

Monitoring Biodiesel Fuel Quality

National Biodiesel Conference
User Track – Fleet Implementation
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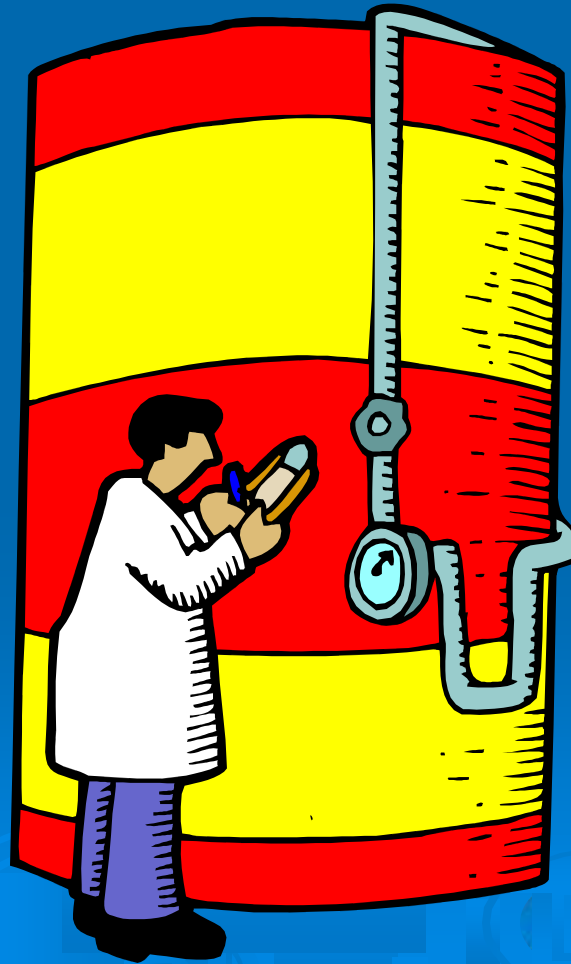
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The (simplistic) Biodiesel Reaction

+ Liquid catalyst
(potassium hydroxide)

Combining

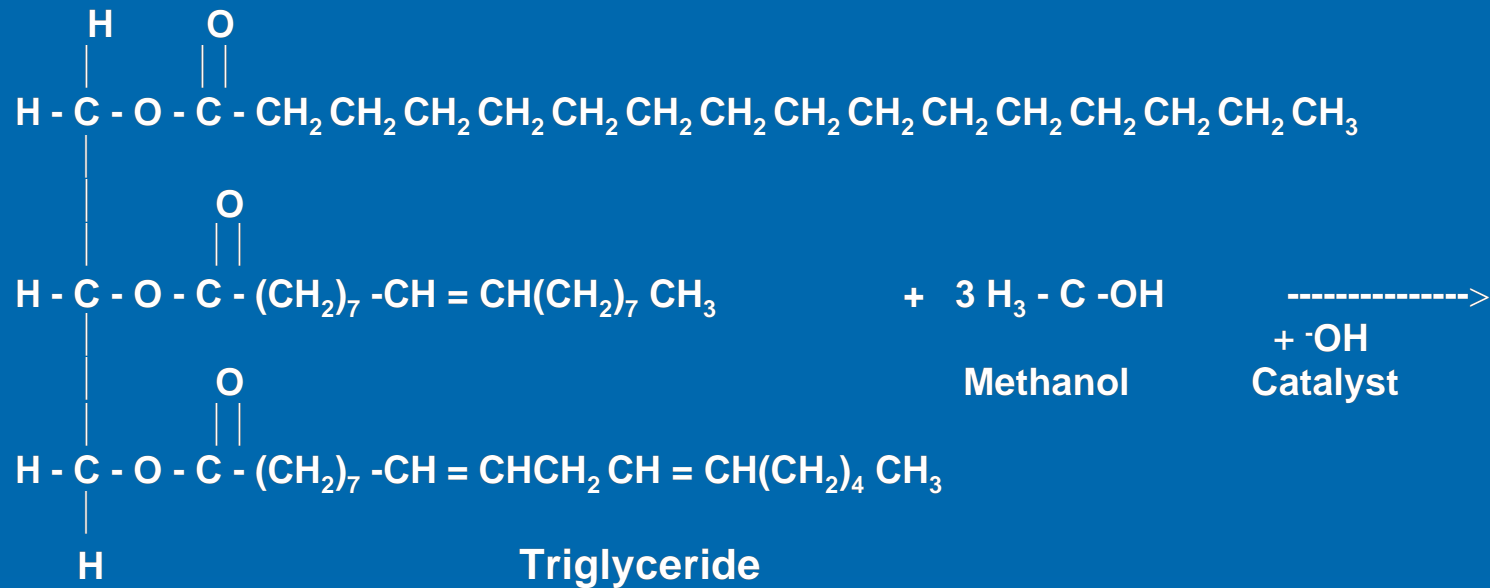
**Virgin crop oil, fat
or recycled
cooking oil
(100 lbs.)
+
Methanol
(10 lbs.)**



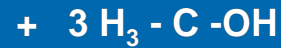
Yields

**Biodiesel
(100 lbs.)
+
Glycerine
(10 lbs.)**

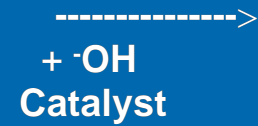
Transesterification Reaction (basic)



Vegetable / Soybean Oil



Methanol

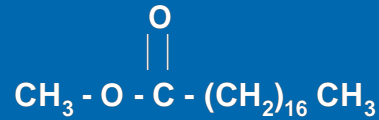


Reaction releases biodiesel methyl esters from glycerin

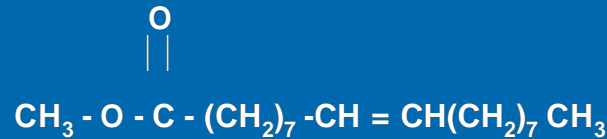


Glycerin

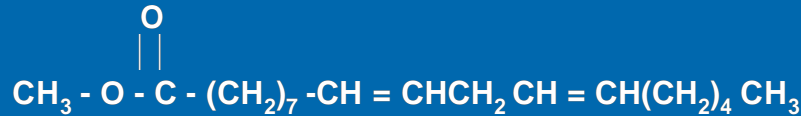
+



Methyl Stearate (saturated ester)



Methyl Oleate (mono-unsaturated ester)



Methyl Linoleate (di-unsaturated ester)

Biodiesel Methyl Esters

Process Control and Batch Testing is Essential

Removing Residuals

- Most transesterification reactions achieve 97-99% conversion of oils & fats to esters
- Co-product glycerin & unreacted reagents are largely removed by gravity separation or centrifugation; dissolved traces remain
- Water washes remove last traces of catalyst, methanol, glycerin and soaps
- Methanol is flashed off and recovered
- Final polishing steps essential to remove traces of oils, mono- and di-glycerides and free glycerin to achieve ASTM spec

ASTM D6751 Highlights

- Acid number – for aged, oxidized fuel
- Flashpoint – for residual methanol
- Water & sediment – fuel fouling, deposits plus moisture in fuel accelerates oxidation
- Sulfated ash – for residual catalyst
- Bound glycerin – for incomplete conversion (mono, di and triglyceride residues in fuel)
- Free glycerin – inadequate fuel polishing
- ASTM updates now include specs for Na^+ , K^+ , Ca^{++} , Mg^{++} & oxidation stability
- NEW “cold soak test” for sterols & glycerides

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 – Still a Quality Control Issue

- 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 lack of proper methods and protocols, from the plant to the distributor to the user

Common Problems Associated with Bad Fuel Quality

- Most problems seen with B100, not B20, but water & sediment are bad for all fuels
- Most precipitates, sediments, bacteria, unreacted fats are macroscopic and caught by fuel filters
- Residual catalyst & methanol degrade seals & gaskets that will harm fuel injection pumps
- Residual glycerides, soaps, long chain saturated esters, unreacted fats leave deposits, foul engine, and degrade crankcase oil or cause polymers
- Bacterial growth in contaminated tanks clogs filters and deteriorates the fuel

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

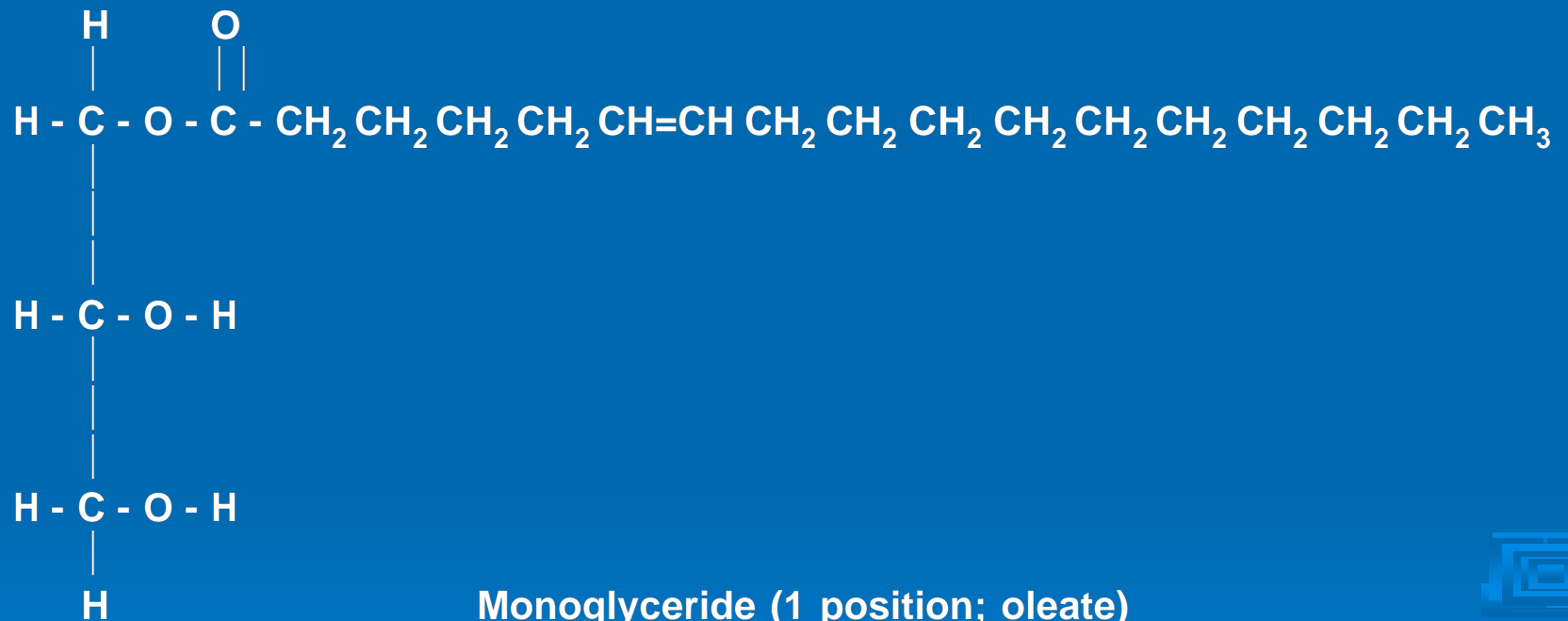
Some problems get caught

- Unreacted fats clog filters
- Sediments, precipitates & bacteria get trapped

But catalyst, methanol, acids, mono/di glycerides, sterols & free glycerin are dissolved in fuel



Mono & di glycerides result from incomplete transesterification



Removal of Saturated Monoglycerides & Sterol Glucosides from Biodiesel

- Avoid problem in first place by removing sterol glucosides & phosphatides from oil during the degumming process
- Polish biodiesel by passing over resins like aluminum silicates or diatomaceous earth
- If precipitates with mono & di glycerides occur (e.g., in transit), cold filter product
- Worse case, chill product, let stand and use gravity to settle ppts, then cold filter

Fuel Quality can Deteriorate

- ASTM spec fuel that is improperly stored, transported and handled can be ruined
- Observed distribution problems include:
 - Storage tanks contaminated with water or old fuel (diesel or biodiesel); bacterial growth
 - Trucks not clean; carry over residues to fuel
 - Improper techniques for blending and fueling
 - Aged fuel – oxidized, precipitates, sediments
 - Mixed batches of fuel from various suppliers
 - Oxidized (ruined) rail car loads last summer

Good Distribution Practices

- Clean dry storage tanks, rigorous tank maintenance and routine testing programs
- Inspection of each transport truck prior to loading; prior fuel only diesel or biodiesel
- Certificate of Analysis for batch delivered
- Proper blending, not just splash blending
- Filtration of fuel to at least 5 microns
- Protocols to prevent contamination
- Paper trails from supplier to end user
- Retain samples of B100 for end user

Field Test Kit Developed for B100: 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 dissolved contaminants; Now a QC protocol test
- Intended to alert a consumer or operator as a ‘firewall’, then they can request a formal lab test

Fuel Quality Test Concepts

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

Soluble contaminants in biodiesel can be:

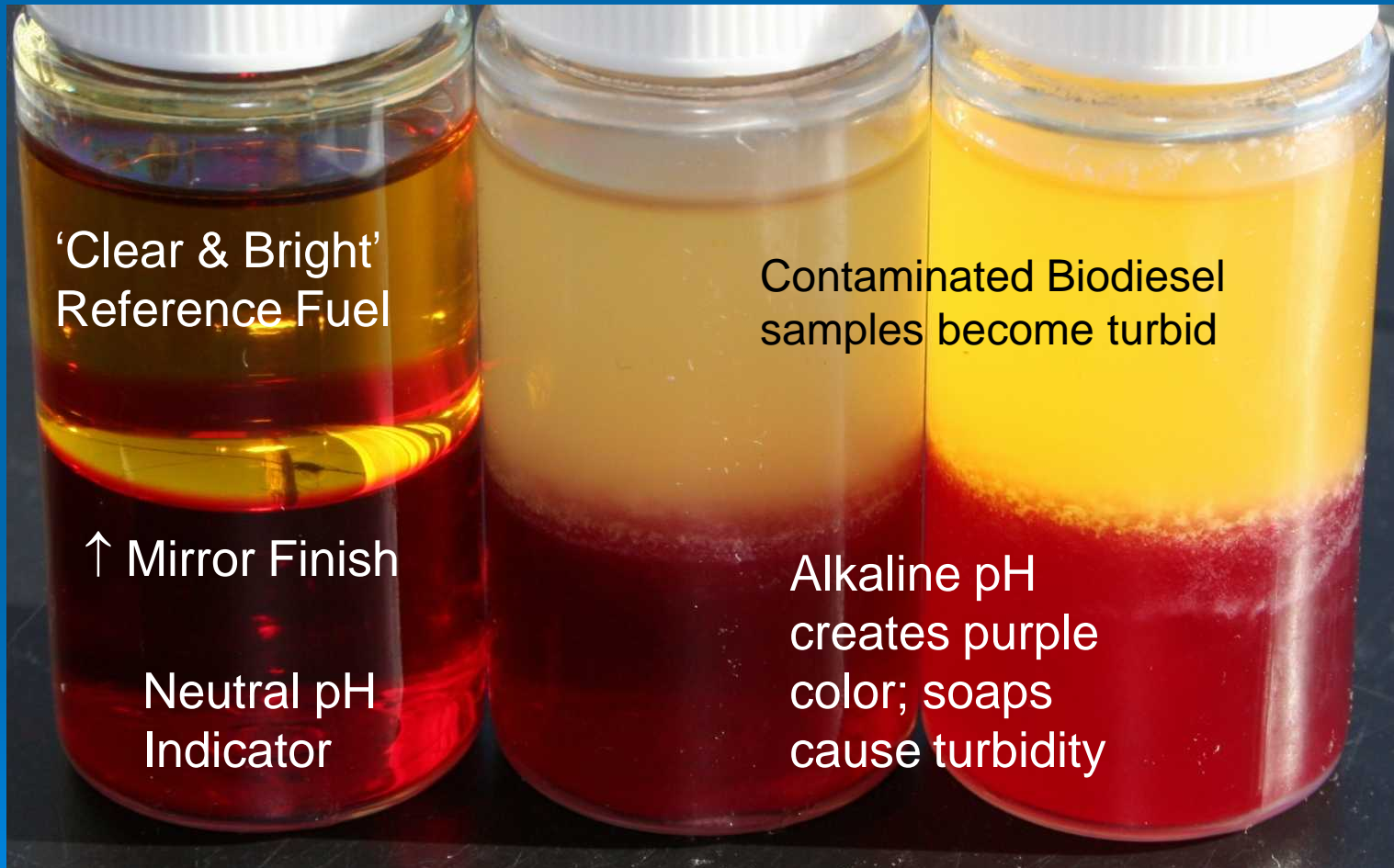
- >Extracted into the aqueous phase (fatty acid soaps) as visible turbidity

- >Concentrated at water-fuel interface (glycerides, sterols, oxidized esters)

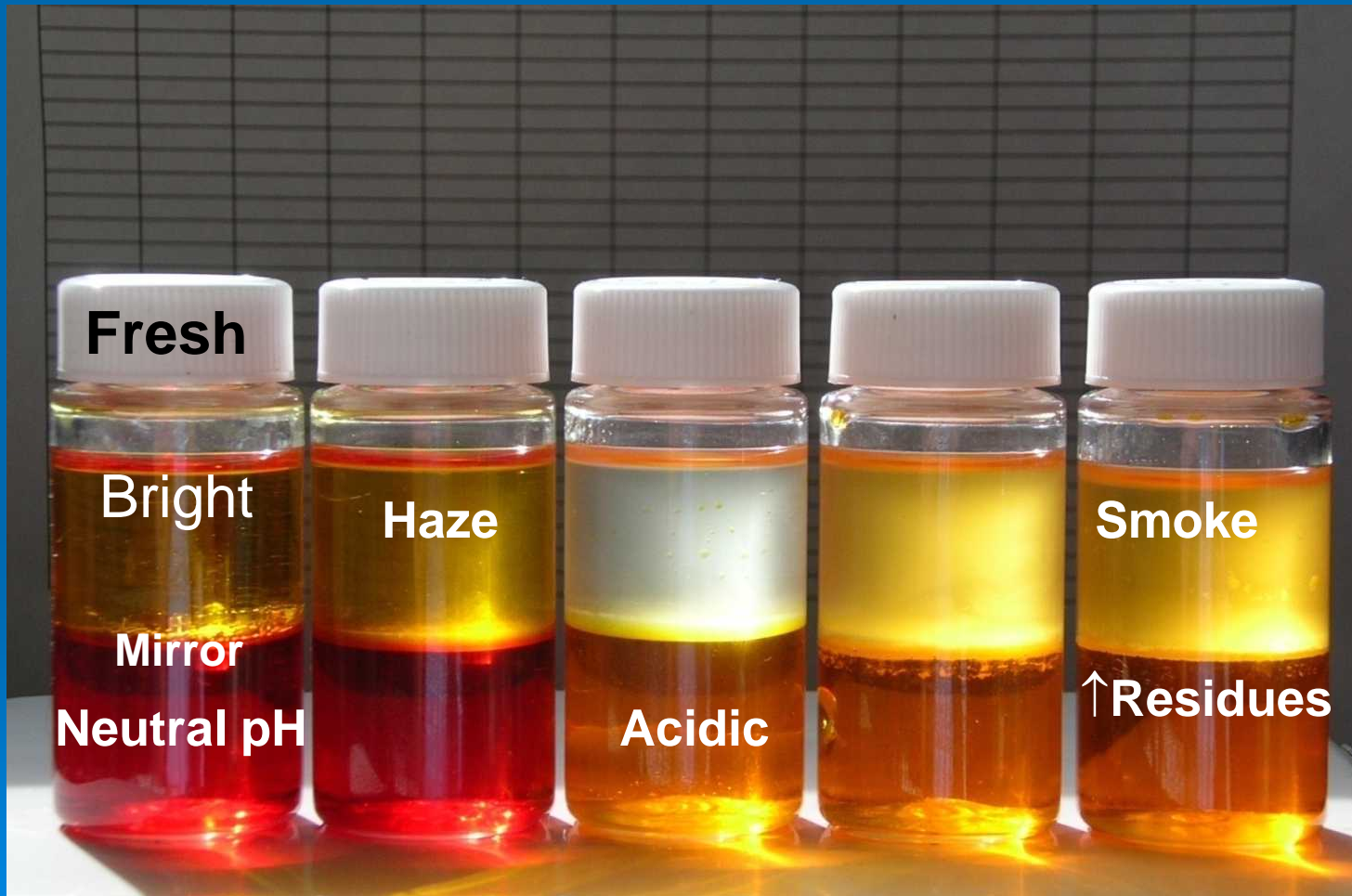
“Lens Effect” = Signal Amplification

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

Detection of catalyst contamination from poorly washed biodiesel fuels



Aging Oxidized B100 Examples Relative to Fresh Bright Reference



Titration of Acidic Aged Biodiesel into Reference Soy Biodiesel



Indicator Solution Color Shifts from Red to Yellow with more Acid

pH = 7.3

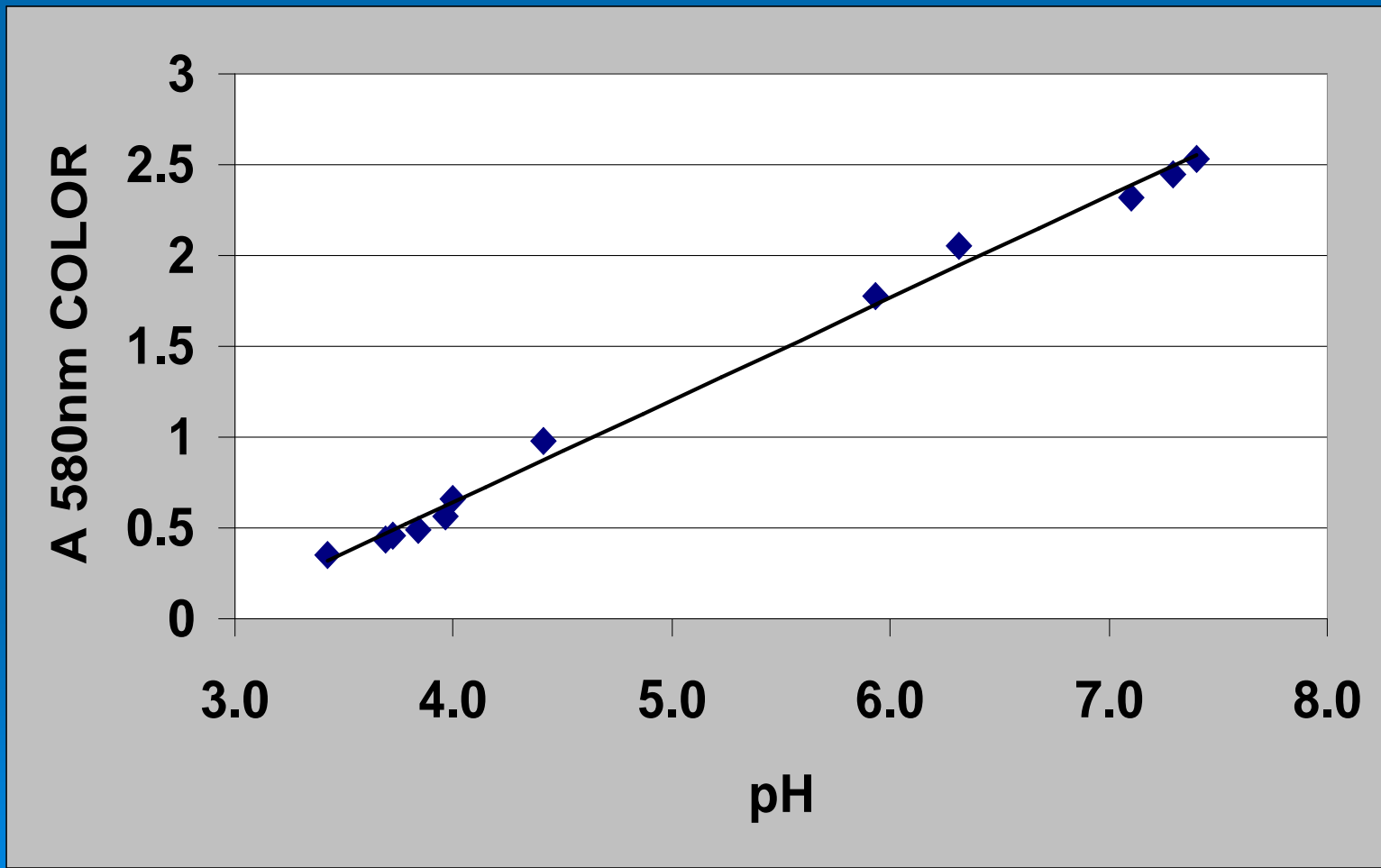
6.4

4.4

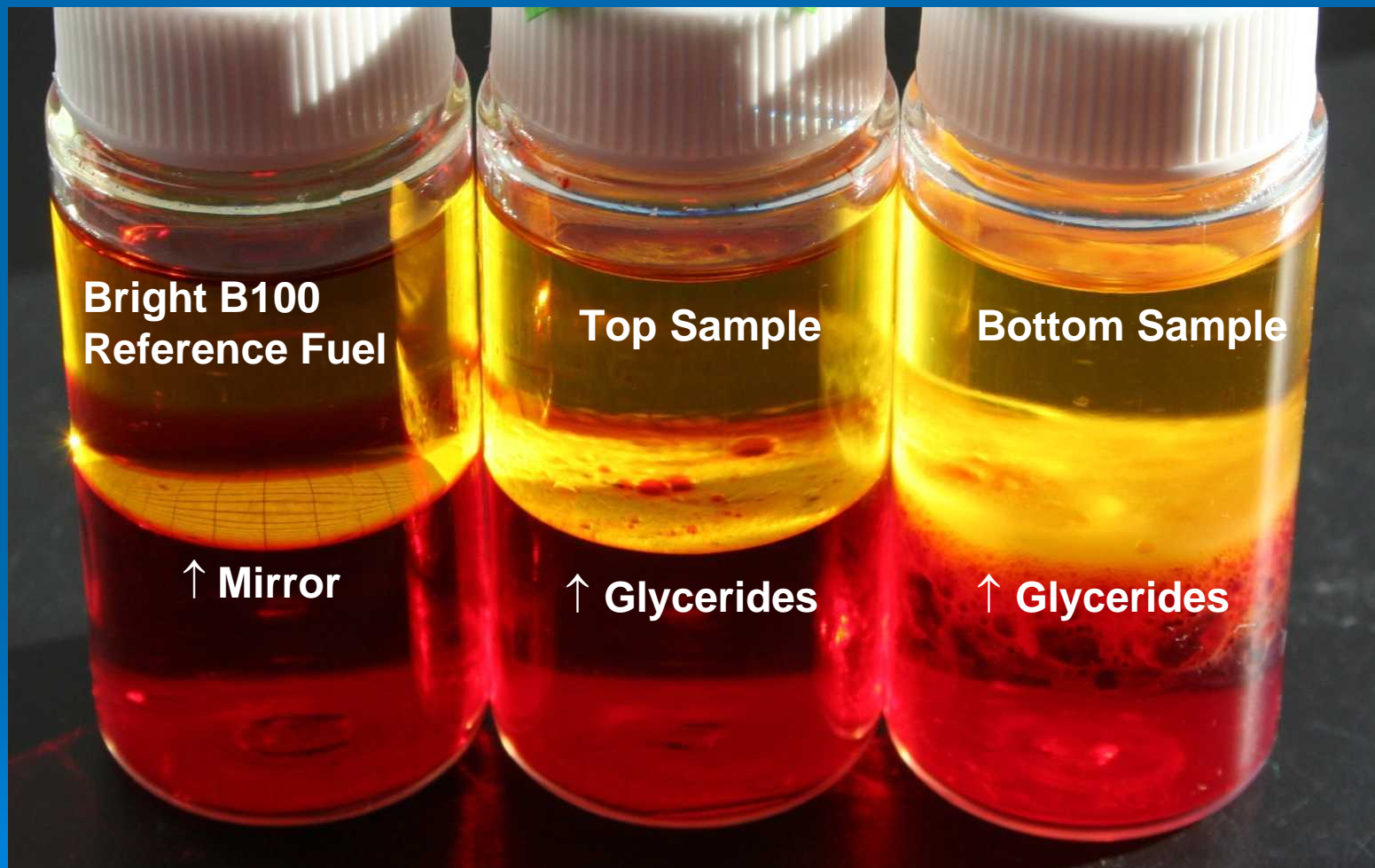
4.0

3.4

Test Color Shift is Linear with pH in Acidic Range



Detecting near-spec and off-spec fuel : top vs. bottom of rail car



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

Typical Results for Commercial ASTM Biodiesel Samples in CA

Often find B100 is “Near Spec” (marginal ASTM fuel)



Various feedstock B100 samples from producers or retail stations

The light “haze” is common for on-spec fuel; few have “Mirror Finish”

Rail Car Check with pHlip Test Corroborates Lab Data (Soy biodiesel)



Bottom

Middle

Top

Bottom Sample Lab Result: PASS

Total Glycerin = 0.16%, Acid No. = 0.12 mg KOH/g

“Biodiesel Quality Status Report”

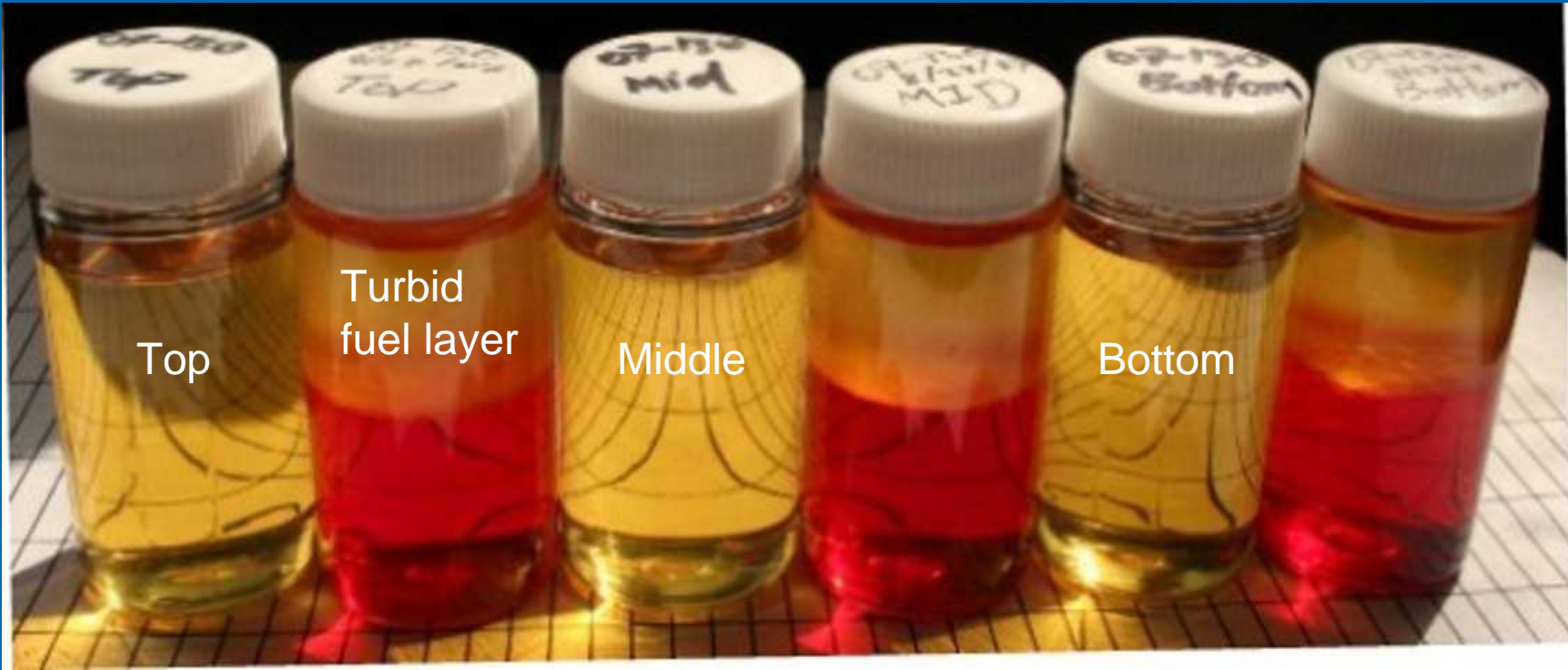
pHLip Test Results and Lab Data



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

All Specifications Tested were PASS – typical rail car load

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	MAX150-250?	470
CSFA Particulate Ct (mg/L)	ASTM D 6217b	< 50?	110



Biodiesel Quality Status Report Jan 31



TAN (mgKOH/g)	ASTM D 664	MAX 0.500	0.13
KF Water (ppm)	ASTM D 6304	MAX 500?	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

Conclusions on Monitoring Biodiesel Fuel Quality

- “Stuff” happens (still!)...during production, distribution, and sitting in end user’s tanks
- Most common production issues: partially reacted fuel (high glycerides) + sterols
- Most common distribution issue: oxidation
- Most common end user’s issue: dirty tanks
- Monitoring is easy, inexpensive and fast
- Field tests work as ‘firewall’ then lab tests
- Work with professional team to set up QA