Co-Production of Fuel Alcohols & Electricity via Refinery Coke Gasification

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Study Objectives

- Evaluate the concept of producing synthetic mixed alcohols which may be suitable for gasoline blending using petroleum coke gasification as feedstock in a refinery setting

- Present overall plant performance data and project economics for co-production of fuel alcohols and electricity for a large facility at a typical Gulf Coast refinery
Topics

- Overview of Potential Gasification Products
- Mixed Alcohols Synthesis Process (PEFI)
- Features of Fuel Alcohols Co-Production
- Mixed Alcohols Synthesis Unit
- Integrated Configuration
- Study Parameters
- Plant Performance
- Economic Evaluation
- Discussion of Results
Potential Gasification Feeds and Products

Potential Feeds
- Natural gas
- Residual oils
- Orimulsion
- Petroleum coke
- Coal
- Waste Oils
- Biomass
- Black liquor
- Sewage Sludge

Gasification Plant
- Slag for Construction Materials

Combined Cycle
- Electric Power
  - Hydrogen
  - Carbon Monoxide
  - Fertilizer (Urea, ammonium nitrate)
  - SNG
  - Industrial Chemicals
  - Methanol, Higher Alcohols
  - Acetic Acid
  - Naphtha
  - Diesel
  - Jet Fuel
  - Wax

Chemical Production

Fischer-Tropsch Synthesis

Potential Products
- Oxygen
- Nitrogen
- Argon
- Carbon Dioxide
- Sulfur/Sulfuric Acid
- Steam

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Mixed Alcohols Synthesis Process

- Process developed by Power Energy Fuels, Inc. (PEFI) of Denver, CO
- Ecalene™ is PEFI’s trade name for mixed alcohols blending stock ((R+M)/2) of approximately 124 as tested
- Ecalene adds oxygen to gasoline required by federal mandates and provides a potentially attractive octane blending compound
- Fluor developed a plant design for a mixed alcohols demonstration unit for the Texaco Cool Water Gasification Project (not constructed)
Reactions for the Synthesis of Alcohols

**Alcohols Synthesis**

\[(n+1)\, \text{H}_2 + (2n-1)\, \text{CO} = C_n\text{H}_{2n+1}\text{OH} + (n-1)\, \text{CO}_2\]

**Shift Conversion**

\[\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2\]
## Hydrogen to CO Ratio

<table>
<thead>
<tr>
<th>Product</th>
<th>H₂/CO Stoichiometric Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>(Full Shift)</td>
</tr>
<tr>
<td>F-T Liquids</td>
<td>2.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>(Full Shift)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.0</td>
</tr>
<tr>
<td>Propanol</td>
<td>0.8</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Features of Fuel Alcohols Co-Production

- The synthesis catalyst is sulfur tolerant making syngas cleanup simpler and less expensive.
- Propanol can be separated for sale as a higher value chemical if market exists.
- Methanol yield is relatively small compared to ethanol production.
- Separated methanol can be utilized as a peak fuel in a stand-alone gas turbine (can be enhanced with a chemical recuperation cycle).
Features of Fuel Alcohols Co-Production (continued)

- High alcohols produced can be used on-site for gasoline blending avoiding transportation and large storage costs
- Alcohol mixture produced has been registered with the EPA as a gasoline and diesel additive
- Production of carbon containing fuel ethanol is an indirect method of carbon capture
Mixed Alcohols Synthesis Unit

Clean Syngas
- CO: 18,380 mol/h
- H2: 18,380 mol/h

MIXED ALCOHOLS SYNTHESIS UNIT

Fuel Gas
- CO: 4,100 mol/h
- H2: 4,900 mol/h
- CO2: 5,500 mol/h
- C1-C4: 890 mol/h

Mixed Alcohols
- Methanol: 95 ST/D
- Ethanol: 1,200 ST/D
- Propanol: 490 ST/D

Steam

BFW
Integrated Gasification Configuration for Co-Production of Power & Mixed Alcohols

- Petroleum Coke Feedstock
- Process Units
  - Air Separation Unit
  - Gasification
  - CO Shift and Heat Recovery
  - Sulfur Recovery Unit
  - Mixed Alcohols Synthesis Unit
  - Fractionation
  - Methanol Storage & Evaporator
  - Power Block (1 x GE 7FA+e combustion turbine)
Block Flow Diagram
Electrical Power Production with Mixed Alcohols Synthesis

**NOTES:**
- BFW = BOILER FEEDWATER
- CO = CARBON MONOXIDE
- CWS = COOLING WATER SUPPLY
- CWR = COOLING WATER RETURN
- H₂ = HYDROGEN
- HP = HIGH PRESSURE
- N₂ = NITROGEN
- O₂ = OXYGEN

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Study Parameters

- Location: Typical US Gulf Coast Refinery Site
- ISO Site Conditions
  - 59°F DB/ 60% RH
  - Barometric Pressure: 14.7 psia
- Cooling Water System: Mechanical Draft Cooling Tower
### Petroleum Coke Analysis

<table>
<thead>
<tr>
<th>Ultimate Analysis, Wt%</th>
<th>Dry Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>89%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>5%</td>
</tr>
<tr>
<td>Ash</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HHV (Dry Basis)</th>
<th>Btu/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15,160</td>
</tr>
</tbody>
</table>
## Overall Performance Summary

<table>
<thead>
<tr>
<th>Description</th>
<th>IGCC w/Mixed Alcohol Synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feed</strong></td>
<td></td>
</tr>
<tr>
<td>Coke Feed Rate st / day (dry)</td>
<td>4,758</td>
</tr>
<tr>
<td>MMBtu/h (HHV)</td>
<td>6,012</td>
</tr>
<tr>
<td>MMBtu/h (LHV)</td>
<td>5,871</td>
</tr>
<tr>
<td><strong>Power Generation</strong></td>
<td></td>
</tr>
<tr>
<td>Gas Turbine</td>
<td>1 x 7FA+e</td>
</tr>
<tr>
<td>Net Output MW</td>
<td>265</td>
</tr>
<tr>
<td><strong>Mixed Alcohols Production(^{(1)})</strong></td>
<td></td>
</tr>
<tr>
<td>Ethanol bbl / day</td>
<td>8,886</td>
</tr>
<tr>
<td>Propanol bbl / day</td>
<td>3,512</td>
</tr>
<tr>
<td>Total bbl / day</td>
<td>12,398</td>
</tr>
</tbody>
</table>

\(^{(1)}\) 700 bbl/day of Methanol is also produced and utilized in the gas turbine.
## Product Pricing Summary

<table>
<thead>
<tr>
<th>Material</th>
<th>$ / lb</th>
<th>$ / MMBtu (LHV)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>$0.17</td>
<td>$14.9</td>
<td>$1.15/gal (w/o subsidy and w/partial credit for octane enhancement)</td>
</tr>
<tr>
<td>Propanol (as chemical)</td>
<td>$0.40</td>
<td>$28.2</td>
<td>$2.70 /gal</td>
</tr>
<tr>
<td>Propanol (as fuel)</td>
<td>$0.21</td>
<td>$14.9</td>
<td>Same $/MMBtu as EtOH</td>
</tr>
<tr>
<td>Methanol</td>
<td>$0.11</td>
<td>$13.0</td>
<td>$0.72/gal (if sold, burned as fuel)</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$0.09</td>
<td>$11.2</td>
<td>$170 / ton</td>
</tr>
<tr>
<td>SNG</td>
<td>-</td>
<td>$5.0</td>
<td>(HHV) Henry Hub</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-</td>
<td>$9.8</td>
<td>$2.7 / MSCF when nat gas is at $5/MMBtu (HHV)</td>
</tr>
<tr>
<td>F-T Liquids</td>
<td>$0.16</td>
<td>$8.9</td>
<td>$1.0/gal</td>
</tr>
<tr>
<td>Electricity (Wholesale)</td>
<td>-</td>
<td>$12.9</td>
<td>4.4 cents/kWh at 3,413 Btu/kWh</td>
</tr>
</tbody>
</table>
Economic Evaluation

◆ Economic Parameters
  – 100% Equity Assumed
  – Wholesale Cost of Electricity: 4.4 cents/kWh
  – Retail Cost of Electricity: 5.0 cents/kWh
  – Price of Ethanol: $1.15/gal
  – Price of Propanol (as chemical): $2.70/gal
  – Tax Rate: 40%
  – Annual Escalation: 3%

◆ Sensitivity Cases
  – All Alcohols at the Same $/MMBtu as Ethanol
  – Alcohols at the Individual Prices
### Economic Results

<table>
<thead>
<tr>
<th>Case</th>
<th>After Tax Return on Investment</th>
</tr>
</thead>
<tbody>
<tr>
<td>All Alcohols at Same $/MMBtu as Ethanol</td>
<td>15.2%&lt;sup&gt;(1)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alcohols at the Individual Prices</td>
<td>15.8%&lt;sup&gt;(2)&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

**Notes:**

1. Base Case with price of Ethanol at $1.15/gal and Propanol the same $/MMBtu as Ethanol with wholesale power price of 4.4 cents/kWh.
2. Price of Ethanol assumed at $0.75/gallon and Propanol at $2.70/gallon with wholesale power price of 4.4 cents/kWh.
After Tax ROI Sensitivity to Electricity Price
All Alcohols at the Same $/MMBtu as Ethanol

Ethanol Price per Gallon

Return on Investment

- 3.5 cents/kWh
- 4.4 cents/kWh
- 5.0 cents/kWh

Ethanol Price per Gallon: $0.90, $1.15, $1.40

Return on Investment: 12.0%, 13.0%, 14.0%, 15.0%, 16.0%, 17.0%, 18.0%, 19.0%
After Tax ROI Sensitivity to Ethanol Price
Alcohols at the Individual Prices

- 3.5 cents/kWh
- 4.4 cents/kWh
- 5.0 cents/kWh

Ethanol Price per Gallon

Return on Investment

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Discussion of Results

- Ethanol, produced with higher alcohols, may be blendable with both gasoline while meeting oxygenate requirements
- Co-production of alcohols and electricity appears to be economically feasible in the Gulf Coast
- Propanol as a chemical by-product improves economics (if a sufficient market exists)
- Ethanol production provides a good synergy in a refinery setting
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