Biofuels

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Topics to be Covered




1. What are biofuels?
2. FAME/Biodiesel
3. Bioethanol
4. Conclusions

1. What are biofuels?

Comparison with Traditional Fuels

- Traditional fuels such as coal and crude oil are derived from biological sources, but are only renewable on geological timescales
- Biofuels are fuels derived from renewable sources of organic matter or biomass, for example:
  - Plant material

  - Waste vegetable/animal oil

1. What are biofuels?

A New Phenomenon?

- Not for enterprising population of South Wales
  - **January 20th 2003**: Dramatic increase in sales of cheap cooking oil has local supermarket staff scratching heads
  - Assumed to be for cooking purposes: "healthy eating has not hit Swansea in a big way" says local supermarket manager, referring to the preference for low quality

  - However, local population mixing cooking oil with diesel for use in their cars
- But what are "official" biofuels?

1. What are biofuels?

Current Official Biofuels

- My talk will focus on two main official categories of liquid biofuels (so-called “first-generation” biofuels):

a. FAME (Fatty Acid Methyl Ester)/Biodiesel

- Produced from oilseed crops, animal fats
- Can be used neat but generally blended with conventional diesel

b. Bioethanol/Bioalcohol

- Produced from sugar and starch crops
- Can be used neat but generally blended with conventional gasoline

1. What are biofuels?

Legislation

- There is an increasing use of biofuels worldwide
- Europe
  - Renewable Energy Directive: 10% automotive fuel consumption from renewable sources by 2020
  - Intertanko estimates some 100 new biodiesel and bioethanol plants in Europe by 2010
- USA
  - Renewable Fuel Standard: Legislates 36 billion gallons of renewable fuel by 2022
- Asia & Latin America
  - Increasing exports of crude vegetable oils and processed FAME
- Hotly debated subject
  - Food versus fuels
  - Questionable environmental impact of biofuels

2. FAME/Biodiesel

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What is FAME/Biodiesel?

- FAME refers to the **Fatty Acid Methyl Ester** produced in the catalysed transesterification reaction of **methanol** with a **vegetable or animal oil**
- Triglyceride + Methanol $\longrightarrow$ Glycerol + Fatty Acid Methyl Esters
- This process brings the properties of vegetable oils (as FAMEs) more in line with conventional diesel
- FAME used in blend with conventional diesel
- Raw material used for production has a significant effect on the properties of FAME produced

2. FAME/Biodiesel

Raw Materials/Feedstock

- FAME can be produced from a number of oils or fats, including:

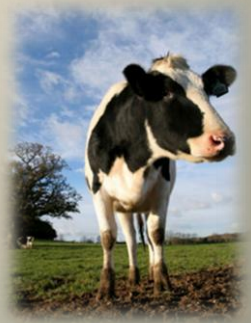
Rapeseed Oil

Sunflower Seed Oil

Soybean Oil

Coconut Oil

Palm Oil



Beef Tallow

FAME Composition

- FAME cargo may be product of processing any one of these oils or a mixture
- Each would give FAME of entirely different composition, yet they are all described as FAME
- High saturated fatty acid content (e.g. FAME from Coconut Oil) corresponds with good stability but poor cold temperature flow properties
- High unsaturated fatty acid content (e.g. FAME from Soybean Oil) corresponds with poor stability but improved cold temperature flow performance

2. FAME/Biodiesel

FAME Composition

- Other compositional characteristics are also important. For example, some believe that FAME with high Vitamin E contents are more stable than others!

2. FAME/Biodiesel

FAME for use as a fuel

- ASTM D6751 Biodiesel Fuel Blend Stock specification details **BXX** nomenclature for describing biodiesel blends (where XX is volume % of biodiesel in fuel)
- Example FAME formulations for automotive fuel use include:
  - **B100: 100% FAME (Neat Biodiesel)**
  - **B20: 20% FAME** & **80% conventional diesel**
  - **B5: 5% FAME** & **95% conventional diesel**
- European Diesel specification EN590 allows up to 5% by volume of FAME in diesel
- Canadian diesel specification CAN/CGSB-3.520 allows between 1.0% and 5.0% biodiesel content by volume
- **No biodiesel limits in US ASTM D975 diesel specification**

2. FAME/Biodiesel

FAME Problems 1 – Water

FAME Problems 1 – Water

- FAME is very prone to water contamination:
  - FAME is hygroscopic – will absorb water from surrounding environment, including from the atmosphere
- Specification limits:
  - EN 14214 B100 biodiesel specification: Maximum **500 mg/kg water**
  - EN 590 diesel specification: Maximum **200 mg/kg water**
  - However, selling specifications often quote a maximum of 300 or 400 mg/kg water (but Inspectors may still quote results against European 500 mg/kg maximum specification)
- Problems:
  - Water promotes hydrolytic reactions forming free fatty acids which can cause filter blockage and corrosion in FAME
  - Water also promotes microbial growth which can cause filter blockage
  - High water content in FAME may cause problems with phase separation when blended with conventional diesel

FAME Problems 1 – Water

- Possible sources of water contamination include:
  - Humidity in storage or ship's tanks
  - Failure of seals and valves allowing atmospheric humidity to enter tanks
  - Leaks in tanks allowing sea water or rain to enter
  - Water residue from tank cleaning operations
  - Possibility of moisture in inert gas blanket (if used – not currently mandated use of inert gas – therefore possibility of absorption of atmospheric moisture from tank ullage space)
  - Transfer operations introduce potential for water contamination e.g. ocean going vessel to barge transfer before final discharge – with two parties involved there is potential problematic recourse for cargo owners/Underwriters in case of contamination

2. FAME/Biodiesel

FAME Problems 2 – Stability

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- FAME is more prone to stability problems than conventional diesel
- FAME can degrade under the influence of air, heat, light and water
- Degree of stability is dependent upon the feedstock used for FAME production
- In general, stability issues will be worst for FAME composed of high proportion of poly-unsaturated fatty acids
- Problems effect both B100 & FAME/Diesel blends

FAME Problems 2 – Stability

- FAME degradation forms insoluble sediments and gums
- These species can increase the viscosity of the FAME, block filters and degrade to other more corrosive species
- Degradation can be promoted by the presence of copper (heating coils) and zinc (tank coatings)
- From Insurers' point of view, perhaps these problems can be considered inherent vice

2. FAME/Biodiesel

FAME Problems 3 – Low Temperature Properties

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FAME Problems 3 – Low Temperature Properties

- At low temperatures certain components of a fuel begin to crystallise and precipitate out as wax/sediments
- The temperature at which wax precipitation occurs in FAME is higher than for conventional diesel
- Low temperature properties of FAME are dependent upon feedstock
  - Saturated FAME worse than unsaturated FAME
- Issues for both B100 and FAME/Diesel blends
- Problems with end use which I won't touch on in this talk
- May be problems for Insurers with precipitation of solids onboard vessel which cannot be easily re-dissolved
  - Specification failure
  - Potential losses

2. FAME/Biodiesel

FAME Problems 4 – Trace FAME in Jet Fuel

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- Use of multi-product pipelines gives potential for FAME carry over into jet-fuel
- FAME is surface active material so can adsorb onto tank or pipeline surfaces and de-adsorb into subsequently carried products
- Trace FAME is currently not permitted in Jet Fuel
- Currently proposals for test methods to measure FAME in jet fuel down to 5 ppm maximum

2. FAME/Biodiesel

FAME Problems 5 – Solvent Properties

FAME Problems 5 – Solvent Properties

- Refers to the ability of a fuel to loosen and take into suspension organic residue, dirt or scale
- FAME, even when blended with diesel at B5 level, can act as “degreaser”
- Can have the effect of “cleaning” storage and pumping systems but contaminating itself
- Re-dissolved and suspended material can clog filters
- This characteristic may lead to claim for particulate contamination

3. Bioethanol

3. Bioethanol

What is Bioethanol?

- Bioethanol is an **alcohol** – ethanol – derived from the fermentation of renewable sources of **sugars** or **starches**
- Raw Materials:
  - Sugars:
    - Sugar cane stalks
    - Sugar beet tubers
    - Sweet sorghum stalks
  - Starches:
    - Corn
    - Wheat
    - Cassava

Sugar Cane

Wheat

Corn

- Ethanol is a single chemical compound unlike FAME, which is a mixture of compounds

Bioethanol Properties

- Properties of ethanol are well understood:
  - Ethanol is the alcohol used in alcoholic beverages
  - Colourless liquid
  - Flammable
  - Miscible with water
  - Considerable experience worldwide of shipping ethanol

Bioethanol for use as fuel

- Can be used neat or as a blend with conventional fossil fuel derived gasoline
- European gasoline specification EN228 allows up to 5% bioethanol by volume (Denoted **E5** gasoline)
- US Colonial pipeline specification allows up to 10% ethanol in gasoline (Denoted **E10** gasoline)
- In countries such as Brazil blends can be much higher – up to 85% to 100% in flexible fuel vehicles

3. Bioethanol

Bioethanol Problems 1 - Water

Bioethanol Problems 1 - Water

- Ethanol is hygroscopic and completely miscible with water
- For bioethanol/gasoline blends, there is a critical threshold level of water that can be dissolved (typically 0.2% v/v at 15^{o}C for E5)
- Once level has been exceeded **irreversible** phase separation into an alcohol rich aqueous phase and alcohol poor gasoline phase will occur
- Alcohol rich aqueous phase will be highly corrosive and accumulate at bottom of ship's tank or storage tank – this phase cannot be used as fuel
- Alcohol poor gasoline phase will possibly be off-specification (reducing ethanol content of gasoline decreases the RON & MON of gasoline)

Bioethanol Problems 1 - Water

- Possible sources of water contamination same for bioethanol as for FAME
- This leads to an important question – where is blending with gasoline going to occur?
- Recommended as close as possible to point of sale to avoid water pick-up issues in transport from refinery to fuel pump

3. Bioethanol

Ethanol Problems 2 – Solvent Properties

Ethanol Problems 2 – Solvent Properties

- Like FAME, bioethanol is a strong solvent
- Bioethanol can loosen and take up organic residues, dirt and scale from storage tanks and line systems, thereby “cleaning out” tanks and lines but contaminating itself
- This can cause subsequent operational problems with filter blocking

4. Conclusions

4. Conclusions

Problems with FAME/Biodiesel

- Very sensitive to **water contamination.**
- Questions with regard to **stability.**
- Poor **low temperature properties.**
- Use of FAME/diesel blends in **multi-product pipelines** gives potential for **jet fuel contamination.**
- Acts as a **solvent** “cleaning out” dirty storage tanks and lines but contaminating itself.
- Inherent vice is an issue.

4. Conclusions

Problems with Bioethanol

- Very sensitive to **water contamination.**
- Acts as a **solvent** “cleaning out” dirty storage tanks and lines but contaminating itself.
- Inherent vice is an issue.