# Fuel Quality Specifications for Biodiesel from Jatropha: Fleet Perspective

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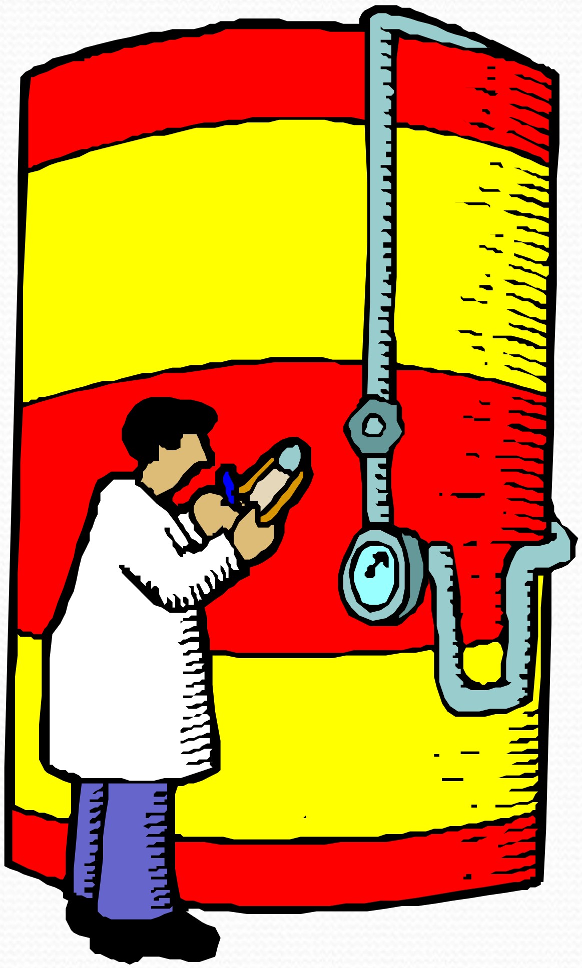
# Basic Biodiesel Reaction

+ Liquid Catalyst 1 kg
(Na or K Hydroxide)

Combining

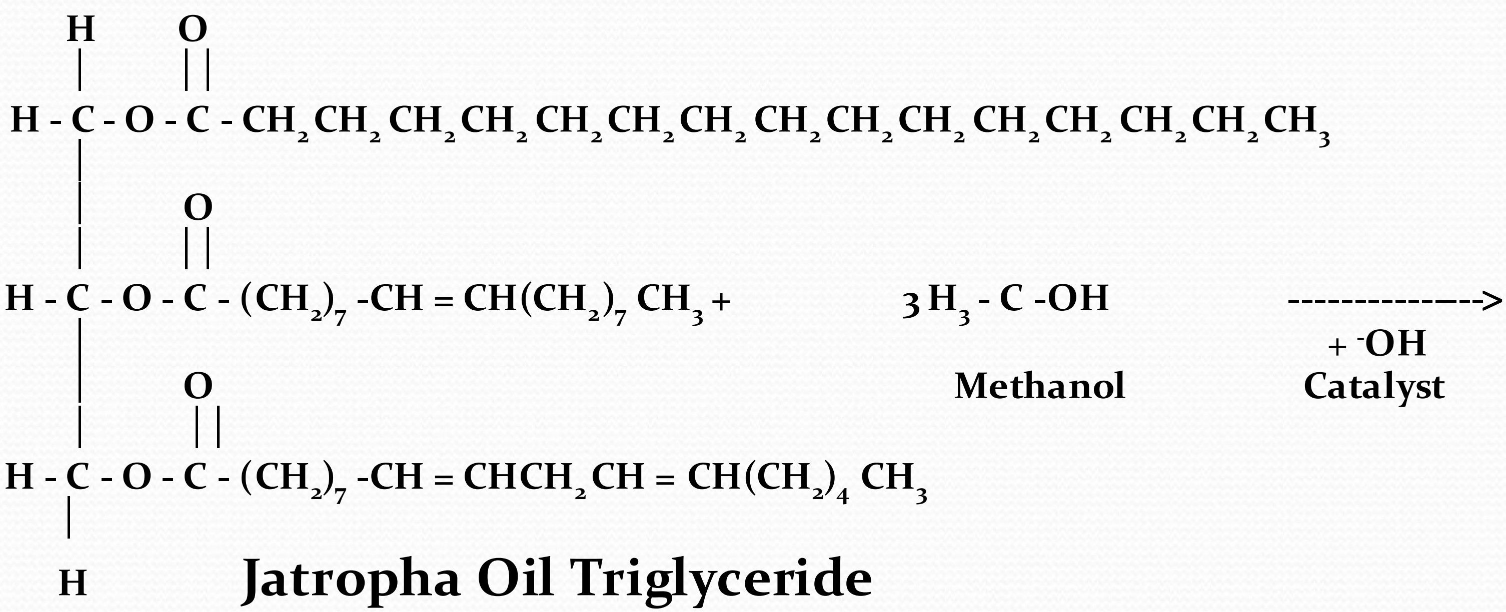
**Jatropha oil**
**(100 kg)**
**+**
**Methanol**
**(12 kg)**



Yields

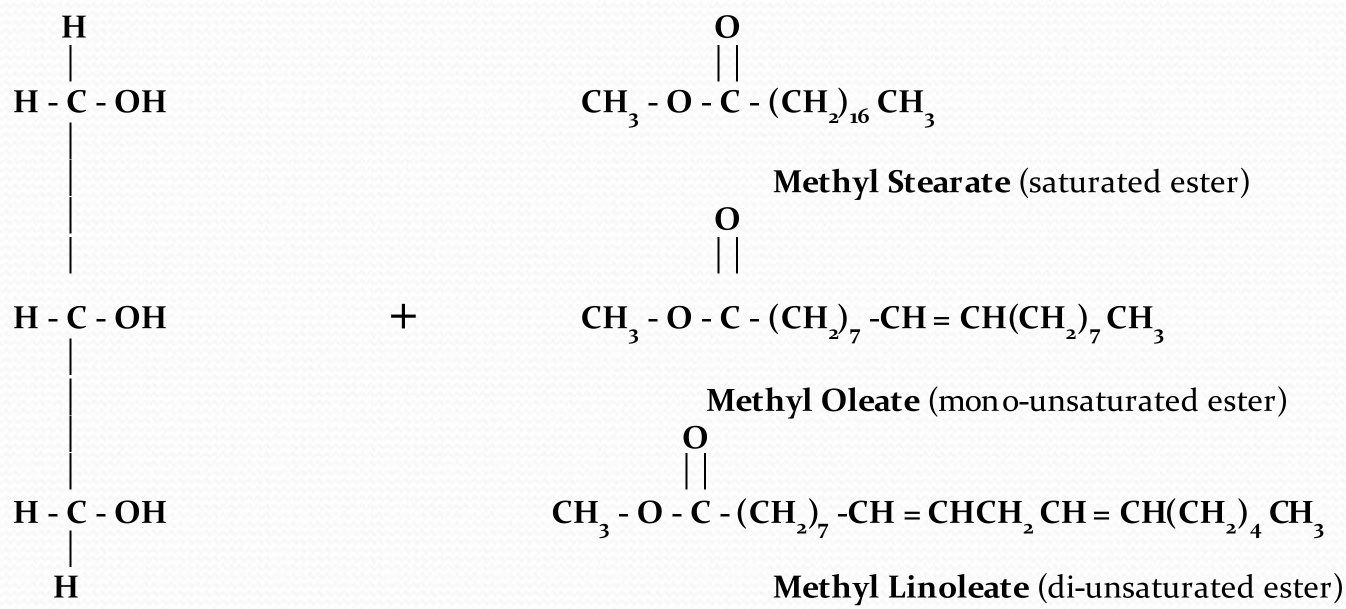
**Biodiesel**
**(95 kg)**
**+**
**Glycerin**
**(11 kg)**

# Transesterification Reaction (basic)




**Jatropha Oil Triglyceride**

# Transesterification reaction releases methyl esters from glycerin




**Glycerin**

**Jatropha Biodiesel Methyl Esters**

**Process Control and Batch Testing is Essential**

# Important Biodiesel Parameters

- Complete conversion – avoid partially reacted fuel!
- High oxidation stability – avoid unwanted reactions
- Removal of glycerin – residues accumulate in engine
- Removal of catalyst – destroys gaskets and seals
- Removal of residual carbon – polymers from oxidation
- Keep low acid number – avoid oxidized fuel
- New pending assay  to test for potential precipitations

- Insured through ASTM D 6751 specs

# ASTM D 6751 2008 "Feedstock Neutral"

| Property | Test Method | Limits | Units |
|---|---|---|---|
| Calcium & Magnesium | EN 14538 | 5 max | ppm (ug/g) |
| **Flash Point** | **D 93** | **130 min.** | **degrees C** |
| **Water & Sediment** | **D 2709 (4176)** | **0.05 max.** | **% volume** |
| Kin. Viscosity, 40C | D 445 | 1.9 - 6.0 | $mm^2$/sec. |
| Sulfated Ash | D 874 | 0.02 max. | % mass |
| **Sulfur S15** | **D 5453** | **0.0015 max (15)** | **% mass (ppm)** |
| Copper Corrosion | D 130 | No. 3 max. | |
| Cetane number | D 613 | 47 min. | |
| **Cloud Point** | **D 2500** | **Report** | **degrees C** |
| Carbon Residue | D 4530 | 0.05 max. | % mass |
| **Acid Number** | **D 664** | **0.50 max.** | **mg KOH/g** |
| **Free Glycerin** | **D 6854** | **0.020** | **% mass** |
| **Total Glycerin** | **D 6854** | **0.240** | **% mass** |
| Phosphorous content | D 4951 | 0.001 max | % mass |
| Distillation, T90 AET | D 1160 | 360 max | degrees C |
| Na/K, combined | EN 14538 | 5 max | ppm (ug/g) |
| **Oxidation Stability** | **EN 14112** | **3 min** | **hours** |
| **(Visual Appearance)** | **D 4176** | **Free of un-dissolved water, sediment and suspended matter** | |

**BOLD = BQ-9000 Critical Specification Testing Once Production Process Under Control**

**Additional testing: KF Moisture to track dissolved water in fuel; Cold Soak Filtration Assay test for particulate**

# ASTM D6751 Highlights for Jatropha oil

- Acid number – fatty acids from oxidation
- Oxidation stability – oxidation intermediates
- Carbon residues – polymers from oxidized chains
- Total glycerin – test for incomplete conversion (mono, di and triglcyeride residues in fuel)
- ASTM and EU specs are likely to tighten for $Na^{+}$, $K^{+}$, $Ca^{++}$, $Mg^{++}$ & oxidation stability
- NEW "cold soak filter test" CSFA pending ASTM approval as operational test for precipitations
- Note: Recommend also monitoring KF Moisture

# Fatty Acid Profiles & Yields of Tropical Oils

| **Fatty Acid (vary w/variety)** | **Jatropha (C.America India)** | **Palm** | **Coconut** |
|---|---|---|---|
| Caprylic Acid, (C8:0) | - | - | 8 |
| Capric Acid, (C10:0) | - | - | 8 |
| Lauric Acid, (C12:0) | - | - | 48 |
| Myristic Acid, (C14:0) | 0.38 | 3.5 | 16.0 |
| Palmitic Acid, (C16:0) | 15-17 | 39.5 | 8.5 |
| Palmetoleic (C16:1) | 1-3.5 | - | - |
| Stearic Acid, (C18:0) | 5-7 | 3.5 | 2.5 |
| Oleic Acid, (C18:1) | **40-43.5** | 46 | 6.5 |
| Linoleic Acid, (C18:2) | **33-35** | 7.5 | 2.0 |
| Linolenic Acid (C18:3) | 0.8 | - | - |
| Production Kg/Hectare | 1590 | 5000 | 2260 |
| % Unsaturated FFAs | 72-79% | | |

# Jathropha oil high in unsaturates

- Double bonds improve cold flow properties but also make the oil (and biodiesel) more sensitive to oxygen
- Oxidation of double bonds can lead to formation of unstable hydroperoxides  which can
  - Breakdown to short fatty acids and other compounds
  - Cross link with each other to form polymers
  - React with engine crankcase oil and increase viscosity
- Keep oil in good condition: separate seed from fruit immediately after harvest, dry seed storage, process oil to biodiesel soon after expelling. Ideally protect oil from oxidation using closes systems or $N_2$ blanket

# Free fatty acids and polymers result from oxidation & cross linking of unsaturated chains

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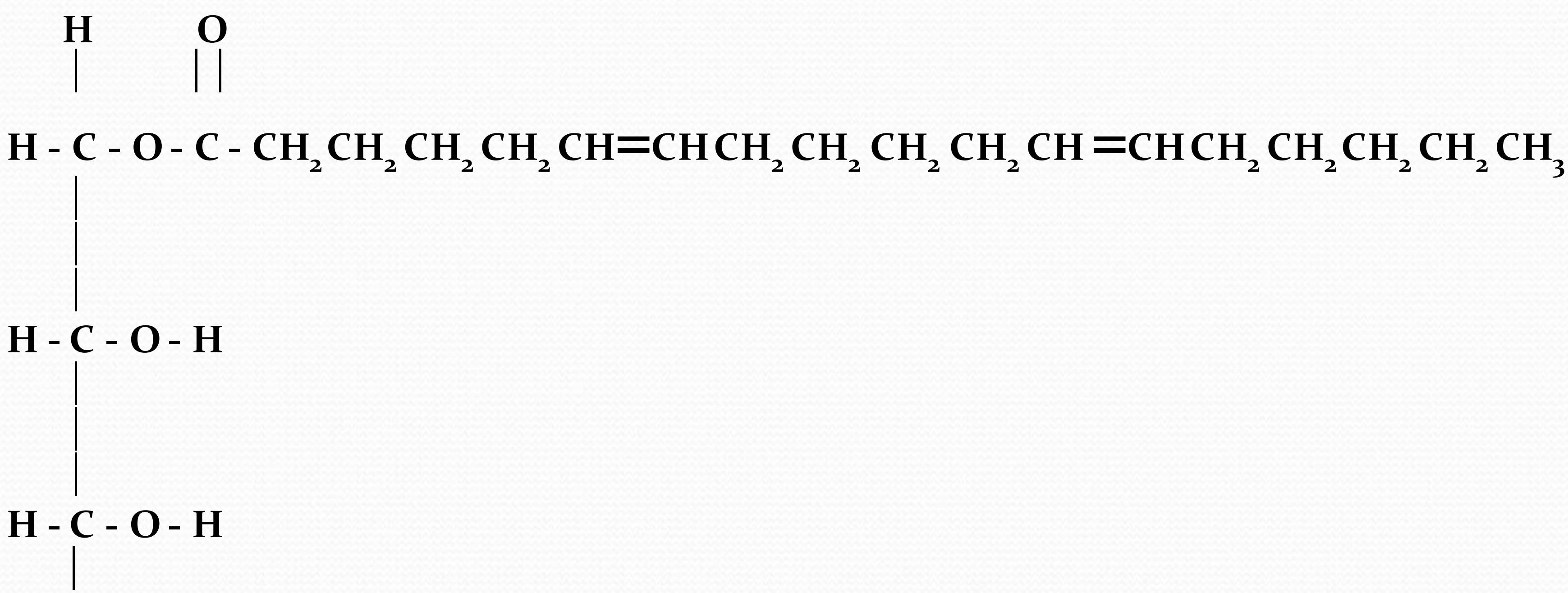
$- O - C - CH_2 CH_2 CH_2 CH_2 CH -- CH\ C\ H_2 CH_2 CH_2 CH_2 CH --CH\ CH_2 CH_2 CH_2 CH_2 CH_3$

Hydroperoxides form by oxidation of double bonds

Breakdown to smaller fatty acids or cross-link to form polymers

Higher free fatty acids (rancid oil) means lower quality biodiesel

# Mono & di glycerides result from incomplete transesterification




- **Monoglyceride (Linoleic: 18:2)**

Free fatty acids in oxidized Jatropha oil contribute to incomplete conversion of oil to esters

# Degumming crude crushed Jatropha oil is crucial to making good biodiesel

- Removal of lecithin and phospholipids, sterols and other impurities is essential to produce good biodiesel
- Impurities in crude fresh oil would interfere
- Typically degumming achieved with phosphoric acid treatment and water, then centrifugation and drying
- Follow with bleaching earth/silicas filter press to absorb out impurities and oxidized unsaturated chains
- Degumming and bleaching would be minimal treatment for using Jatropha oil for use as SVO for 'in country' as biofuel or fuel for modified diesel engines

# Reports of biodiesel production issues using Jatropha oil, despite a 'friendly feedstock'

- Prior oxidation and cross linking of Jatropha oil chains can result in polymer problems with biodiesel
- Low, out of spec oxidation stability index even in fresh biodiesel made from Jatropha oil that was oxidized
- Higher viscosity than normal = polymer formation
- Higher carbon residue numbers = polymer residues
- Failed distillation tests = polymer residues
- Need to keep seeds dry; Process Jatropha oil soon after crushing and minimize contact with air

# Oxidized Jatropha Oil results in lower quality, more expensive Biodiesel

- Oxidation of double bonds in unsaturated triglyceride chains leads to formation of hydroperoxides
- Hydroperoxides break down to form ketones, aldehydes and, eventually, shorter free fatty acids
- Hydroperoxides can also cross-link with each other to form polymers and precipitates
- Natural tocopherols (Vitamin E components) protect oil from oxidation in soy, rapeseed and palm
- Need to protect Jatropha oil from heat, moisture and metal ions that promote oxidation and deterioration

# Pretreatment of Jatropha Oil

- Freshly expelled Jatropha oil is perishable and sensitive to moisture, oxidation and deterioration leading to rancid (oxidized, degraded) unsuitable feedstock
- Degumming is critical and more challenging than making the biodiesel from the degummed oil
- Degumming removes: Lecithin, phospholipids, protein, phorbol esters and sterols/sterol glucosides
- Degummed oil must be dried and stored under $N_2$
- Impurities in crude Jatropha oil will vary with wild type varieties, so need to optimize degumming process

Courtesy of Satish Lele, India

# Optimizing oil extraction and biodiesel production as an integrated process

- Maximize extraction of Jatropha oil from seeds using combination of mechanical press & solvent extraction
- Protect oil from oxidation ($N_2$ blanket, closed system)
- Co-locate biodiesel production plant at oil processing facility to minimize deterioration of oil, transport costs
- Pre-treat crude oil (acid degumming & silica DE resin) to remove all traces of lecithin, phospholipids, protein and phorbol esters (toxic); Properly dry treated oil
- Keep FFA levels < 2, optimize transesterification to achieve complete conversion of oil to methyl esters

# Fuel Quality Control: A Mindset at 3 Levels from Plant to Fleet

- Production at the plant: feed stock to fuel
  - BQ 9000 or other rigorous QA program
  - ASTM 6751 specs and certification

- Distribution, storage and handling
  - BQ 9000 or other rigorous QA program
  - Protocols, documentation, monitoring

- Consumer storage, dispensing & use
  - Protocols, documentation, monitoring

# Biodiesel Fuel Specifications: It's all about Quality Control

- Most or all problems associated with biodiesel use are due to fuel quality issues, not to the biodiesel per se
- Quality control problems largely a result of a rapidly growing industry, inexperience and lack of diligence.
- The problems are NOT caused by inadequate specifications or the lack of proper protocols, from the plant to the distributor to the user – just do it right

# Common Problems with Biodiesel in Transit & Storage

- Biodiesel, blends of biodiesel all suffer from water & sediment in poorly maintained tanks (condensation water and contamination from delivery are common)
- Bacterial growth (not 'algae') in water layer will deteriorate the fuel, generate acids and precipitations
- Acids caused by bacterial biodegradation of fuel (carboxylic acids) can damage engine components
- Anaerobic conditions in damp tanks promote sulfate reduction forming traces of corrosive sulfuric acid
- Older tanks or tanks accidentally contaminated with infected, deteriorated diesel fuel can infect biodiesel

# Fuel Problems Associated with Increasingly Out of Spec Biodiesel

- Residues in storage tanks, filters and lines
- Clogged filters can stop vehicles on road
- Dissolved contaminants foul injectors
- Coking of injectors and varnish on valves
- Rough engine operation, smoke, wear
- Catalyst, methanol ruin fuel injection pump
- Crankcase oil deterioration, polymerization
- Long term or catastrophic engine damage

# Some problems get caught

Sediments, bacterial slime, precipitates and free water can be trapped by filters along with any insoluble impurities associated with the fuel

But…deteriorated fuel & acids can damage engines

# Field Test Kit Developed for checking Biodiesel B100 Quality: pHLip Test

- A Quick Check in the field for detecting traces of catalyst, mono/di/triglycerides, soaps, acids and oxidized (aged) fuel = hydroxyesters, peroxides
- 10 min test; Simply add B100 to test vial, mix by 'flipping" & let the fuel float to create two phases
- **Visual** indication only but quantitative capability
- Unrelated to ASTM yet surprisingly sensitive for <u>dissolved</u> contaminants; Now a QC protocol test
- Intended to alert a consumer or operator as a 'firewall', then they can request a formal lab test

# pHLip Test Kit Concepts

Extraction of catalyst or acid from fuel to aqueous pH indicator elicits color change from neutral red color

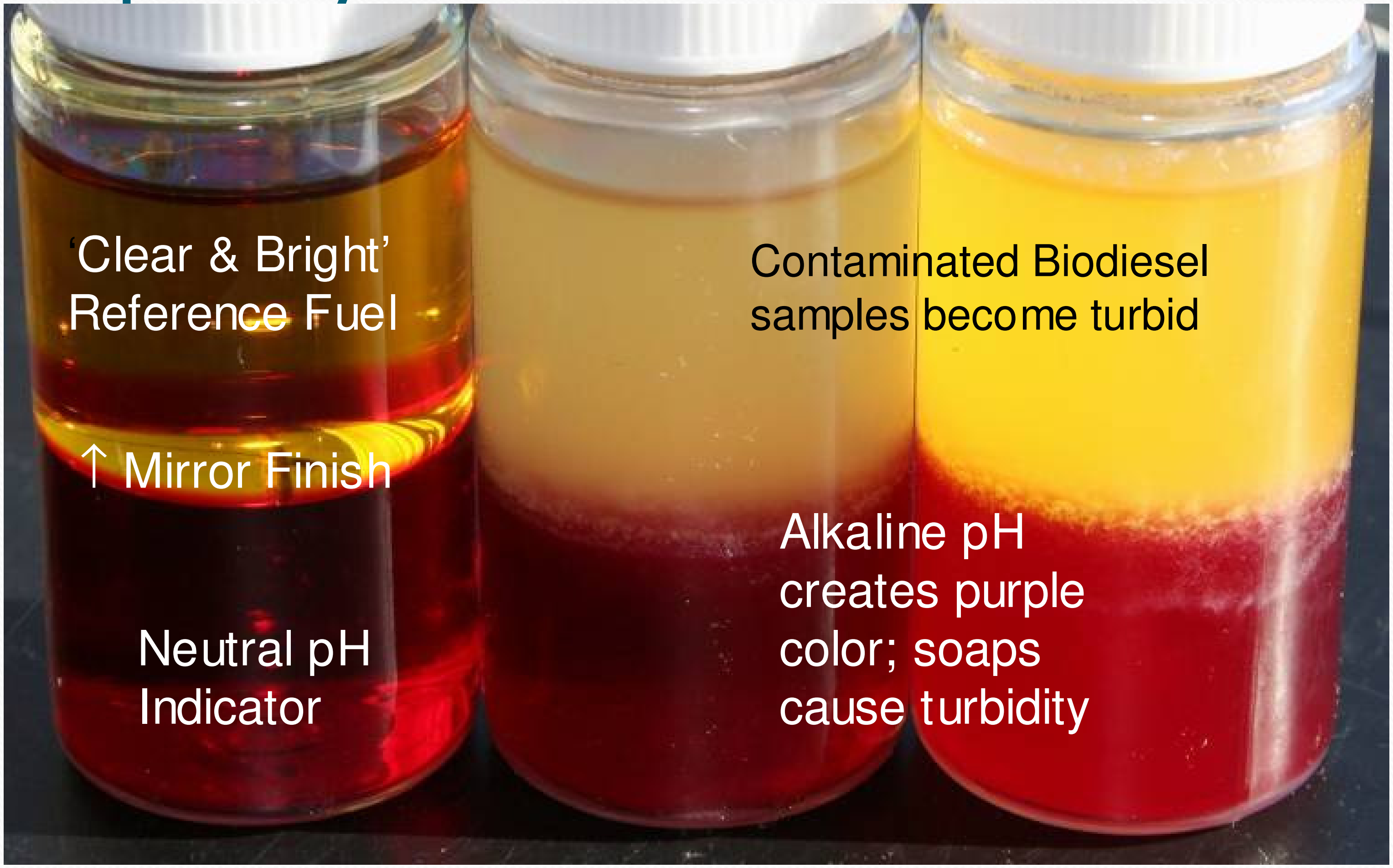
Soluble contaminants in biodiesel can be:

>Extracted into the aqueous phase (fatty acid soaps) as visible turbidity

>Concentrated at water-fuel interface (glycerides, sterols, oxidized esters) "Lens Effect" = Signal Amplification

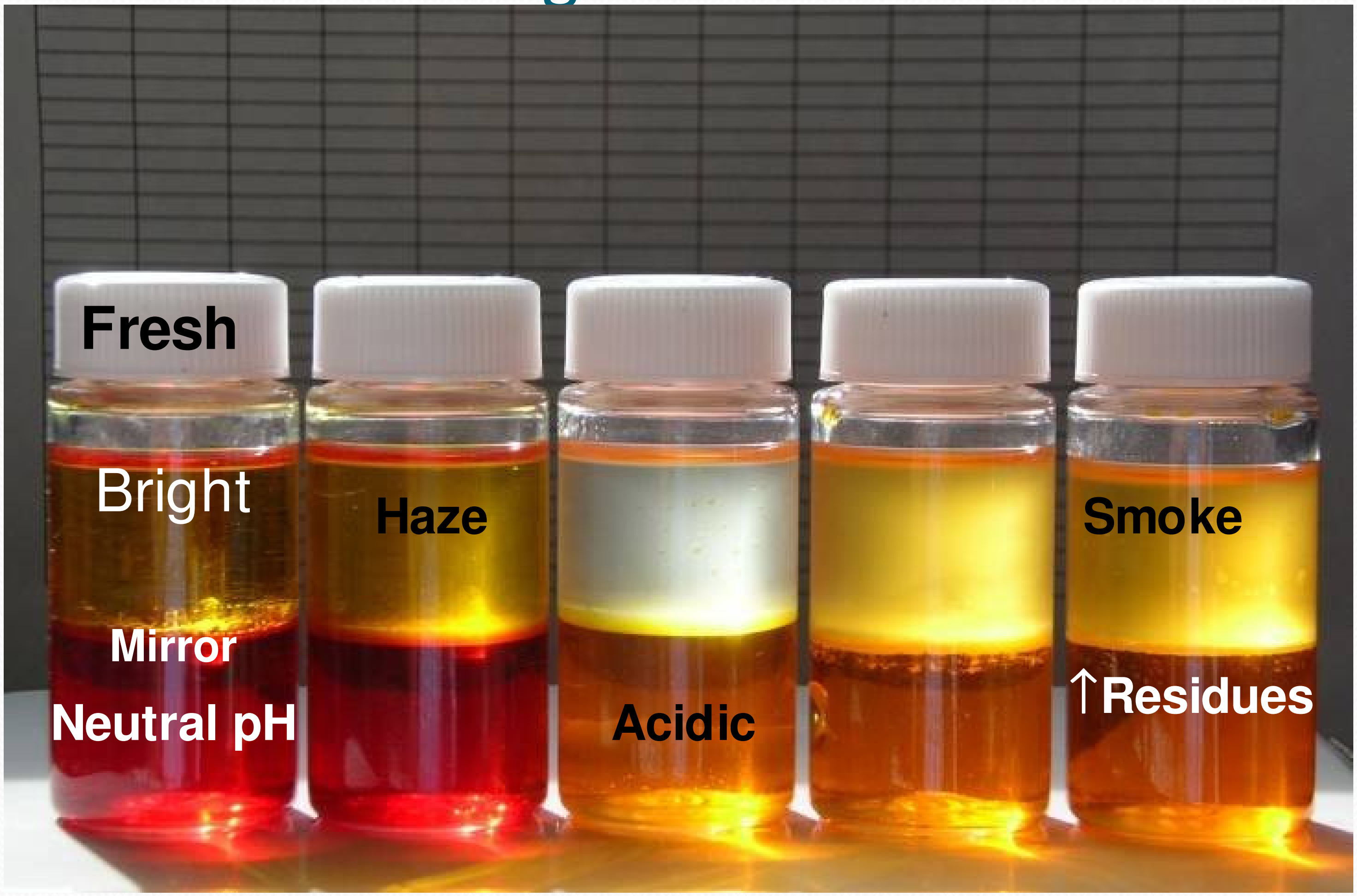
>Hydrated in the fuel as visible turbidity (mono, di & triglycerides; fatty acids, oxidized)

# Detection of catalyst contamination from poorly washed biodiesel fuels



# Aging Oxidized B100 Examples

## Relative to Fresh Bright Reference Fuel

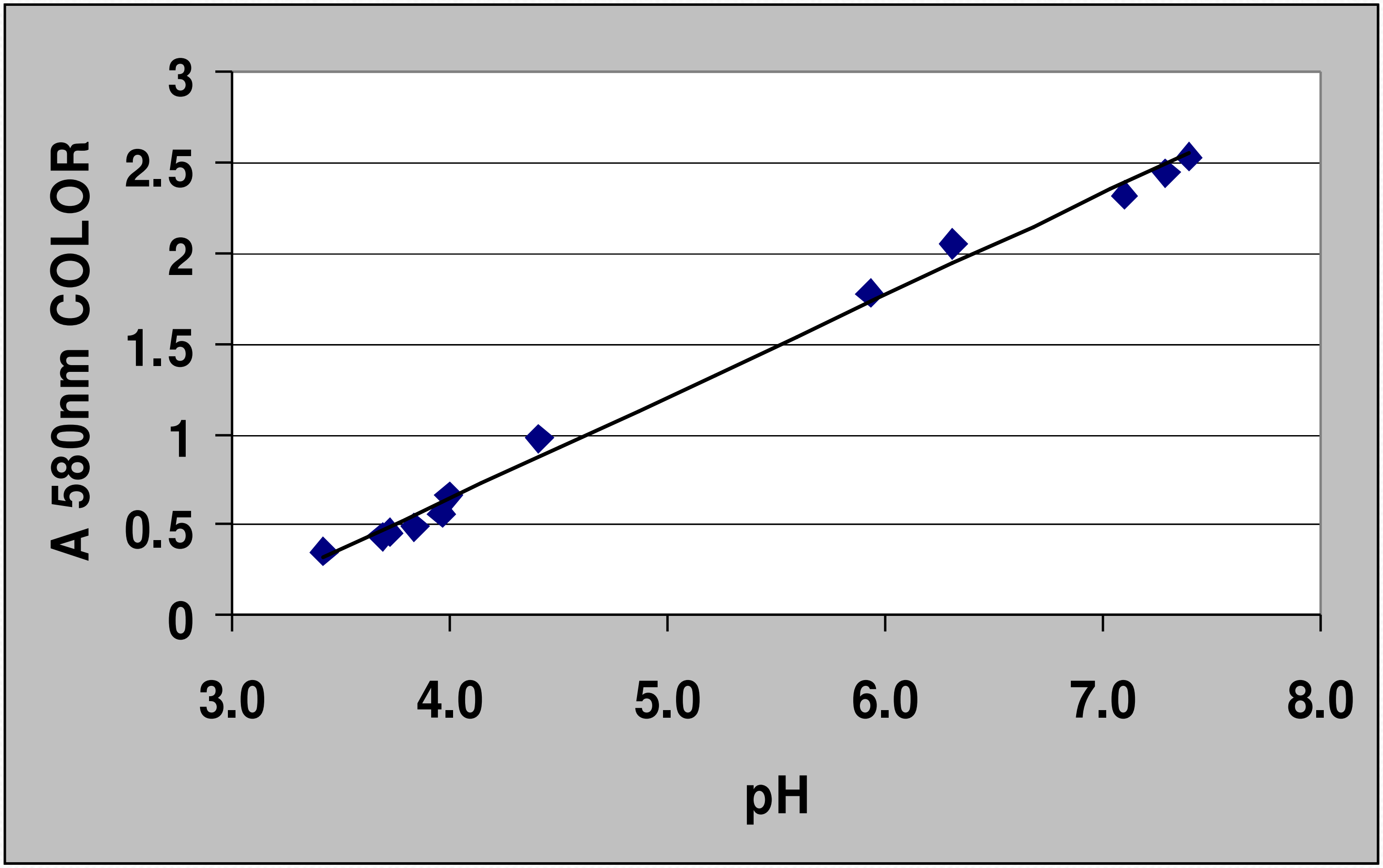


# Titration of Acidic Aged Biodiesel into Reference Soy Biodiesel

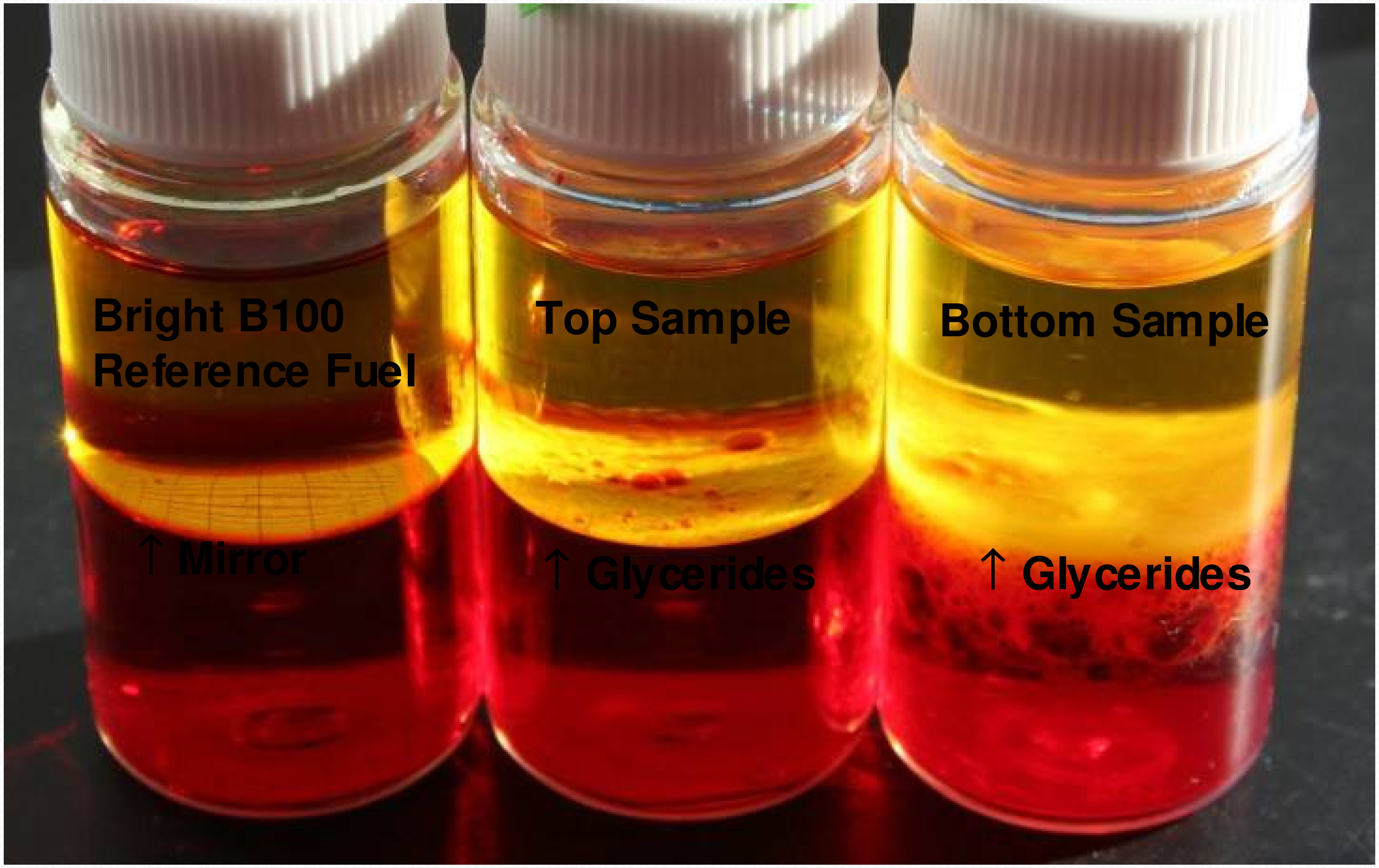

Indicator Solution Color Shifts from Red to Yellow with more Acid

pH = 7.3 6.4 4.4 4.0 3.4

# Test Color Shift is Linear with pH in Acidic Range



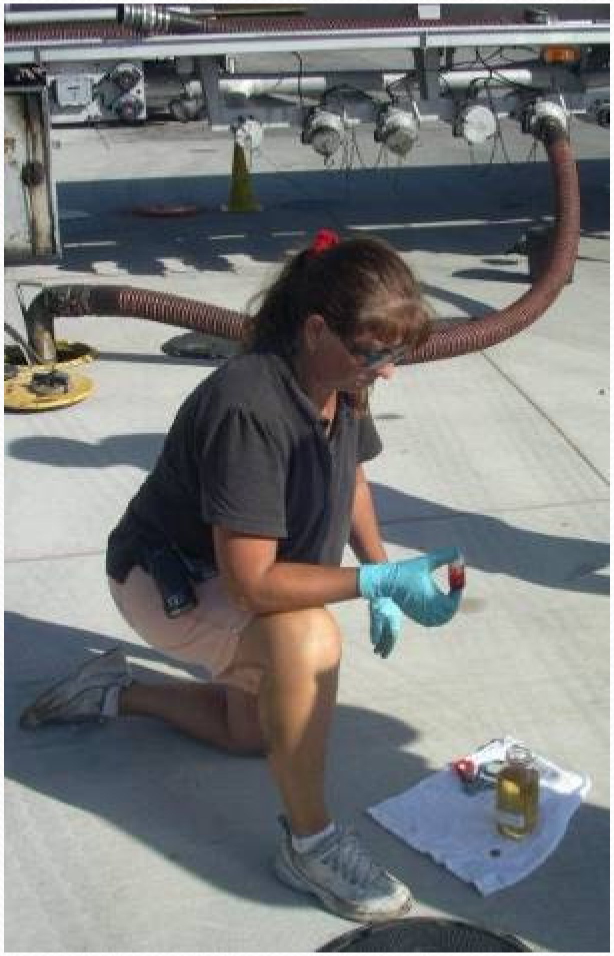
# Detecting near-spec and off-spec fuel: top vs. bottom of storage tank of B100




0.76% Monoglycerides, 0.38% Diglycerides, 0.62% Triglycerides
0.31% Total Glycerin with <0.005% Free Glycerin in composite

# Monitoring Biodiesel Quality for Fleet Deliveries by Truck/Rail

Bus Fleet Managers Testing B99 on delivery

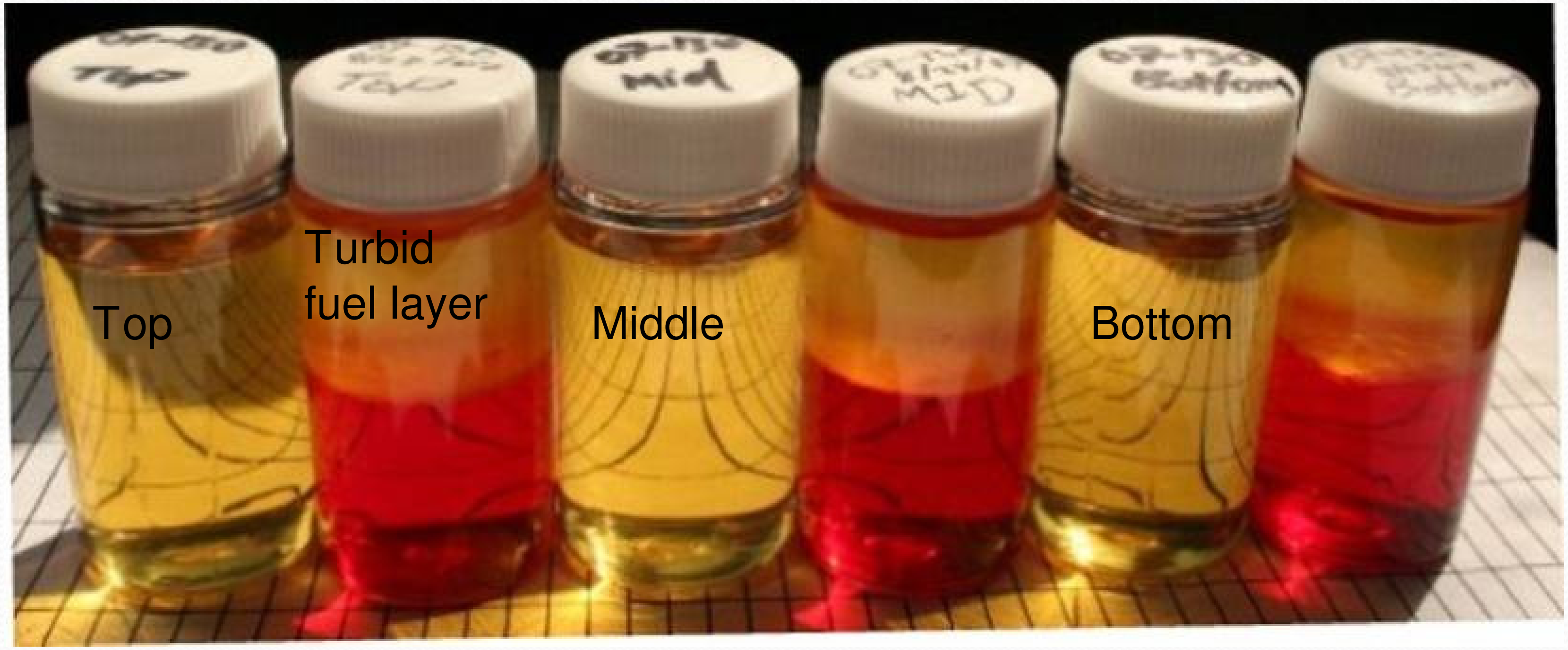


# Biodiesel Quality Status Report (BQSR)

| | | | |
|---|---|---|---|
| TAN (mg KOH/g) | ASTM D 664 | **MAX 0.500** | **0.12** |
| KF Water (ppm) | ASTM D 6304 | **N/A** | **205** |
| Free Glycerin (mass %) | ASTM D 6584 | **MAX 0.020** | **0.003** |
| Monoglycerides (mass %) | ASTM D 6584 | **N/A** | **0.144** |
| Diglycerides (mass %) | ASTM D 6584 | **N/A** | **0.010** |
| Triglycerides (mass %) | ASTM D 6584 | **N/A** | **0.004** |
| Total Glycerin (mass %) | ASTM D 6584 | **MAX 0.240** | **0.160** |
| Flash Point (deg C) | ASTM D 93 | **MIN 130** | **186** |

Typical B100 imported to CA, similar to NREL 2007 Survey

# Out-of-spec, incompletely reacted B100




| | | | | |
|---|---|---|---|---|
| Free Glycerin (mass %) | ASTM D 6584 | MAX 0.020 | 0.000 | PASS |
| Monoglycerides (mass %) | ASTM D 6584 | N/A | 0.215 | N/A |
| Diglycerides (mass %) | ASTM D 6584 | N/A | 0.523 | N/A |
| Triglycerides (mass %) | ASTM D 6584 | N/A | 1.867 | N/A |
| Total Glycerin (mass %) | ASTM D 6584 | MAX 0.240 | 2.605 | FAIL |
| Flash Point, Closed Cup (°C) | ASTM D 93 | MIN 130 | 50 | FAIL |

Note 'clear and bright' B100 samples vs. Turbid fuel layer in pHLip Tests

# Oxidized (ruined) ASTM spec B100

| | | | |
|---|---|---|---|
| TAN (mg KOH/g) | ASTM D 664 | **MAX 0.500** | **0.29** |
| KF Water (ppm) | ASTM D 6304 | **MAX 500?** | **736** |
| Free Glycerin (mass %) | ASTM D 6584 | **MAX 0.020** | **0.000** |
| Monoglycerides (mass %) | ASTM D 6584 | **N/A** | **0.072** |
| Diglycerides (mass %) | ASTM D 6584 | **N/A** | **0.007** |
| Triglycerides (mass %) | ASTM D 6584 | **N/A** | **0.000** |
| Total Glycerin (mass %) | ASTM D 6584 | **MAX 0.240** | **0.085** |
| Flash Point (deg C) | ASTM D 93 | **MIN 130** | **168** |
| Oxidation Stability Index (Hr) | EN14112 | **MIN 3** | **2.89** |
| Cold Soak Filter Time (min) | ASTM D 6217b | MAX**150-250?** | **470** |
| CSFA Particulate Ct (mg/L) | ASTM D 6217b | < 50? | **110** |

# Biodiesel Quality Status Report 2008

| | | | |
|---|---|---|---|
| TAN (mgKOH/g) | ASTM D 664 | **MAX 0.500** | **0.13** |
| KF Water (ppm) | ASTM D 6304 | | **725** |
| Free Glycerin (mass %) | ASTM D 6584 | **MAX 0.020** | **0.000** |
| Monoglycerides (mass %) | ASTM D 6584 | **N/A** | **0.000** |
| Diglycerides (mass %) | ASTM D 6584 | **N/A** | **0.019** |
| Triglycerides (mass %) | ASTM D 6584 | **N/A** | **0.000** |
| Total Glycerin (mass %) | ASTM D 6584 | **MAX 0.240** | **0.019** |
| Flash Point (deg C) | ASTM D 93 | **MIN 130** | **184** |

**All Specifications Tested were PASS – Excellent (but moist) B100**

# Jatropha Oil is a promising feedstock for biodiesel…and fleets

- Jatropha should make high spec biodiesel provided the oil is in good condition: properly degummed, low in oxidation, low in free fatty acids, free of polymers
- Oxidation issues will be critical and will be monitored
- Cold flow properties are encouraging
- Cold soak filter assay (CSFA) pending ASTM approval
- Specifications could tighten for future engines: oxidation stability, trace metals ($K^+$, $Na^+$, $Mg^{++}$, $Ca^{++}$)
- 'Sustainability' , land use changes, GHG emissions & carbon footprints are important criteria for big fleets

# Research on Jatrohpa as feedstock oil

- Develop practical and inexpensive methods to protect crushed oil from oxidation including low-heat expeller system, minimal air contact and improved storage
- Improved efficient degumming methods
- Effective methods to filter/polish raw oil prior to transesterification to biodiesel; improved transport
- Determine risks of phorbol esters in raw oil and explore extraction/detoxification with methanol
- Selecting varieties of wild type plants to favor ratios of 18: 1 / 18:2 to optimize oil / biodiesel oxidative stability

# National Biodiesel Expo Conference San Francisco: February 1-4, 2009

www.biodiesel.org