BIODIESEL

A Technical Report

As of September 3, 2008

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  - –Why is Biodiesel material compatibility difficult to determine?
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- ENVIRONMENTAL IMPACTS:
  - –Air emissions vs. ULSD
  - –Aquatic toxicity vs. ULSD
- "Green" alternatives to Biodiesel?

Water Boards

Why is biodiesel material compatibility difficult to determine?

Water Boards

… because there are

>1,500,000 possible biodiesel formulations!

Water Boards

Biodiesel: The definition

1. a substitute for petroleum diesel
2. made from **vegetable oils** and/or **animal fats**
3. through the process of **transesterification**
4. resulting in **methyl esters** and
5. conforming to performance specification **ASTM D 6751-07b,** but …

Water Boards

... the reality is

... each batch is
chemically unique

Water Boards

Many feedstocks = many combinations of 8 fatty acids:

Vegetable oils: soybean, rapeseed (canola), palm oil, sunflower, safflower, peanut, etc

Animal Tallow: animal fat from rendering

"Yellow Grease": recycled cooking oil

"Brown Grease": trap grease, highly variable

Algae oils: nitrogen fixing algae may be a sink for power plant CO_2, no water loss, requires no farm land, does not compete with food crops, no increase in food price – but what about economics and reliability?

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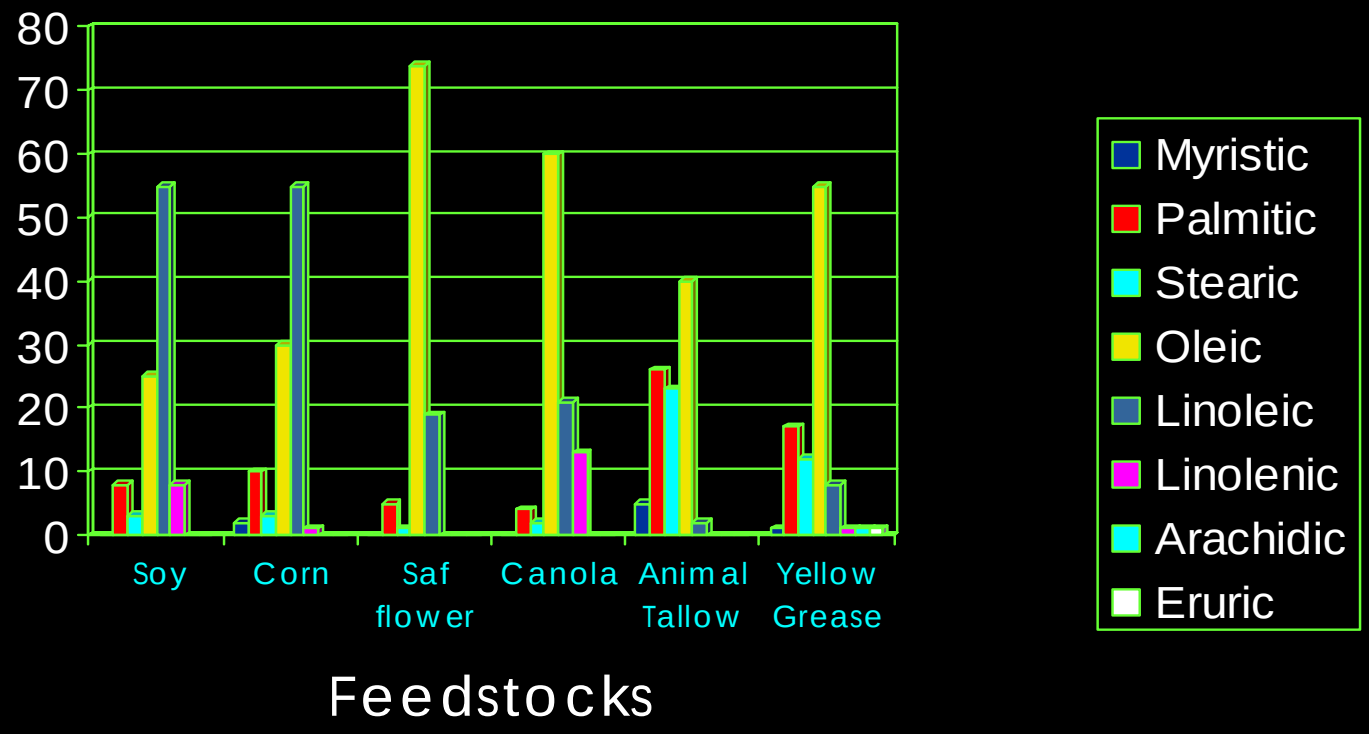
Feedstocks are combinations of **8** different fatty acids



Water Boards

... and there are ...

chemical variations due to process variables

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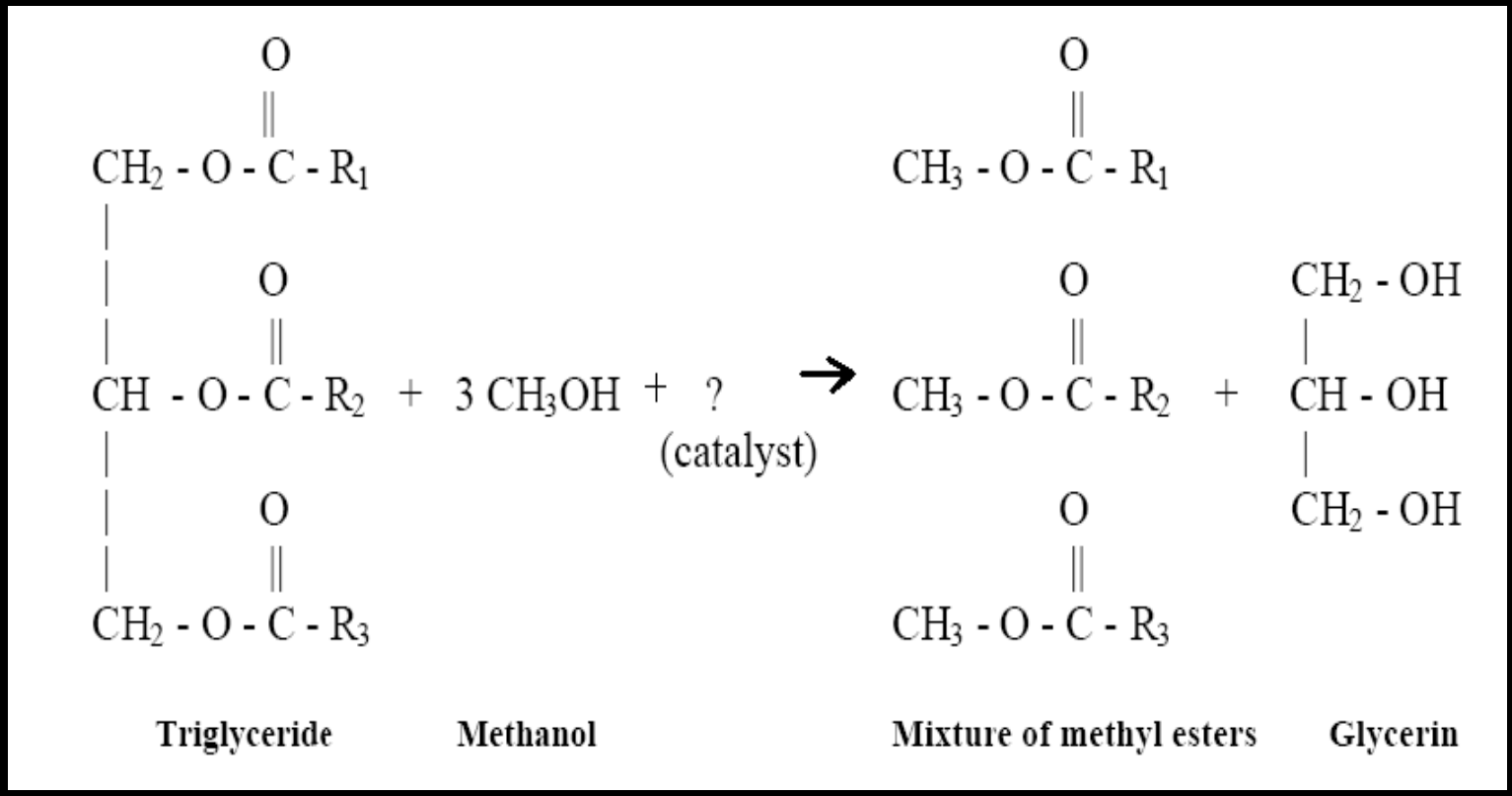
Transesterification can produce either methyl esters or ethyl esters



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… and there are …

… chemical variations due to poor quality control

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How reliable has commercial scale Quality Control been?

NOT VERY … In 2007 National Renewable Energy Lab [NREL] published a survey of B100 fuel quality from 37 different producers nationwide in which **>50%** B100 samples did NOT meet ASTM D6751

A more recent NREL report indicates a remarkable QC improvement in nine months of nearly **98% compliance** among B100 producers cooperating in the study

- NOTE: Off spec fuel may contain corrosive contaminants such as peroxides and water, batches also vary due to contaminants and poor quality control

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How reliable is the Quality Control of the home scale biodiesel production?

EVEN LESS… the following is paraphrased from an online blog:

First put your **trap grease, tallow, yellow grease** etc. in a 45L pot.

Then pour in lots of **methanol** (*keep the 40 gallon drums in your garage out of site of the Fire Marshall*)

Stir in some **sodium hydroxide** and let simmer for a few hours.

Then pour in some **hydrochloric acid** to separate the glycerin and to avoid making soap.

BTW, There's no market for all that glycerin, so ***just dump it down the storm sewer****.*

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home brew biodiesel QC– reliable?

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... another blog raises issues of QC

... never mind safety

"Here's a image of my basic processor - please disregard the OH&S issues!!

I just love your easy access to the NaOH on the floor which you simply shovel into the processor!

I was emptying my processor one day when I went up the street for lunch and while taking my first bite into the pizza, remembered I'd left the 135L processor emptying into a 25L drum. So, it takes a fair bit of kitty litter to absorb 110L of slop vegie oil.

I have a similar setup but use a drill pump. The drill pump is leaking and I would like to use a better pump."

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… and there are…

… chemical variations due to additives

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each batch may contain many different additives

1. **Antioxidants,**
2. **Biocides,**
3. **Cold flow enhancers,**
4. **Cetane enhancers,**
5. **NOx reducers,**
6. **Water dispersants,**
7. **Anti-foaming agents**

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Additives?

... 2160 possible combinations

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… and there are…

… chemical variations due to additives that aren't effective and create contaminants

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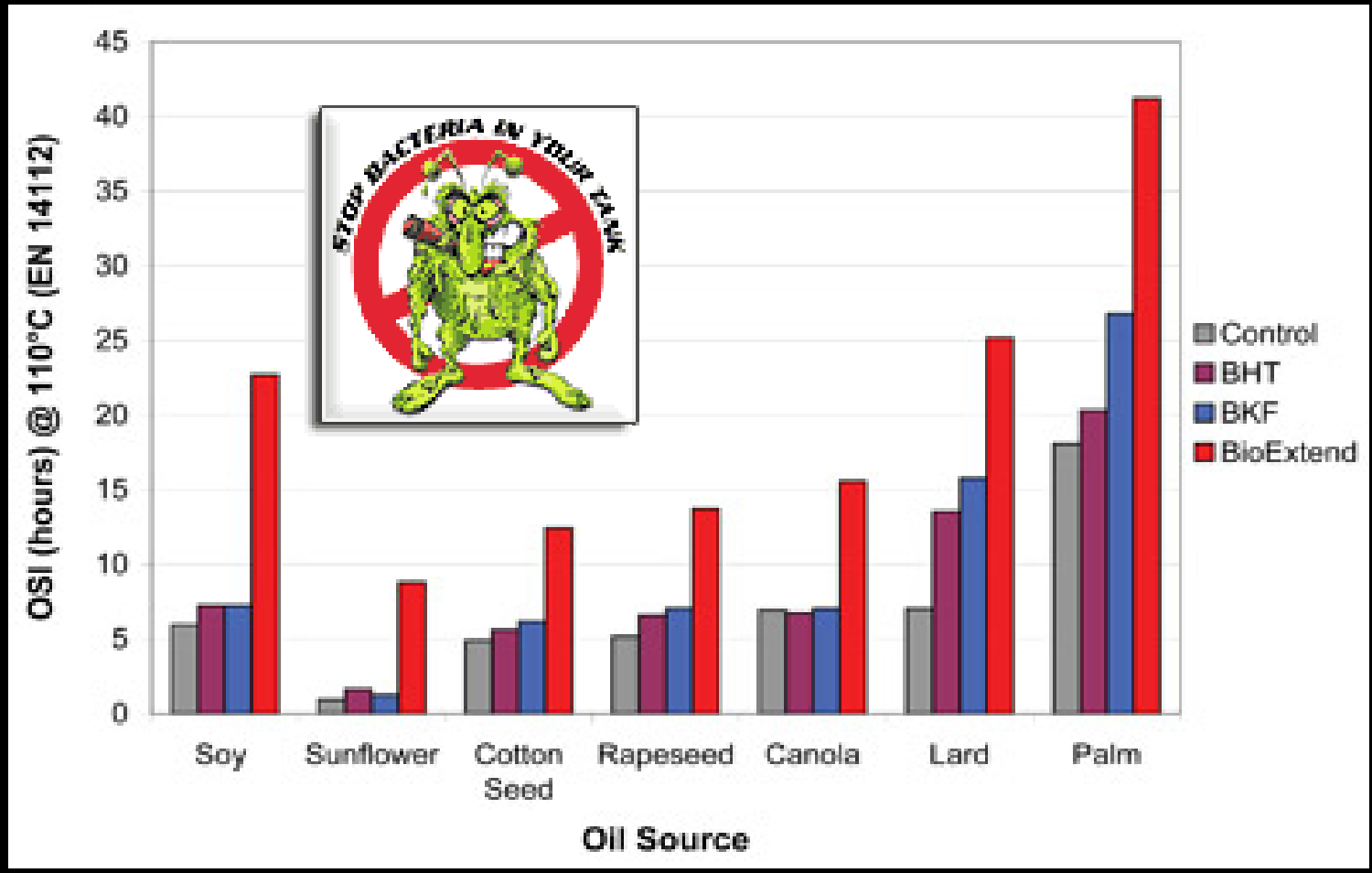
additives and effectiveness



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combinations and permutations?

2160 possible combinations of additives

8 possible combinations of fatty acids

2 possible esters types – methyl or ethyl

4 possible contaminants (O=O, Cl, TAN, H_20)

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>1,500,000 possible biodiesel formulations!

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How does Biodiesel's

MATERIAL COMPATIBILITY

compare to petroleum diesel's?

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Biodiesel vs. Petroleum Diesel

Biodiesel is 600x more electrically conductive and that = > corrosivity

Biodiesel oxidation produces greater corrosive conditions

Biodiesel swells some elastomers 100% -- elastomers that are stable in petroleum diesel

Elastomer swelling takes ~3x longer to manifest, and then suddenly fails catastrophically

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... and

Is more aggressive when water contaminated

Is more aggressive in acidic conditions

Is more aggressive with age

Water Boards

Biodiesel is more electrically conductive than petroleum diesel

= greater potential for corrosion

for example.....

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Conductivity of Various Biodiesel Blends vs. #2 Fuel Oil

(pS/m)

#2 Fuel Oil	Biodiesel %	Biodiesel %	Biodiesel %	Biodiesel %	Biodiesel %
0 %	2 %	20 %	40 %	60 %	100 %
2	7	75	358	775	1209

Courtesy of the National Biodiesel Board. Testing conducted by Williams Pipeline.

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Biodiesel is a solvent that may attack some elastomers under specific conditions

- Volume change may exceed 100%
- Hardness and tensile strength may decrease > 50%

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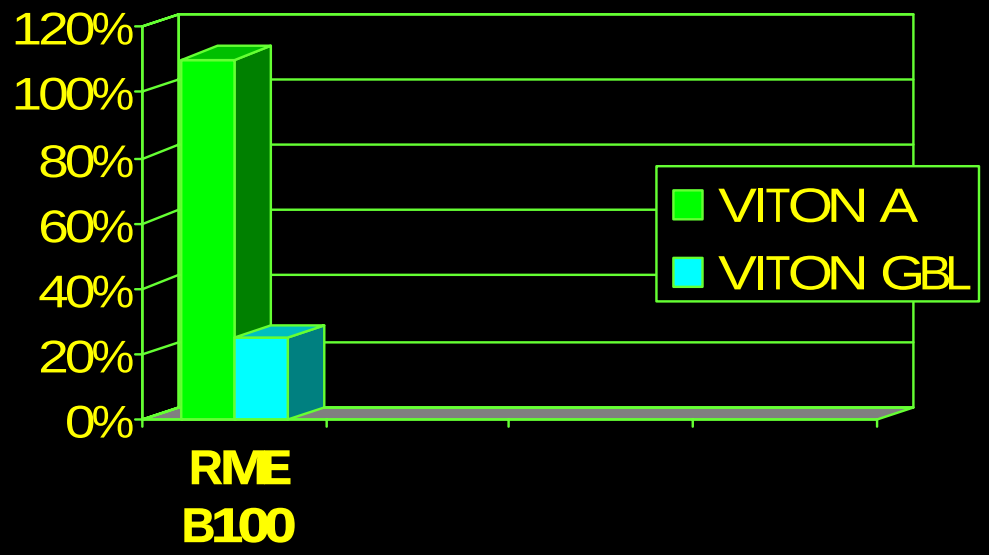
B100: Elastomer Swelling in Viton ®

note: these data result from DuPont Performance Elastomer tests at 125C



Viton® is a trademark of DuPont Performance Elastomers L.L.C

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Changes in elastomer properties due to biodiesel may be delayed

... new accelerated test data indicate

significant changes occur only after

300 to 1000 hours

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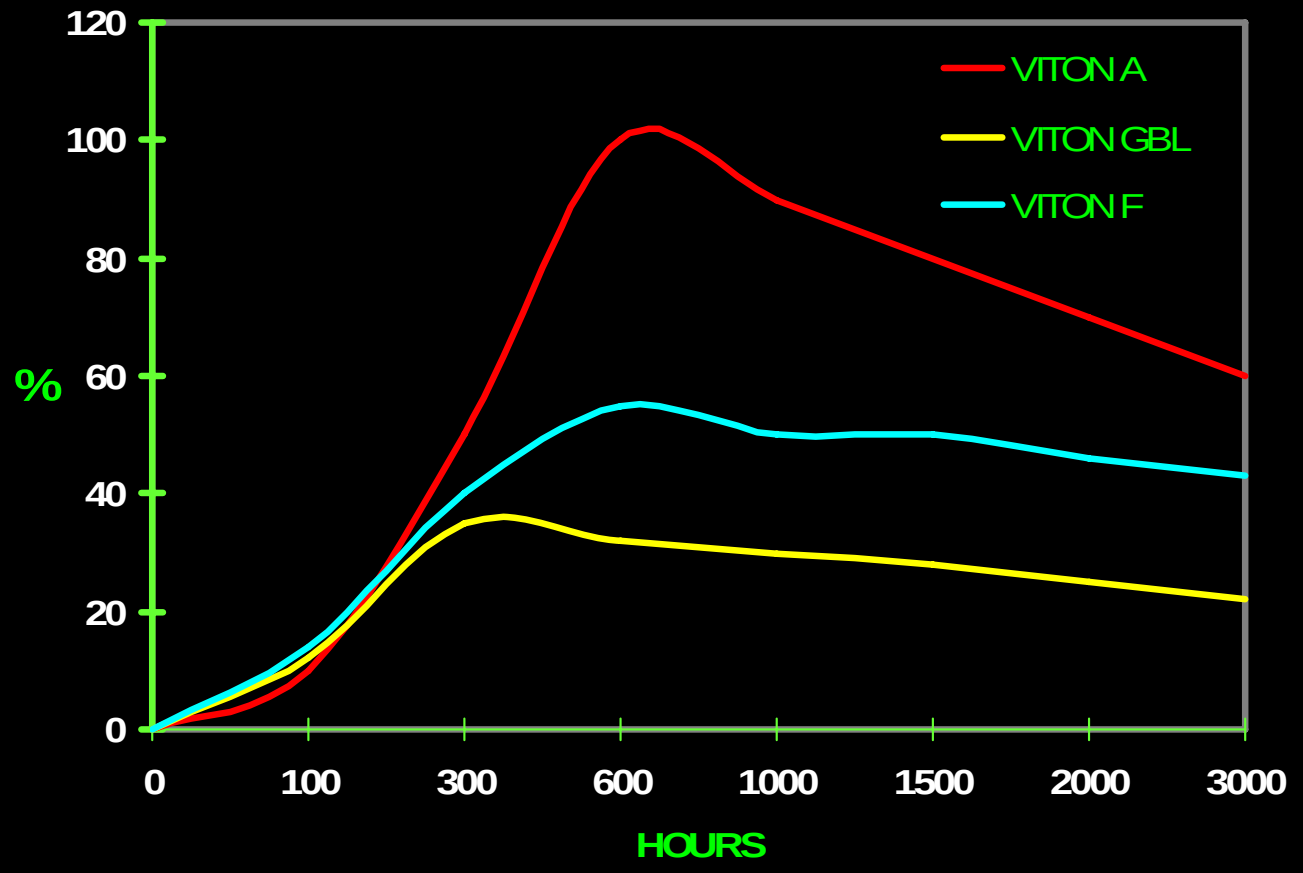
B100: Volume Change over 3000 hours

note: these data result from DuPont Performance Elastomer tests at 125C



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Biodiesel may degrade elastomers cured using metal oxides

data furnished by DuPont Performance Elastomers LLC in personal communications

- ... for example, VITON® GBL-S cured **with** metal oxides swells nearly 10X greater
- ... than the same VITON® GBL-S cured **without** metal oxides.
- *Metal oxides are routine ingredients in all fluoroelastomer formulations and needed for bisphenol cured fluoroelastomers such as VITON® A401C.*

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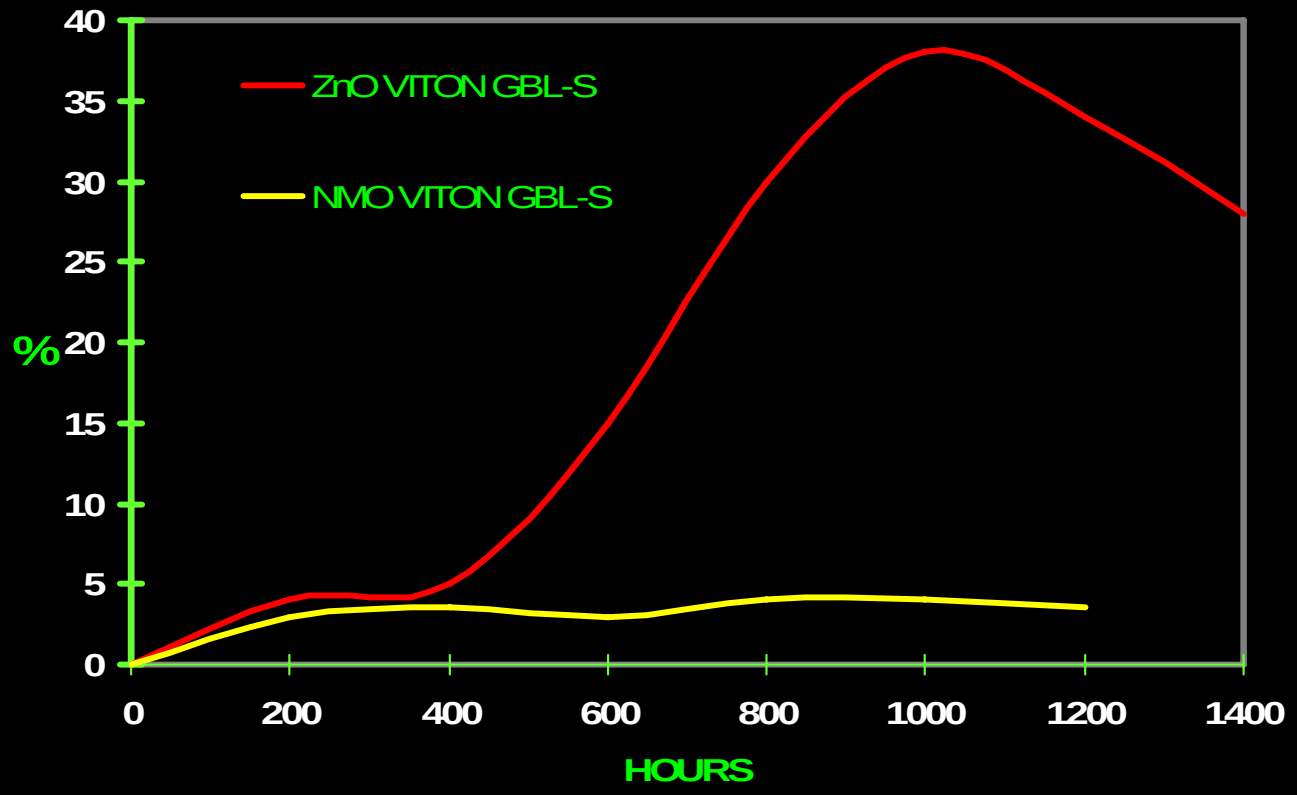
- Kalrez® and Viton® are trademarks of DuPont Performance Elastomers L.L.C.

B20: Swelling w/wo Zinc Oxide Curing

note: these data result from DuPont Performance Elastomer tests at 125C



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Water contamination makes biodiesel more aggressive

- **Water** facilitates electrical conductivity
- **Water** accelerates oxidation
- **Water** may contain corrosive contaminants

... maintain **dry tanks** and insist on **dry fuel**

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Acidic conditions may make biodiesel more aggressive

- ASTM 6751-07a TAN spec = **0.5 max** (mg KOH /kg)
- Biodiesel oxidation may increase acidic conditions
- Exceeding the TAN spec may increase swelling,

... for example ...

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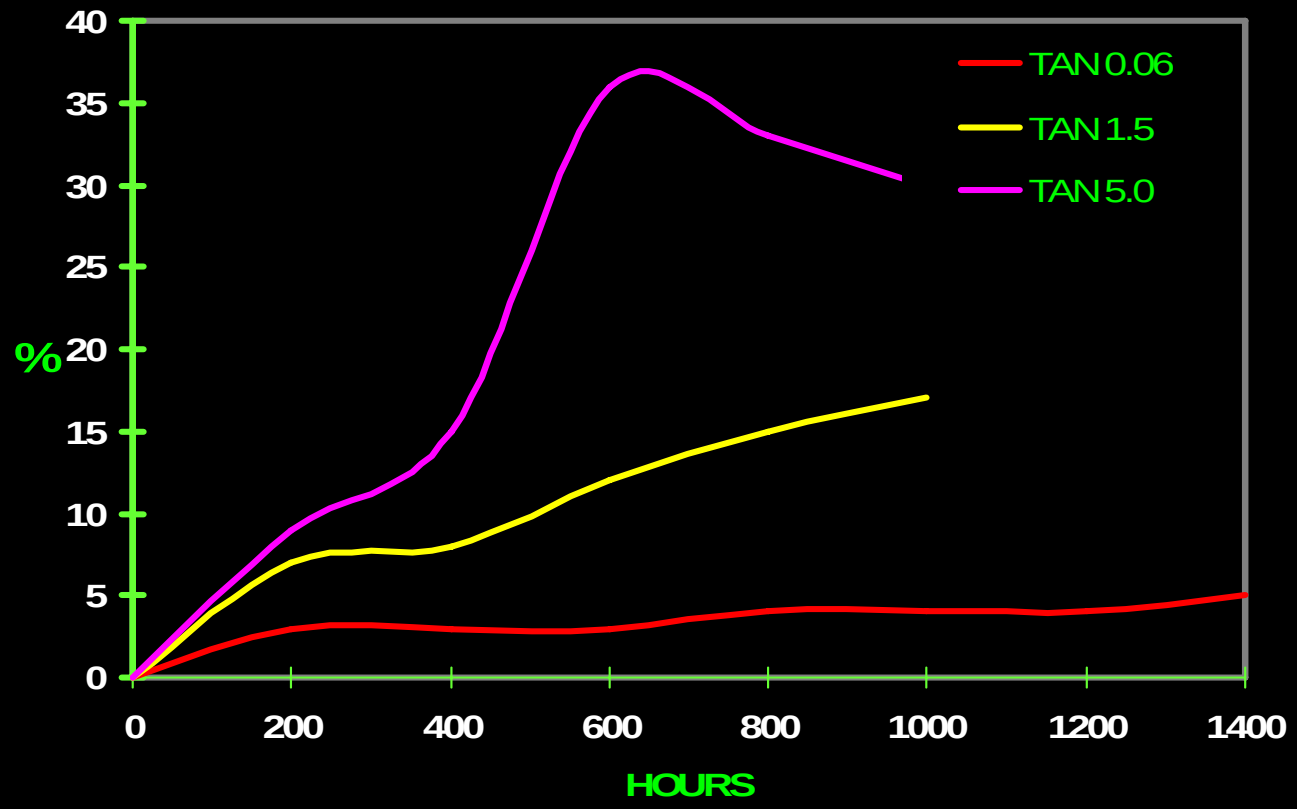
B20: Effect of Acidity on Swelling in VITON A ®

note: these data result from DuPont Performance Elastomer tests at 125C



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Aging makes biodiesel more aggressive

data furnished by DuPont Performance Elastomers LLC in personal communications

- "Old" biodiesel causes greater damage to elastomers than "new" biodiesel
- "Old" = 6-8 weeks since production
- Tensile strength decreases **70%-80%**
- Volume increases more than **100%**

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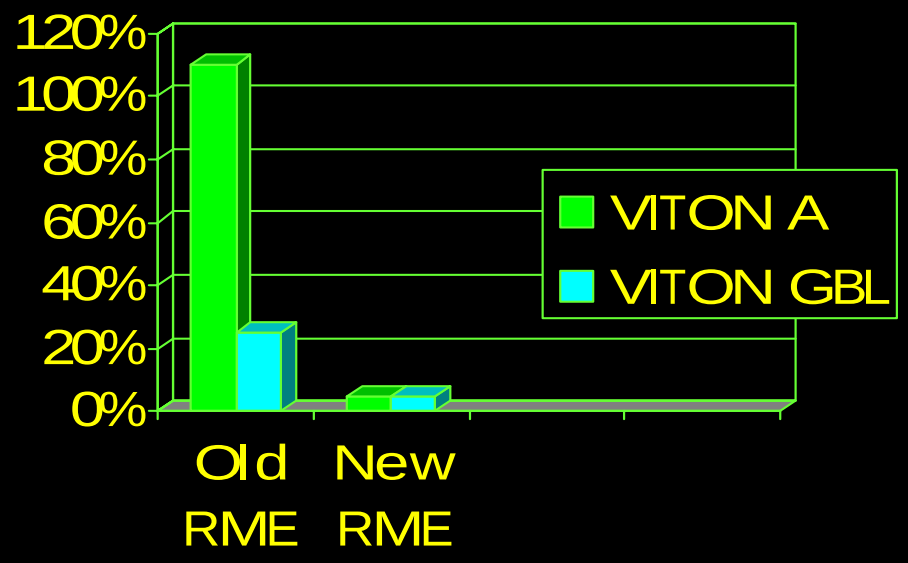
... for example,

B100: Effects on Swelling; Old vs. New

note: these data result from DuPont Performance Elastomer tests at 125C



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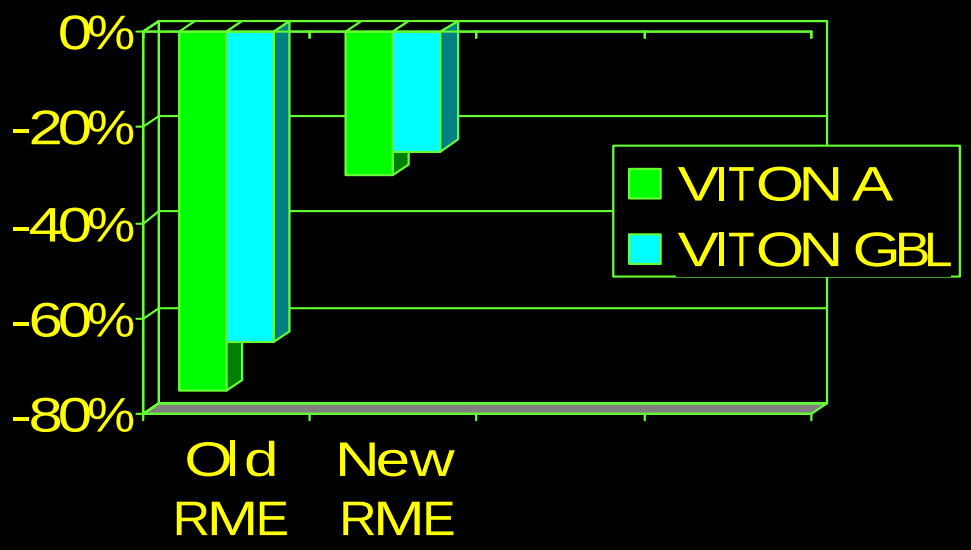
B100: Tensile Strength Loss; Old vs. New

note: these data result from DuPont Performance Elastomer tests at 125C



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How does one choose elastomers for storing biodiesel?

Consult polymer manufacturers for recommendations on the most cost effective **elastomer** and **grade** for the **fuel blend** stored.

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What practical actions can we take now to improve biodiesel material compatibility with USTs?

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Tips for improving material compatibility

Biodiesel is more electrically conductive; UST system must avoid vulnerable metals and water

Biodiesel instability makes it prone to oxidation: avoid off-spec fuel, “old” fuel, and water in UST (*biodiesel not recommended for standby generators*)

Biodiesel has a history of poor QC: demand distributor's guarantee of ASTM D6751 fuel quality

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… more Tips for improving material compatibility

Biodiesel is a solvent that attacks elastomers: UST should contain only elastomer components recommended by DuPont et al for storing biodiesel. Avoid rubber, Nitrile, certain grades of Viton, etc.

Effects may be slow to appear: UL testing should be longer than 100 hours exposure.

Attacks elastomers depending on curing method: ask polymer manufacturer's advice on Viton grades

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… even more Tips for improving material compatibility

Biodiesel is more aggressive in the presence of water: avoid water in UST and fuel.

Is more aggressive in acidic conditions: avoid off-spec fuel, water, and vulnerable metals

Is more aggressive as it ages: o/o should require their supplier to provide **"Rancimat"** test certification on each fuel drop

Water Boards

CONCLUSIONS: Compatibility with USTs

1. Factors in biodiesel-elastomer stability
    1. Acidity (TAN),
    2. Elastomer Curing Method, and
    3. Elastomer Grade

2. **<u>Some</u>** elastomers are highly vulnerable

3. Factors in greater biodiesel corrosion
    1. Water,
    2. Contaminated fuel,
    3. Peroxides, and
    4. Greater Electrical Conductivity

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RECOMMENDATIONS
for storing BIODIESEL in USTs:

1. **Consult elastomer manufacturers re most cost effective options (not component mfgrs.)**

2. **Avoid and replace vulnerable UST metals!!**

3. **Insist on fuel quality guarantees!!!**

4. **Keep the UST water-free!!!**

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... and

... Trust data, not intuition

The effects of biodiesel on UST material stability are NOT intuitive ...

DuPont data are a good case in point

Intuitively 100 or 200 hours of exposure testing should be adequate to detect significant elastomer instability, but it wasn't in this case.

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What are Biodiesel's environmental impacts?

- Air emissions vs. petroleum diesel
- Water quality impacts vs. petroleum diesel

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Biodiesel Air Emissions

"There are not yet sufficient data to assert that the use of biodiesel will reduce the emissions of criteria and toxic air pollutants."

- Source: California Biodiesel Multimedia Evaluation: Tier I Report DRAFT March 2008

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HC, PM, NOx, CO

Emission data are available on HC, PM, NOx and CO, but

- –most of these data were generated using older technology engines.
- –Very little detailed exhaust data exists beyond … regulated pollutants, and …
- –Which biodiesel formulations should we test – or does it matter?

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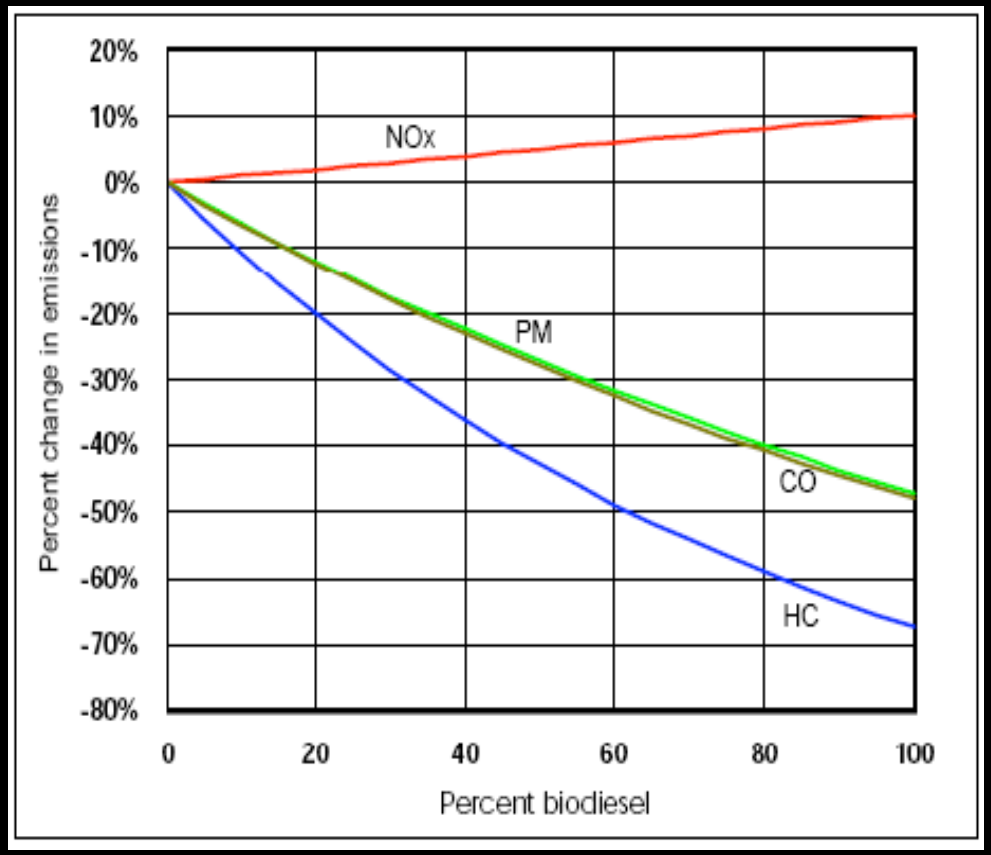
Source: California Biodiesel Multimedia Evaluation: Tier I Report DRAFT March 2008

Average Biodiesel Emissions from Heavy-Duty Vehicle Engines

Source: USEPA 2002; California Biodiesel Multimedia Evaluation: Tier I Report March 2008



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Do feedstocks affect emissions?

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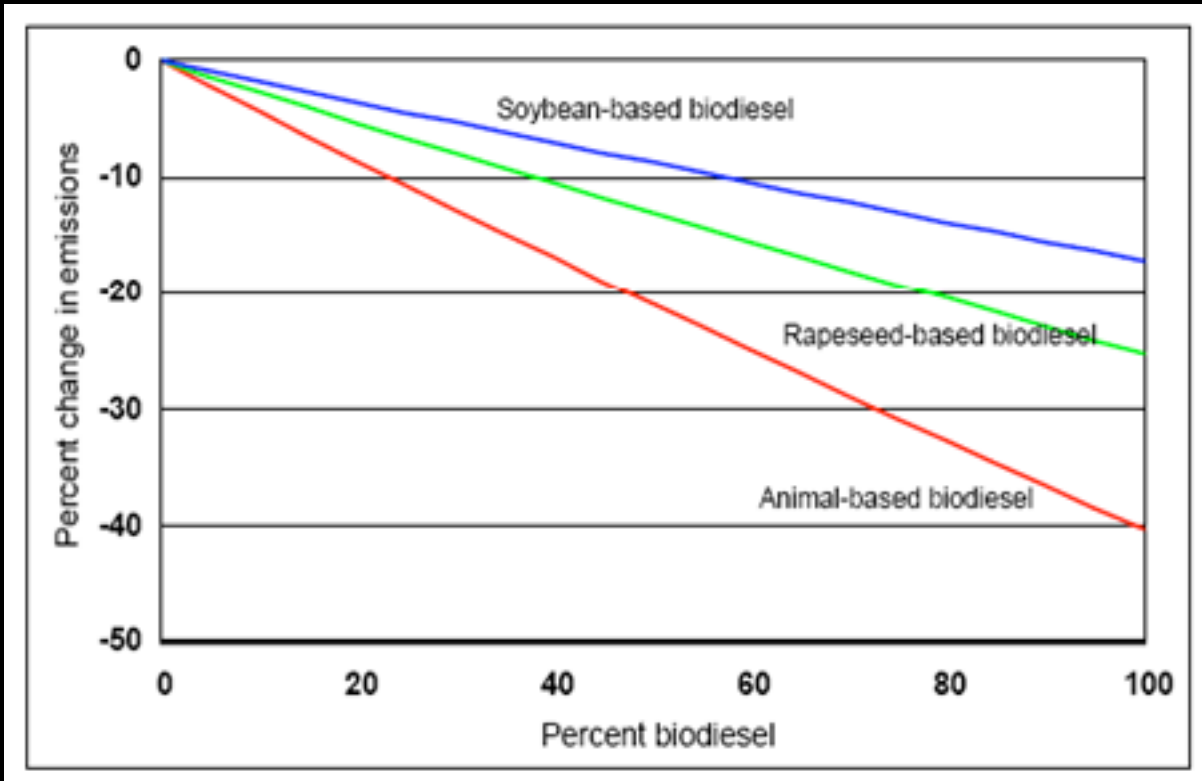
Feedstock Effect on CO Emissions

Source: USEPA 2002; California Biodiesel Multimedia Evaluation: Tier I Report March 2008



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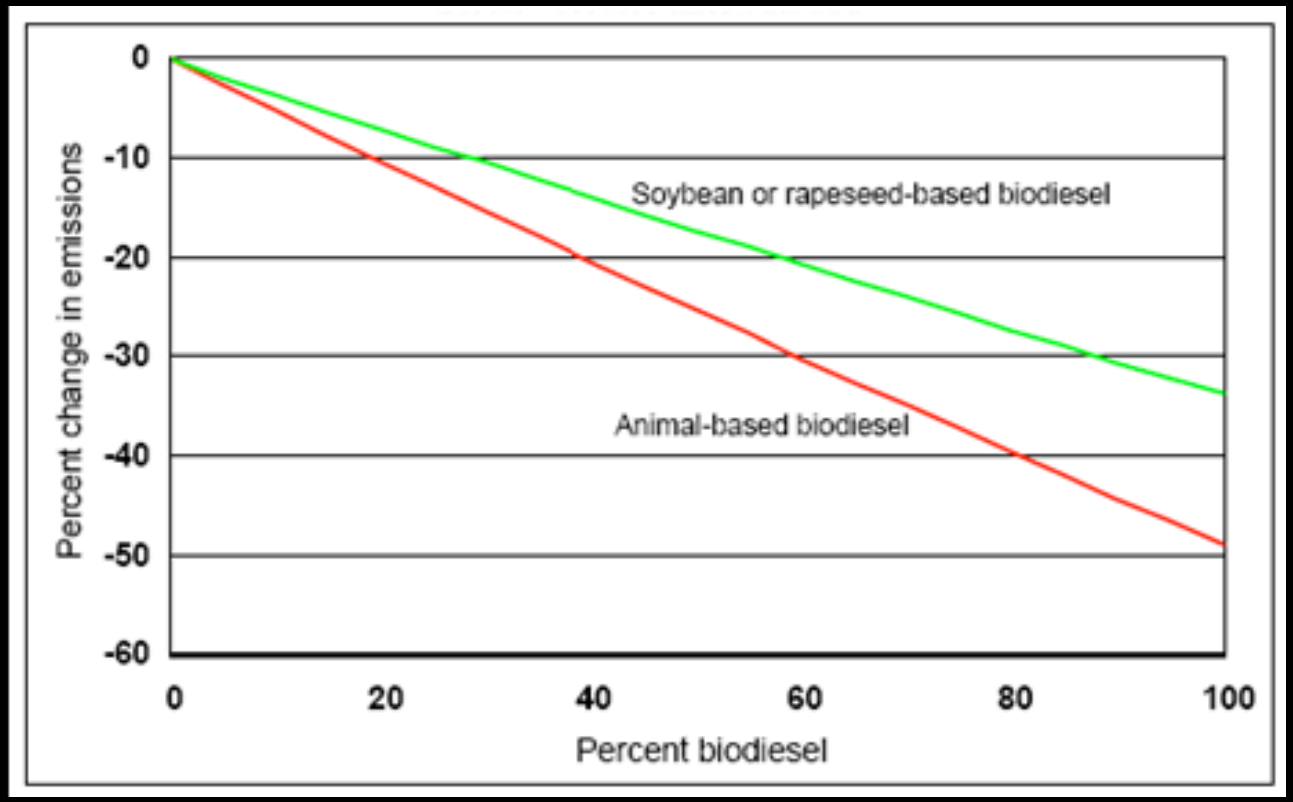
Feedstock Effect on PM Emissions

Source: USEPA 2002; California Biodiesel Multimedia Evaluation: Tier I Report March 2008



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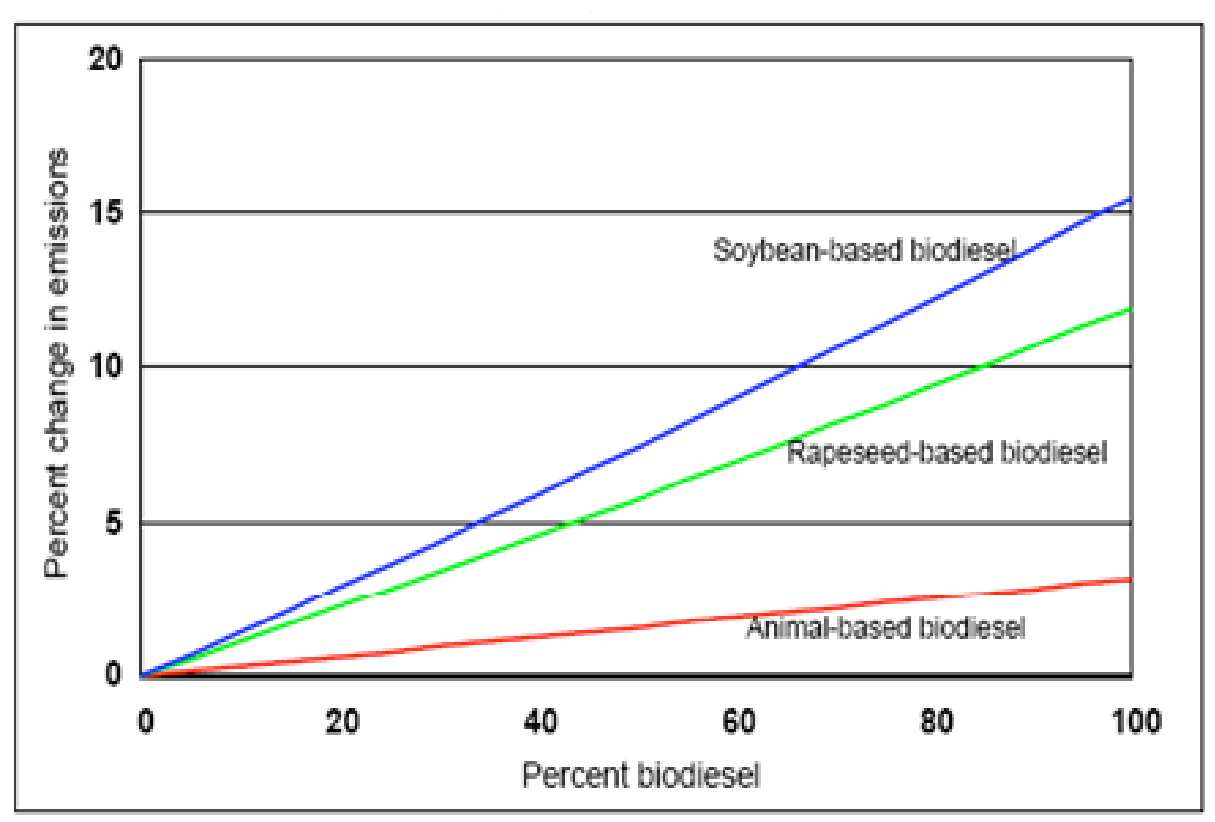
Feedstock Effect on **NOx** Emissions

Source: USEPA 2002; California Biodiesel Multimedia Evaluation: Tier I Report March 2008



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soil and water impacts vs. petroleum diesel

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aerobic biotransformation in soil

days	CO_2 evolution (%)				
	REE100	R80/d20	R50/d50	R20/d80	d100
0	0%	0%	0%	0%	0%
7	64.09%	52.33%	37.85%	25.24%	12.08%
14	77.51%	61.26%	45.74%	31.59%	14.96%
28	84.37%	67.82%	51.90%	35.67%	18.18%

Zhang et al, 1998; California Biodiesel Multimedia Evaluation: Tier I Report March 2008.

Water Boards

anaerobic biotransformation in soil

Degradation after 60 days incubation in argon:

- 48% diesel
- 79% sunflower oil
- 80% beef grease
- 81% B100

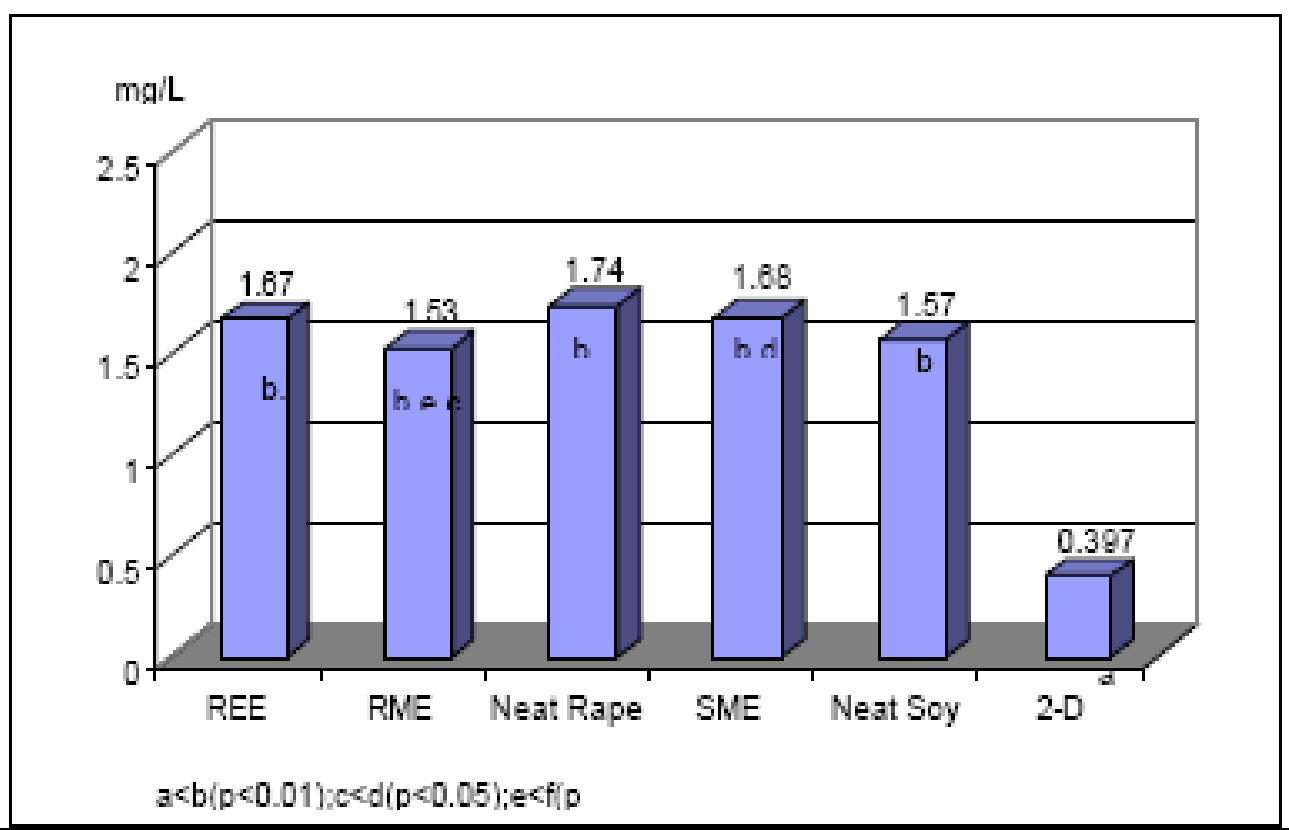
Water Boards

Lapinskiene and Martinkus (2007)

BOD_5: diesel vs. biodiesel

Source: Knothe et al 2005; California Biodiesel Multimedia Evaluation: Tier I Report March 2008

Biodiesel has higher BOD_5 than petroleum diesel



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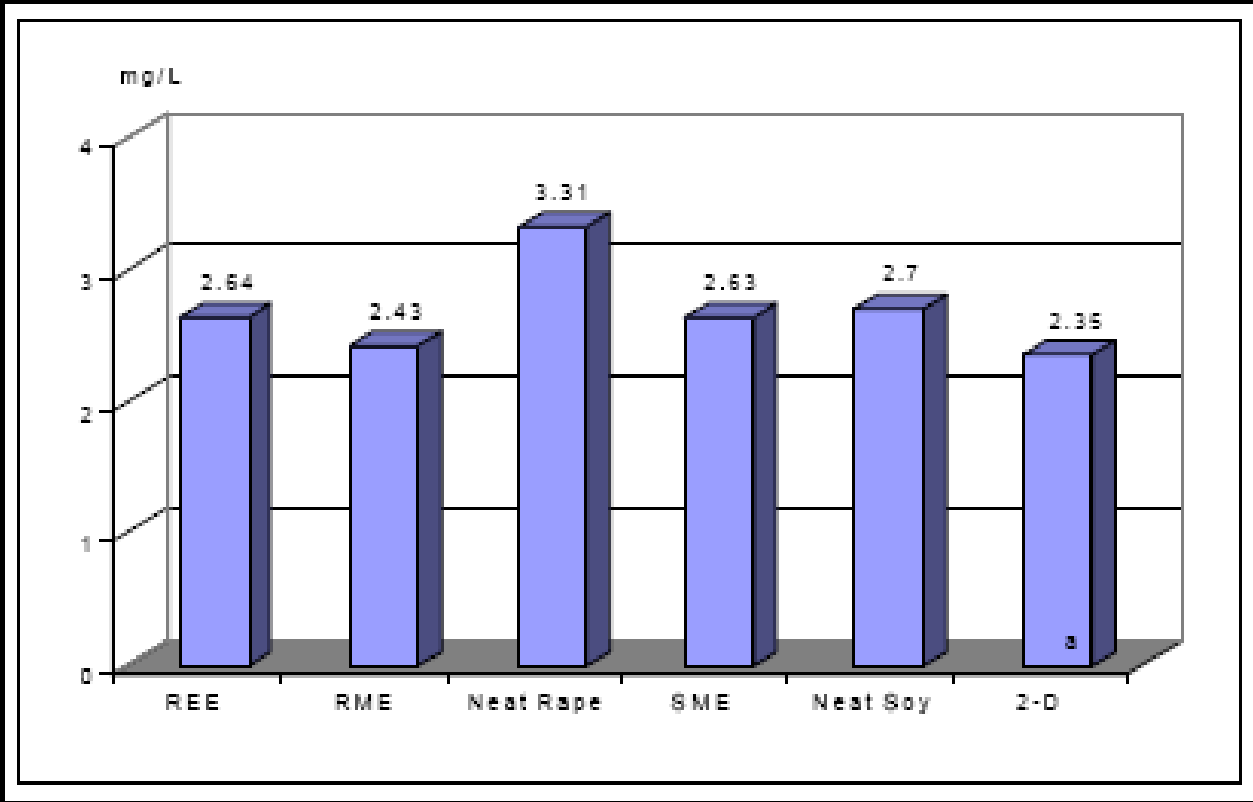
COD: diesel vs. biodiesel

Source: Knothe et al 2005; California Biodiesel Multimedia Evaluation: Tier I Report March 2008

Biodiesel has slightly > COD than petroleum diesel



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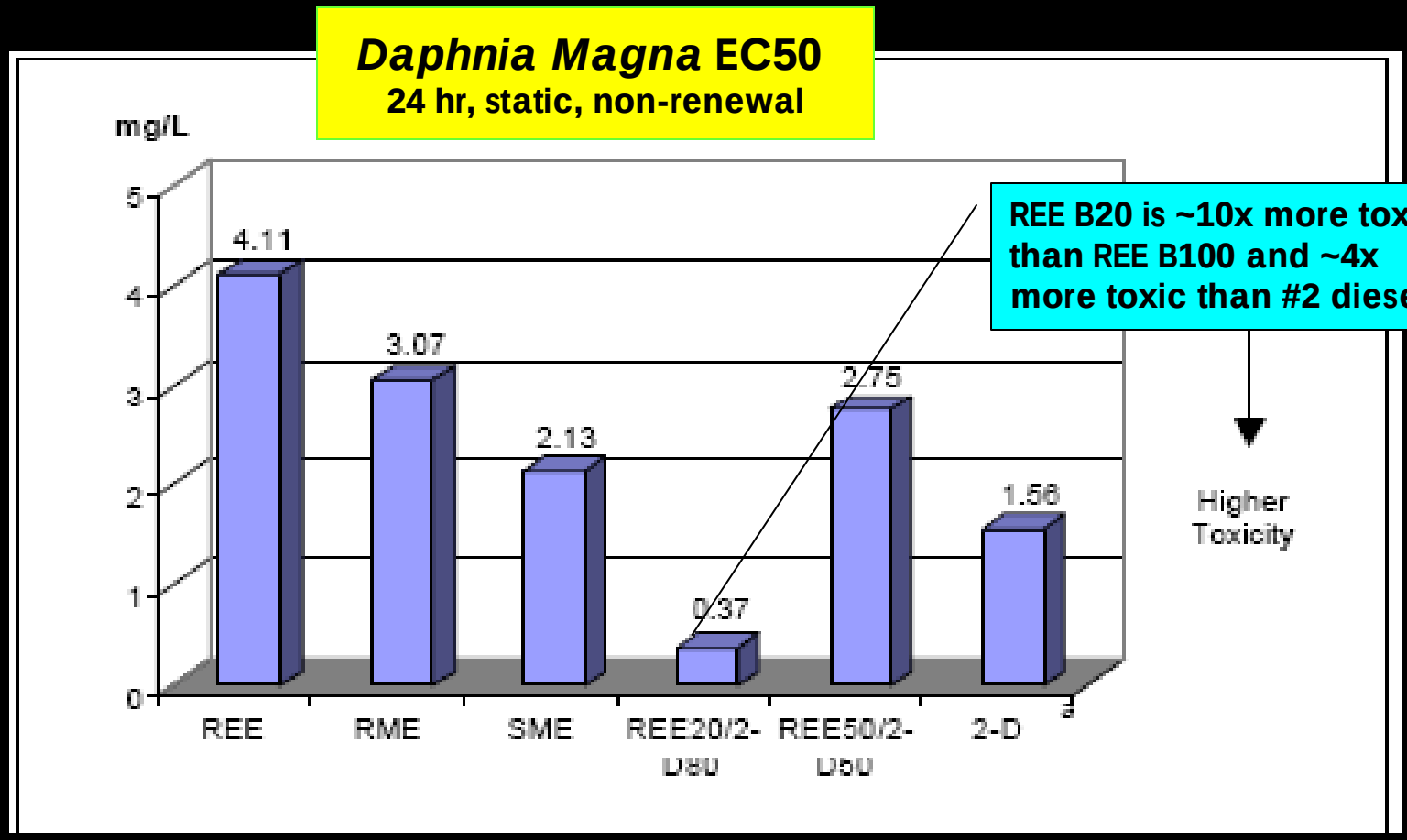
Aquatic Toxicity:

Source: Knothe et al 2005; California Biodiesel Multimedia Evaluation: Tier I Report March 2008



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Reported NPDES Permit violation:

Biodiesel plant discharging wastewater to the Black Warrior River, Al

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What are the potential impacts on human health?

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Risks to Human Health

- **Global adverse impacts on GHG, land use, and food insecurity**
  - Food shortages in developing countries blamed on food-to-fuel concept
  - Biodiesel demand causing deforestation and soil erosion in crop areas
  - Increased CO_2 emissions due to soil erosion
  - UN Rappateur calls biofuels "…a crime against humanity"
- **Toxicity of fuel additives and processing**
  - Toxicity of additives is unknown
  - Engine emissions of additives unknown
  - Oil processing uses solvent extraction method resulting in hexane emissions
- **Toxicity of fuel and contaminants**
  - Possible chemical components: MeOH, Peroxides, NaOH, HCl
  - Natural toxins in feedstocks: **aflatoxins** and **prions** (very unlikely)

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LD_{50} Toxicity
Biodiesel vs. Diesel Fuel

- B100, B50, B20, and 100% #2Diesel samples administered to rats via gastric intubation

- **LD_{50} of Biodiesel and petroleum diesel is ~ equal,**
  > 5 g/kg

... but data are inconclusive because they tested only biodiesel from rapeseed oil [rapeseed methyl ester and rapeseed ethyl ester].

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Biodiesel Mutagenicity?

Unknown!

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Q: is there a “greener” alternative to “biodiesel”?

A: *Maybe* -- **“Renewable Diesel”**

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“Renewable Diesel”: The definition

Source: Communications with Conoco-Phillips, BP, Nesté)

1. Also a substitute for petroleum diesel
2. Also made from **vegetable oils** and/or **animal fats**
3. But via a process of **thermal depolymerization**
4. Which results in **alkanes** and
5. Conforms to **ASTM D 975** (CARB ULSD)

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How will "renewable diesel" be different than biodiesel?

RD is reportedly a "linear paraffin" (alkane), "3 diesel and 1 propane molecule"

...instead of biodiesel which is multiple esters.

RD being developed by major oil company refineries;

...no backyard breweries or other quality control issues

RD reportedly meets ASTM D 975 for petroleum diesel;

... no need for new standards

RD reportedly is diesel, not a chemical to be blended with diesel:

therefore the material compatibility is known

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Source: Communications with Conoco-Phillips, BP, Nesté)

which is more benign "Biodiesel" or "Renewable Diesel"?

Renewable diesel emissions, fate and transport, UST compatibility, stability, toxicity, human health and other impacts

should be very similar to petroleum diesel.

Renewable diesel will be produced at a major refinery, no home brew batches

should be much better quality control.

... but not yet enough data to say definitively,

...the Water Board Tier I "biodiesel" tests will compare biodiesel and renewable diesel.

Water Boards

First do no harm...

Water Boards

Thank you for your attention!!

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