Emerging and Future Biofuels

Robert L. McCormick, Matthew Ratcliff, Bradley T. Zigler

CRC Advanced Fuel and Engine Efficiency Workshop

Baltimore, MD
February 26, 2014
The Big Picture: Achieving 80% CO₂ Reduction

Constraints: Cost, Scale, Safety, Consumer Choice, Environmental Impact, Policy (Urban Planning)

Reduced Carbon Intensity

Vehicle Energy Consumption (kWh/km) vs. Carbon Intensity of Energy Carrier (g/kWh)

Typical Car Today

2010

345 g/km

2030

129 g/km

2050

38 g/km
Fuel Enabled Trends in Engine Efficiency

**Spark Ignition**

- Current CR limited to about 10 because of engine knock at higher values
- Smaller, highly boosted engine operated at low-speed is more efficient and also knock limited
- Enabled by higher knock resistance fuel (RON, HOV, flame speed)

**Compression Ignition**

- Lower compression ratio reduces friction, engine size/weight, and NOx
- Lower weight parts-higher engine speed
- Trend towards reduced CR, but CR<15 is not achieved, primarily due to cold start problems
- Lower CR and higher speed enabled by higher cetane number fuel
Biomass-Based Gasoline Options

Sugar: corn, cane, or biomass
- Biochemical Conversion → Ethanol, Isobutanol
  - Commercial scale
- Catalytic Reforming → Renewable Gasoline
  - Pilot scale

Lignocellulosic Biomass
- Fast Pyrolysis-Hydrotreating → Renewable Gasoline
  - Pilot scale
- Gasification-Alcohol Synthesis → Mixed Alcohols
  - Bench scale
- Acid/Base Depolymerization-Upgrading → Gasoline Oxygenates
  - Bench scale

Algal Biomass
- Hydrothermal Liquefaction-Hydrotreating → Renewable Gasoline
  - Pilot Scale?

Sunlight
- Photosynthesis-Metabolic Engineering → Ethanol, Renewable Gasoline
  - Pilot Scale?

NATIONAL RENEWABLE ENERGY LABORATORY
Ethanol Enables Efficient Engine Technologies

• Ethanol research octane number is higher than that of today’s hydrocarbon gasoline
• For direct injection engines fuel evaporation occurs in the cylinder – cooling the charge and reducing knock tendency
• Alcohols have significantly higher heat of vaporization (HoV) leading to a higher “effective RON”


Isobutanol

- Higher energy content, much lower water solubility
- Similar or identical GHG emission reduction as ethanol
- Refiners make sub-octane hydrocarbon blendstock
  - Meets AKI requirement when ethanol is added
  - Isobutanol may not be high enough octane
- Butanols lower RVP of gasoline
  - Allows blending of higher levels of butane and pentane – year round
  - *Worth billions of dollars annually to North American refiners?*
- Heat of vaporization lower than ethanol (579 kJ/kg vs 837 kJ/kg), but greater than hydrocarbon (350 to 400 kJ/kg)
Cellulose-Derived Oxygenates

- Acid catalyzed deconstruction of cellulose/hemicellulose, or pyrolysis
- Some potential oxygenate products have very high octane numbers, insoluble in water, low heat of vaporization

**Knock Resistance Metrics**
- Multiple high octane bio-derived materials
- RON, HOV, Flame Speed must all be considered (and other factors?)
- How to specify knock resistance in a fuel standard?

![Chemical reactions diagram](image)
Biomass-Based Diesel Options

- **Sugar:** corn, cane, or biomass
  - Biochemical Conversion
    - Biodiesel / Renewable Diesel
  - Catalytic Reforming
    - Renewable Diesel

- **Lignocellulosic Biomass**
  - Fast Pyrolysis-Hydrotreating
    - Renewable Diesel
  - Gasification-FT Synthesis
    - FT-Diesel/Renewable Diesel

- **Algal Biomass**
  - Hydrothermal Liquefaction-Hydrotreating
    - Renewable Diesel

- **Sunlight**
  - Photosynthesis-Metabolic Engineering
    - Renewable Diesel

- **Oils and Greases (Algae)**
  - Biodiesel Production
    - Biodiesel
  - Hydrotreating
    - Renewable Diesel

- **Commercial scale**
- **Pilot scale**
- – Demonstrated
  - – Pilot Scale?
  - – ?
High Cetane Biomass-Based Diesel: Biodiesel, Hydrogenated Esters and Fatty Acids, Terpenoids

- HEFA fuels are highly isomerized (85%+) to lower CP
- Terpene hydrogenation/ring-opening leads to a very limited group of hydrocarbon products
- Large life-cycle GHG emission reduction for fats/oils, unknown for terpenes

Terpenoid-Derived:
- 2,6 dimethyl octane
- Farnesane

Biodiesel (FAME):
Lignocellulosic Biomass

- Hardwoods
- Grasses
- Crop residues
- Softwoods
- MSW

- Over 1 billion annual tons available in US by 2050
- Potentially 80+ billion annual gallons of biofuel
- 400 million tons available today
- Wide range of costs
Ligno-Cellulosic Biomass to Hydrocarbon Biofuels?

- Biomass has high oxygen content:
  - 40 to 60 wt%
  - Molar O/C about 0.6
- Economically rejecting this oxygen may not be possible
- Hydrotreating costs for fast-pyrolysis oils can be very high

Lignin: 15%–25%
Hemicellulose: 23%–32%
Cellulose: 38%–50%

Biomass-Derived Oxygenate Boiling Points

Cellulose-Derived Diesel Oxygenates

**Pyrolysis**
- Propyl and other alkyl phenols:

- Low CN, bp 200-250°C
- Do not appear to negatively affect fuel stability, cold weather performance, etc
- Are renewable benefits worth the cost of higher CN blendstock or CN additives?

**Acid deconstruction**
- Pentyl ethers and esters

- Little or no effect on diesel properties other than CN

\[\text{CN}=111\ \text{bp}=204^\circ C\]
\[\text{CN}=96\ \text{bp}=173^\circ C\]
\[\text{CN}=30\ \text{bp}=204^\circ C\]
Summary

• A broad range of new biofuels are at different stages of research and development

• These include high octane number molecules that may be appropriate fuels for highly efficient SI engines
  - An important research need is for a knock resistance metric that encompasses RON, heat of vaporization, and flame speed

• Emerging renewable diesel fuels include:
  - High cetane number paraffins derived from triglycerides and terpenoids, as well as relatively high cetane biodiesel
  - Low cetane number aromatic streams that would require higher cetane blendstocks or cetane improving additives
  - High cetane number isoamyl and pentyl ethers

• While not discussed, fuel properties that might enable low-temperature combustion (HCCI or PCCI) need to be better defined