Biodiesel from Crude Corn Oil (CCOE)

Dr. Louis A. Kapicak
Senior Research Scientist
Product and Process R&D
Lou.kapicak@matricresearch.com
800-611-2296 x-853

Chemical and Environmental Technologies
Health and Life Sciences
Advanced Engineering Systems

www.matricresearch.com
Current US Raw Material Costs

- RBD Soy Oil: $3.04/gal
  - Transesterification only

- Crude Soy Oil: $2.81/gal
  - Pretreatment, Transesterification

- Crude Corn Oil (CCOE): $2.05/gal
  - Esterification, (Pretreatment), Transesterification

- Yellow Grease: $1.97/gal
  - Esterification, (Pretreatment), Transesterification
Continuous Biodiesel Production Using Crude Corn Oil from Ethanol Plants (CCOE)

- **Esterification**
  - Two Stage Esterification
    - Residual FFA < 1%
- **Pretreatment (Optional)**
  - Removal of residual FFA/other impurities
- **Transesterification**
  - Multi-staged + intermediate decantation
- **Refining/CSFT Remediation**
  - Glycerin/soap/methanol removal & recovery
  - Removal of unique “cold flow culprits”
    - Increasingly tougher ASTM CSFT specifications
ASTM CSFT Specifications

- Test: Filter 300 ml pre-chilled (16 hrs.@ 4.5°C) B-100 through a 0.7µ filter at 21-25 in. Hg within a specified time, after warming the sample back to room temperature within a two hour period

- Of questionable value for predicting cold temperature performance

- Winter filtration time specification..................<200 Seconds

- Non-winter filtration time specification..............<360 seconds
Numerous Known “Cold Flow Culprits”

- Steryl glucosides in soy & canola (rapeseed) oils
  - High melting point solids
  - Aggregate with additional time and/or cooling

- Saturated monoglycerides, especially at higher BG values
  - Monopalmitate and Monostearin crystallize at low temperature
  - Readily re-dissolve at warmer temperature

- Residual soap, especially when very dry
  - Usually an outcome of incomplete washing & drying
  - Often found associated with glycerin

- General category often referred to as “Waxes”
What are “Waxes?”

- True vegetable waxes - Hydrophobic esters of high MW acids and alcohols
  - Located in skins of seed and their purpose is to repel water
  - Usually removed during food oil purification (winterization)
  - If present, would not survive transesterification reaction conditions
  - Are NOT a recognized CSFT problem

- “Wax” in CCOE is very different and very troublesome in B-100
  - Present in CCOE as supplied from the Ethanol plants
    - Concentrated in the “sludge” that separates from CCOE upon standing/cooling
    - Still soluble enough in pure CCOE to cause CSFT problem in resulting biodiesel
  - Remains chemically unchanged in the biodiesel process
    - Survives acidic esterification and basic transesterification
  - Very soluble in warm biodiesel
  - Plugs filters rapidly and completely when B-100 is cooled
  - As little as 25-35 ppm causes CSFT failure
What is this CCOE Wax?

- Readily soluble in hexanes/heptane; insoluble in polar solvents (MeOH, acetone)
  - Suggests material itself is very non-polar

- Melts over a range of temperatures (60-100°C)
  - Suggests a mixture of compounds

- GC confirms a “family” of similar compounds.

- GC retention times suggest molecular weights in 700-1000 amu range

- Unreactive to acidic and basic conditions

- Infrared also suggests material is very “hydrocarbon-like”
  - No functional groups detected besides C-H and “skeletal” vibrations
GC Scan of “Corn Wax”

Standard Biodiesel GC Program per ASTM D6584
IR Scan of “Corn Wax”

Re-crystallized multiple times from ethanol

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<th>Peak finding results for: Corn Wax</th>
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<td>1472.39</td>
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% Transmittance

- 1733.37
- 1462.189
- 1172.56
- 955.83
- 729.59
Are these Phytosterol Derivatives?

- Free phytosterols present in Corn Oil at ~ 1.2wt %
  - Campesterol..........................2691ppm
  - Stigmasterol...........................702ppm
  - beta-sitosterol.........................7722ppm
  - \( \Delta^5 \)-avenesterol...............468ppm
  - \( \Delta^7 \)-Stigmasterol..............117ppm

- Traditional refining of corn oil known to convert sterols into steradienes (dehydration) and disteryl ethers (etherification)
  - Occurs during acidic bleaching process
CCOE Waxes Could Be a Family of Disteryl Ethers

“Influence of processing on minor components of vegetable oils,”
Prof. Roland Verhé, University of Ghent
Free Sterols to Disteryl Ethers

**Test:** Mixture of commercial sterols was dissolved in “pure” biodiesel and heated to 80°C for one hour with benzene sulfonic acid present.

**Result:** Some of the sterols reacted to produce several of the peaks found in the GC of “corn wax”.

**Conclusion:** “Waxes” in CCOE and Biodiesel made from it appear to be a family of disteryl ethers, most likely formed during high temperatures at acid pH in the evaporation train of the ethanol plant.
Work performed by MATRIC on behalf of

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