The potential and challenges of “drop in” biofuels

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International Energy Agency Bioenergy Task 39 (liquid biofuels)
Commissioned Task 39
‘drop in’ biofuel report

- OVERVIEW
  - Definition
  - Role of Hydrogen in drop in biofuels
  - Role of Hydrogen in petroleum industry

- TECHNOLOGIES
**Definition of a “drop-in” biofuel**

- Bioethanol: Biogenic ethyl alcohol
- Biodiesel: Fatty acid methyl esters (FAME)
- Drop-in biofuels are liquid hydrocarbons that are **functionally** equivalent and as **oxygen-free** as petroleum-derived transportation blendstocks (fuels)
- Examples:
  - Hydrotreated Vegetable Oils (HVO)
  - Hydrotreated Pyrolysis Oils (HPO)
  - Fischer Tropsch Liquids (FT liquids)
Properties of transportation fuels

Drop-in biofuels need to have similar properties to petroleum fuels:

- Fit the **carbon number** range
- Low to **No oxygen**

Unlike conventional biofuels, “drop-in” biofuels should be indistinguishable from petroleum fuels **for end uses**!
Oxygen Challenge

- Oxygen is present in biomass in the form of hydroxyls, esters, and ethers
- Can oxidize fuel components, reactors and pipeline metallurgy to cause corrosion
- Oxygen content reduces energy density

Ethanol

\[
\text{CH}_3\text{C}_n\text{H}_{2n+1}\text{O}_n\text{H}
\]

Biodiesel (fatty acid methyl ester)
Increasing Oxygen content reduces fuel energy density

- Crude oil (No O_2)
- Biodiesel (11% O_2)
- Butanol (21.5% O_2)
- Ethanol (35% O_2)
- Biomass/Sugar (50% O_2)

R^2 = 0.99438

The graph shows the relationship between Oxygen content and energy density.
Deoxygenating biomass dilemma
...add $H_2$ or lose yield?

Insert Hydrogen

$H_2$  \(-H_2O\)

A Carbohydrate e.g. Glucose

$C_6H_{12}O_6$

Oxidize Carbon

“sacrificing” feedstock

-\(CO_2\)

A Hydrocarbon e.g. Butane

$C_4H_{10}$

High H/C $\approx 2$

Objective is to deoxygenate and enrich $H_2$ content of biomass
Effective hydrogen to carbon ratio ($H_{\text{eff}}/C$)

- A high Effective Hydrogen to Carbon ratio is desired for drop-in biofuels

- $H_{\text{eff}}/C = \frac{n(H) - 2n(O)}{n(C)}$

**Carbohydrate**

$H_{\text{eff}}/C = 0$

**Hydrocarbon**

$H_{\text{eff}}/C \approx 2$

(e.g. Butane, Diesel)
The Effective H/C ratio staircase...

More H₂ inputs required

High O₂ or low H/C feedstocks require more processing and H₂ inputs
“Drop-in biofuels” is a loose term referring to liquid biofuels containing low or no oxygen content.

Deoxygenation requires hydrogen inputs or “oxidizing/burning” of feedstock carbon.

High $H_{\text{eff}}/C$ ratio feedstocks such as lipids are well suited for drop-in biofuel production.
What will determine the success of “drop in biofuels”?

- Drop-in biofuel technologies complexity/selectivity and hydrogen demand
- Commercialization challenges such as capital, yield and refinery insertion
- Crude oil is becoming increasingly hydrogen deficient (‘heavier’ and ‘sourer’)

Crude oil quality declining...

"Heavy" and "Sour" oil increasing

Purvin & Gertz forecast for world crude oil quality (Source: data from EIA)

"Sour" = High Sulfur

Purvin & Gertz forecast for world crude oil quality (Source: data from EIA)
The H/C ratio staircase for petroleum...

Lower quality fossil feedstocks = lower H/C ratio = higher H₂ inputs
Hydrotreating and Hydrocracking

- Hydrotreating (Removes sulfur impurities as $\text{H}_2\text{S}$)
- Hydrocracking (breaks heavy oil to lighter molecules)
US Hydrotreating capacity 1990-2030

Rapid increase in H₂ consumption in US refineries

Source: EIA, Annual Energy Outlook 2006
Natural gas: Where $H_2$ comes from

- 90% of commercial $H_2$ comes from **steam reforming natural gas**

\[
\text{CH}_4 \rightarrow \text{Steam reforming} \rightarrow H_2 \]

\[\text{CO}_2\]

ENERGY INTENSIVE PROCESS!!
Role of $\text{H}_2$ in upgrading petroleum and drop-in biofuels

<table>
<thead>
<tr>
<th>Petroleum</th>
<th>Drop-in Biofuels</th>
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<tbody>
<tr>
<td>Increasing <strong>Sulfur</strong> content</td>
<td>No Sulfur</td>
</tr>
<tr>
<td>Increasing <strong>heavy</strong> oil needs cracking</td>
<td>High <strong>Oxygen</strong> content of feedstock needs hydrogenation</td>
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Both require Hydrogen for upgrading to finished fuels

Hydrogen will likely come from Natural Gas
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The commercialization potential of Drop in Biofuel platforms and their $H_2$ dependence

- Oleochemical (HVO, algae)
- Thermochemical (Pyrolysis - HPO, Gasification FT-liquids)
- Biochemical (Advanced Fermentation)
- Hybrid platforms (e.g. Virent, Zeachem, Lanzatech)
Technology pathways to “drop-in”

**CONVENTIONAL INTERMEDIATES**
- Sugar crop
- Hydrolysis → Sugars
- Gasification → Syngas
- Pyrolysis → Biooil
- Animal digestion
- Oilseed crop
- Autotrophic algae

**Technology Pathways**
- Sun photons, water, CO₂ and nutrients
- Biomass fiber

**Bio**
- Fermentation
  - Higher alcohols (e.g. Gevo)
- Catalytic conversion
  - Isoprenoids (e.g. Amyris)
- Upgrading
  - FT liquids (e.g. CHOREN)
  - HPO (e.g. ENSYN)

**Thermo**
- Hydroprocessing
- Blending
- FT liquids (e.g. CHOREN)
- HPO (e.g. ENSYN)

**OLEO**
- Materials
- Processes

**LEGEND**
- drop-in fuel

Forest Products Biotechnology/Bioenergy at UBC
Oleochemical Platform
Hydrotreated Vegetable Oils or HEFAs

Major advantages

- “Simple” technology, low risk (processes already commercial)
  - Bio SPK ASTM certification
- High Hydrogen to carbon ratio (low Oxygen) of Feedstock
  - Palm oil
  - Tallow (rendered animal fat)

Challenges

- Costly feedstock (approx. $500-1000/t)
- Sustainability?
Commercial drop-in biofuel companies

- All based on oleochemical
  - Neste Oil: 2,400,000,000 L diesel from palm oil
  - Dynamic Fuels: 280,000,000 L diesel from animal fat
Many examples of commercial biofuel flights

- Virtually all based on oleochemical
  - US Navy: Sept 2011 Solazyme algae oil and palm oil
  - Continental Airlines: Nov 2011 Solazyme algae oil
  - Alaska Airlines: Jan 2012 tallow and algae
  - Lufthansa: July 2011 Jatropha, Camelina
  - Finnair: July 2011 Used Cooking Oils
- Many more
Thermochemical drop-in biofuel platforms

INTERMEDIATES

- Pyrolysis oil
  - 500°C
  - No O₂
- Gasification Syngas
  - 900°C
  - Some O₂

CATALYTIC UPGRADING

- Hydro treatment 1
- Hydro treatment 2
- FT liquids
- HPO

HYDROCRACKING

- Gases
- Gasoline
- Jet
- Diesel
Example of pyrolysis drop in facility: KiOR

- 50,000,000 L per year in Mississippi (in operation)
Forest BtL Oy and Choren’s Carbo-V

- 130,000,000 L per year of Gasification FT liquids by 2016 (Finland)
Feedstock and Capital cost of drop-in Biofuels

Feedstock intensive vs Capital intensive platforms

Source: Kazi et al. 2010, Pearlson et al. 2011, Jones et al. 2009
“Over the fence” Hydrogen inputs can reduce capital and feedstock costs

Over the fence Hydrogen inputs can reduce capital and feedstock costs.

Pyrolysis is highly dependent on access to cheap Hydrogen.

Source: Kazi et al. 2010, Pearlson et al. 2011, Jones et al. 2009
Drop in biofuels leveraging on Oil refineries

OLEOCHEMICAL
- Lipids

THERMOCHEMICAL
- Biomass
  - Pyrolysis oil
- Gasification
  - Syngas
  - Fischer-Tropsch
    - FT liquids
    - HPO

OIL REFINERY
- Hydrocracking
  - Over the fence $\text{H}_2$
  - Gases
    - Gasoline
  - Jet
  - Diesel

Forest Products Biotechnology/Bioenergy (FPB/B)
Drop in biofuels leveraging on Oil refineries

**DISTILLATION**
- Crude oil
- Distillation tower
  - Light ends
  - Heavy ends
- Vacuum unit

**(CATALYTIC) UPGRADING**
- Lipids
- FT liquids
- HPO
- Reformer
- Hydrocracker
- Fluid catalytic cracking
- Hydrotreatment
- H₂

**BLENDING**
- Gasoline
- Jet
- Diesel, Jet
- Diesel, Jet
- Gasoline
- Coke

**Product blending**

Forest Products Biotechnology at UBC
Challenges of hydroprocessing biofeed: The Haldor Topsoe experience

- Higher Hydrogen consumption
  - requirements more than doubled when just 5% of feed was replaced with biofeed!

- Presence of oxygenated gases such as CO and H$_2$O

- Heterogeneity of feedstock (Catalyst design challenges)

Source: Haldor Topsoe, 2009
Major scale up challenges for each platform

- Pyrolysis
  - Hydrogen
  - Hydrotreating catalyst

- Gasification
  - Capital / scale
  - Feedstock / yields

- HVO oleochemical
  - Feedstock

- Refinery insertion challenges

Sources: Jones et al. 2009; Swanson et al. 2010; Pearlson et al. 2011
Biochemical: Sugar fermentation to drop-in

- **Major advantages**
  - Pure and “functionalized” product streams suitable for value added markets

- **Major challenges**
  - Volumetric productivity about \(10\times\) lower than ethanol
  - Recovery challenges: e.g. recovery from fermentation broth and intracellular expression
  - Sugar feedstock **highly oxidized** \((H/C = 0)\)
Fermentation pathways for deoxygenating Carbohydrates

Compared to ethanologenic yeast:

- Energy intensive
- High requirement for reducing power (derived from NADPH or Hydrogen)

Lanzatech CO₂ + H₂ example
Climbing fewer steps on the $H_{\text{eff}}$ /C staircase...

‘Drop-in’ biofuels

- Lipids: 1.8
- Butanediol: 1.4
- Ethylene glycol: 1.2
- Levulinic acid: 0.8
- Adipic acid: 0.6
- Wood: 0.4
- Sugar: 0

Diesel: 2.0

Value-added biorenewables

$H_{\text{eff}}$ /C ratio

Value added chemicals have lower $H_{\text{eff}}$ /C ratios than fuels.
Summary

- Oleochemical: commercial now and less H\textsubscript{2}-dependent with considerable potential for growth (feedstock challenges?)

- Thermochemical well suited for long term drop-in biofuels
  - H\textsubscript{2} and catalyst challenges (Pyrolysis), Scale challenges (Gasification)
  - Leveraging on oil refineries: more challenging than expected

- Biochemical “drop-in” products more valuable in rapidly growing chemicals markets

- Accessing cheap/renewable Hydrogen will be a key challenge for both drop-in biofuels and crude oil of decreasing quality
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www.Task39.org
Future competition for Hydrogen inputs...

- Heavy oil processing
e.g.
Venezuela and Alberta

- Ammonia industry

- Drop-in biofuels?