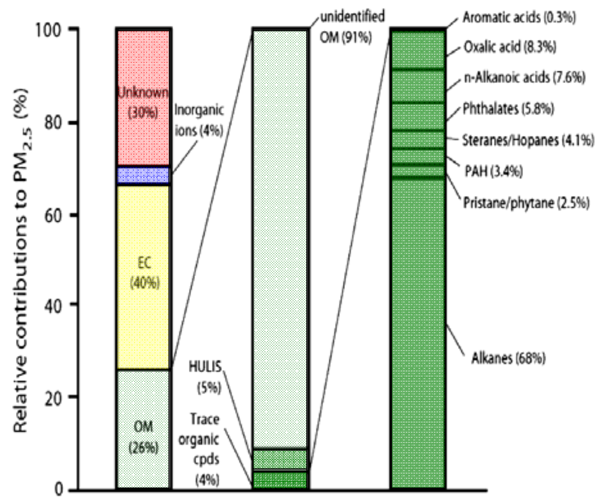
Chemical Complexity of Diesel Particles



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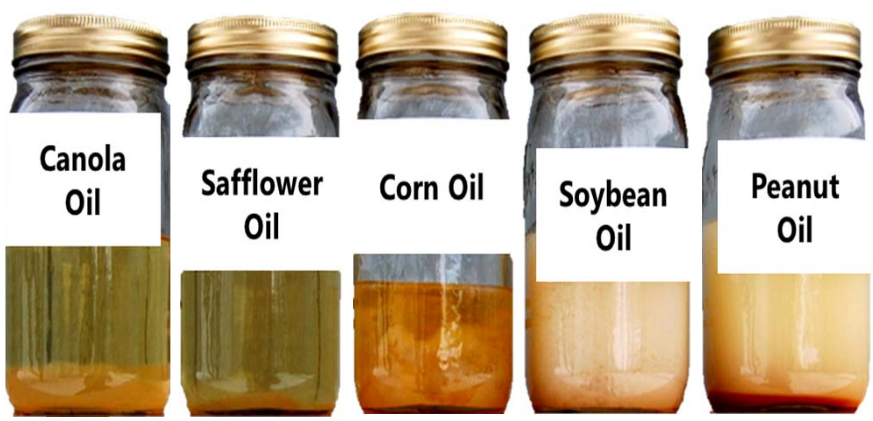
Methyl Ester Physical Properties



Temperature = 2 ^{0}C

— Increased Gelling →

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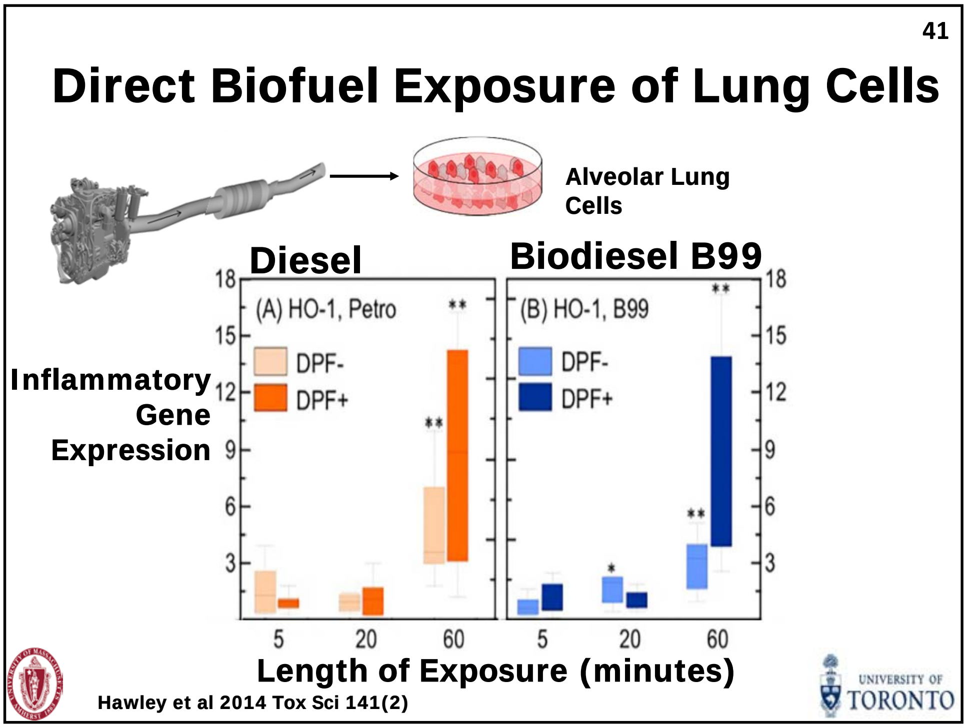
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Direct Biofuel Exposure of Lung Cells
Alveolar Lung Cells
Diesel
Biodiesel B99
(A) HO-1, Petro
(B) HO-1, B99
DPF-
DPF+
Inflammatory Gene Expression
18
15
12
9
6
3
5
20
60
Length of Exposure (minutes)
Hawley et al 2014 Tox Sci 141(2)
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