Hydrogen Generation for Refineries

DOE Phase II SBIR

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Project Overview

• **Timeline**
  - Project start date: 8/14/09
  - Project end date: 8/14/14
  - Percent complete: 90
  - P.I. : Dr. Girish Srinivas

• **Budget**
  - DOE share: $850,000
  - Cost Share: ~$450,000 (ongoing management time for commercialization efforts)
  - Funding received in FY13: $0
  - Total funding planned for FY14: $0
  - Spent as of 3/31/14
    - $656,145 (Ph II)
    - $100,000 (Ph I)
    - $756,145 (total)

• **Barriers**
  - Demonstration of continuous operation with circulating fluidized bed reactor system
  - Engineering scale up
  - Pilot scale demonstration

• **Partners**
  - Matheson Tri-Gas
Hydrogen from Heavy, Renewable and Waste Oils – TDA HyRes Process

TDA’s HyRes Process
Steam Reforming Vacuum Tower Bottoms

Steam/carbon = 5
70% H₂
20% CO₂
10% CO
~2% CH₄

Refinery for Hydrotreating

This presentation does not contain any proprietary, confidential, or otherwise restricted information
• Refineries are processing increasingly sour, heavy crudes

• Catalytic reforming of paraffins to aromatics and hydrogen cannot supply enough H₂ for hydrotreating

• Typical 100,000 bbl/day hydrocracking refinery will be short 23 million ft³/day of H₂

• TDA HyRes process can generate additional H₂ from residuum
## H₂ Required for Heavy Crudes

### Table: Carbon Residue, Sulfur, Conradson, and Hydrogen for Heavy Crudes

<table>
<thead>
<tr>
<th>Residuum type</th>
<th>°API</th>
<th>Sulfur (wt%)</th>
<th>Conradson (wt%)</th>
<th>Nitrogen (wt%)</th>
<th>Hydrogen (scf/bbl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Venezuela, atmospheric</td>
<td>15.3–17.2</td>
<td>2.1–2.2</td>
<td>9.9–10.4</td>
<td>—</td>
<td>425–730</td>
</tr>
<tr>
<td>Venezuela, vacuum</td>
<td>4.5–7.5</td>
<td>2.9–3.2</td>
<td>20.5–21.4</td>
<td>—</td>
<td>825–950</td>
</tr>
<tr>
<td>Boscan (whole crude)</td>
<td>10.4</td>
<td>5.6</td>
<td>—</td>
<td>0.52</td>
<td>1100</td>
</tr>
<tr>
<td>Tia Juana, vacuum</td>
<td>7.8</td>
<td>2.5</td>
<td>21.4</td>
<td>0.52</td>
<td>490–770</td>
</tr>
<tr>
<td>Bachaquero, vacuum</td>
<td>5.8</td>
<td>3.7</td>
<td>23.1</td>
<td>0.56</td>
<td>1080–1260</td>
</tr>
<tr>
<td>West Texas, atmospheric</td>
<td>17.7–17.9</td>
<td>2.2–2.5</td>
<td>8.4</td>
<td>—</td>
<td>520–670</td>
</tr>
<tr>
<td>West Texas, vacuum</td>
<td>10.0–13.8</td>
<td>2.3–3.2</td>
<td>12.2–14.8</td>
<td>—</td>
<td>675–1200</td>
</tr>
<tr>
<td>Khafji, atmospheric</td>
<td>15.1–15.7</td>
<td>4.0–4.1</td>
<td>11.0–12.2</td>
<td>—</td>
<td>725–800</td>
</tr>
<tr>
<td>Khafji, vacuum</td>
<td>5.0</td>
<td>5.4</td>
<td>21.0</td>
<td>—</td>
<td>1000–1100</td>
</tr>
<tr>
<td>Arabian light, vacuum</td>
<td>8.5</td>
<td>3.8</td>
<td>—</td>
<td>—</td>
<td>435–1180</td>
</tr>
<tr>
<td>Kuwait, atmospheric</td>
<td>15.7–17.2</td>
<td>3.7–4.0</td>
<td>8.6–9.5</td>
<td>0.20–0.23</td>
<td>470–815</td>
</tr>
<tr>
<td>Kuwait, vacuum</td>
<td>5.5–8.0</td>
<td>5.1–5.5</td>
<td>16.0</td>
<td>—</td>
<td>290–1200</td>
</tr>
</tbody>
</table>

- Processing heavy crudes requires large quantities of hydrogen
- The lower the API gravity, the heavier the crude
- Heavy crudes contain high sulfur and high molecular weight hydrocarbons
Example: $\text{H}_2$ Shortage

(Basis: 100,000 bbl/day crude feed)

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Throughput 1000 Barrels per Day (MBPD)</th>
<th>Hydrogen Usage Million Standard Cubic Feet per Day (MMSCF/D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Crude Distillation</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Vacuum Distillation</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>Light Ends; Gasoline Isomerization</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Naphtha Hydrotreater (Atmospheric and Delayed Coker naphtha)</td>
<td>20</td>
<td>2 (consumed)</td>
</tr>
<tr>
<td>Catalytic Reforming</td>
<td>22</td>
<td>22 (supplied)</td>
</tr>
<tr>
<td>Light Distillate to Hydrotreating for Kerosene/Jet Fuel</td>
<td>10</td>
<td>2 (consumed)</td>
</tr>
<tr>
<td>Heavy Distillate &amp; Cycle Oil to Hydrotreating for Diesel/Heating Oil</td>
<td>10</td>
<td>3 (consumed)</td>
</tr>
<tr>
<td>Atmospheric Gas Oil to Gas Oil Hydrotreating</td>
<td>10</td>
<td>5 (consumed)</td>
</tr>
<tr>
<td>Light Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>12</td>
<td>6 (consumed)</td>
</tr>
<tr>
<td>Heavy Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>13</td>
<td>7 (consumed)</td>
</tr>
<tr>
<td>Delayed Coker Gas Oil to Gas Oil Hydrotreating</td>
<td>7</td>
<td>4 (consumed)</td>
</tr>
<tr>
<td>Cycle Oil to Hydrocracking</td>
<td>8</td>
<td>16 (consumed)</td>
</tr>
<tr>
<td>Catalytic Cracking</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>Resid to Delayed Coking</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Resid to Resid Hydroprocessing</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**H$_2$ shortage** 23 (supplied)

Source: AIChE petroleum refining CD

- A 100,000 bbl/day refinery that has hydrocracking is typically **short** about 23 million standard ft$^3$/day of H$_2$
- TDA process can be used to generate the extra hydrogen from bottom of the barrel vacuum residuum
Hydrogen Prices

- TDA’s process for residuum steam reforming to generate hydrogen a.k.a. *HyRes*
  - Cost of hydrogen approximately $4/1000 SCF
  - Lower capital cost than small steam methane reforming plant
  - Suitable for smaller refineries (~50,000 bbl/day)
  - Less expensive alternative for expanding H₂ capacity

### Target market

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pipeline</td>
<td>2 to 50</td>
<td>$1.25</td>
<td>$2.25</td>
<td>$1.95</td>
<td>$3.51</td>
</tr>
<tr>
<td>Large on-site SMR</td>
<td>10 to 100</td>
<td>$1.50</td>
<td>$2.75</td>
<td>$2.34</td>
<td>$4.28</td>
</tr>
<tr>
<td>Small on-site SMR</td>
<td>0.5 to 10</td>
<td>$3.00</td>
<td>$6.00</td>
<td>$4.67</td>
<td>$9.35</td>
</tr>
<tr>
<td>Delivered Liq H₂</td>
<td>0.01 to 1</td>
<td>$6.00</td>
<td>$18.00</td>
<td>$9.35</td>
<td>$28.04</td>
</tr>
<tr>
<td>Delivered gas H₂</td>
<td>0.001 to 0.1</td>
<td>$12.00</td>
<td>$15.00</td>
<td>$18.70</td>
<td>$23.37</td>
</tr>
</tbody>
</table>
Approach: Generating $\text{H}_2$ from Resid

- Diagram shows a complete, *stand alone* hydrogen plant
- Unit operations already in the refinery can be used
Catalyst

- Catalyst is cycled between reforming and regeneration with air.
- Same charge of catalyst used been tested in the laboratory over the course of 2.5 years with NO deactivation.
- Feeds processed include:
  - Atmospheric residuum (aka: atmospheric tower bottoms (ATB), long residuum)
  - Vacuum residuum (aka: vacuum tower bottoms (VTB), vacuum resid)
  - Dilbit (tar sand bitumen diluted with 30% condensate)
  - Biomass fast pyrolysis oil (whole raw oil)
  - Norpar 12 ($C_{11}/C_{12}$ paraffinic solvent – used as naphtha simulant)
Laboratory Scale Test Apparatus

- Cooling coil for gas prior to venting
- Fire resistant curtains
- Furnace and Reactor
- Oil and Pet coke Slurry Injection
- Boiler Furnace and coil
- ISCO high pressure syringe pumps for oil, water and pet coke slurry
- Pressure control valve
- Online gas analyzer
- Gas manifold & MFCs
- Process control electronics

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Accomplishments

• Steam reforming of atmospheric tower bottoms (ATB)
  • ATB is the stream from atmospheric distillation of crude oil that boils at $T > 650^\circ F$
  • ATB is normally sent to vacuum distillation (or sometimes the fluid catalytic cracker)
    • No catalyst deactivation

• Steam reforming of vacuum tower bottoms (VTB)
  • VTB is the stream from vacuum distillation of ATB that would boil at $T > 1050^\circ F$ at atmospheric pressure
    • $1050^\circ F$ is an extrapolated boiling point because in reality VTB would pyrolyzes before boiling at atmospheric pressure
    • No catalyst deactivation
  • Same catalyst sample used in all the tests for more than 2.5 years
Characteristics of ATB

$H:C \approx 1.68$

<table>
<thead>
<tr>
<th>Huffmann elemental analysis</th>
<th>1.68</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis: 100 grams Oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>#2</td>
<td>Average</td>
</tr>
<tr>
<td>Carbon</td>
<td>wt%</td>
<td>86.58</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>wt%</td>
<td>12.04</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>wt%</td>
<td>0.11</td>
</tr>
<tr>
<td>Oxygen</td>
<td>wt%</td>
<td>0.58</td>
</tr>
<tr>
<td>Sulfur</td>
<td>wt%</td>
<td>0.80</td>
</tr>
</tbody>
</table>

- Elemental analysis primarily done to determine sulfur content of the feed
- Chemistry of ATB, VTB etc. is more important than H:C content and is reflected in API gravity and boiling point, however…
- Only the H:C ratio affects $HyRes$ (and only slightly)

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GC Analysis of ATB

- A few high boilers (very highest boilers cannot elute from GC column)
- ATB is liquid at room temperature
Single Cycle Shown for ATB
Steam/Carbon = 3

- ATB reforming
- Steam/carbon = 3
- Syngas generated during reforming
  - 70% H₂
  - 20% CO
- Syngas composition agrees with thermodynamic equilibrium predictions (dry basis)
  - Purge with N₂*
  - Regenerate with air (stop when O₂ levels off)
  - Purge with N₂*
  - Start another reforming cycle

*N₂ purges used for fire prevention because experiments are done in a single reactor vessel
Multiple Reforming Cycles: ATB
Steam/Carbon = 5

- ATB reforming at T = 865°C (1589°F) & P = 50 psig
- Hydrogen ~70 vol%
- No catalyst deactivation in 83 hours (26 cycles)
Vacuum Tower Bottoms (VTB)

- Two sources of VTB were tested
  - Liquid at 50°C “medium”
  - Not liquid until T = 150°C “extra heavy”

H:C ≅ 1.71

<table>
<thead>
<tr>
<th>Huffmann elemental analysis</th>
<th>1.71 C/H ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Basis: 100 grams Oil</td>
</tr>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>Carbon  wt%</td>
<td>86.99</td>
</tr>
<tr>
<td>Hydrogen wt%</td>
<td>12.37</td>
</tr>
<tr>
<td>Nitrogen wt%</td>
<td>0.21</td>
</tr>
<tr>
<td>Oxygen wt%</td>
<td>0.30</td>
</tr>
<tr>
<td>Sulfur wt%</td>
<td>0.27</td>
</tr>
</tbody>
</table>

- Elemental analysis primarily done to determine sulfur content

Viscosity at 50°C (solid at room temp)

“Medium VTB”
GC Analysis of “Medium VTB”

- Some “high boilers”
- Solid at room temperature
- Heat to 50°F to feed to lab-scale reactor as a liquid
“Medium VTB” reforming at $T = 865°C$ (1589°F) & $P = 50$ psig
- Steam/carbon = 5
- Hydrogen ~70 vol%
- $H_2$ production rate (red) is constant during each reforming step indicating there is no catalyst deactivation in 280 hours (96 cycles)
“Extra Heavy” Vacuum Residuum (VTB)

- Slightly lower H:C than ATB
- Elemental analysis primarily done to determine sulfur content
- 2.5X as much sulfur as ATB
- Had to cut with 20 wt% xylene because we cannot operate our pump at 150°C which would be needed to reduce viscosity enough to feed whole oil to test reactor

H: C ≈ 1.53

<table>
<thead>
<tr>
<th>Huffman Elemental Analysis</th>
<th>1.53</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>#2</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>85.99</td>
<td>86.09</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>10.89</td>
<td>10.98</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>0.49</td>
<td>0.52</td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>2.02</td>
<td>2.02</td>
</tr>
</tbody>
</table>

20% xylene added to make fluid; heated to 50°C to feed to reactor

“Extra Heavy VTB” Solid at room temperature

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GC Analysis of “Extra Heavy VTB”

- Largely “high boilers” (however, most of sample cannot elute from column)
- Solid at room temperature
- Had to cut with 20% xylene to be able to feed to the reactor (cannot maintain 150°C in the heat high pressure feed pump)
Reforming Cycles: “Extra Heavy VTB”
Steam/Carbon = 5

- Hydrogen ~70 vol%
- H₂ production rate (red) is constant during each reforming step indicating there is no catalyst deactivation in 115 hours (37 cycles)
Feedstock Flexibility: Norpar 12

• **Norpar 12**
  - ExxonMobil product
  - ~1:1 C\textsubscript{11} and C\textsubscript{12} alkanes (paraffins)
  - Demonstrates using TDA’s *HyRes* process to generate hydrogen from middle distillates
  - Very easy feedstock for hydrogen generation using *HyRes*

Colorless, low viscosity liquid at RT
**H₂ Generation from Norpar 12**  
(simulates steam naphtha reforming)

- **Very easy feedstock to process**
- **71% H₂ agrees with thermodynamic equilibrium prediction (dry basis)**
- **Operates at very low steam to carbon ratios (S/C < 2)**
- **Lower CAPEX alternative to conventional fixed bed steam naphtha reforming (e.g. in Europe)**
Hydrogen Generation from Bitumen

- **DILBIT** (bitumen diluted with 30% condensate)
  - Liquid at room temperature
  - Tested in TDA’s HyRes process
  - Performance essentially identical to that obtained with refinery residuum ATB and VTB (i.e. 70 vol% H₂ in raw syngas and no catalyst deactivation)

- **Sales oil** (diluted with 15% condensate)
  - Currently testing, expect good performance

- **Emulsion**
  - Cannot test directly with apparatus in current configuration (two phase mixture of tar in water)
  - Might not be possible to test raw bitumen (after water removal) in the lab because of feed heating limitations
DILBIT Test Results

- Approx. 70 vol% H₂ in syngas
- No catalyst deactivation
- Results essentially identical with those obtained when testing the refinery feedstocks (ATB, medium and heavy VTB)
Biomass Fast Pyrolysis Oil

- Two cycles shown to see details
- Slightly lower H₂ in syngas than obtained with hydrocarbon feeds because bio-oil contains oxygen, which is rejected as water
- Steam to carbon = 2 (low S/C reduces energy required to raise steam)
- No catalyst deactivation in subsequent cycling
- Whole raw oil can used without any prior processing (except filtering)
Team Members and Future Work

- Biomass pyrolysis oil testing
- Continued oil sands bitumen testing
- Waste oil testing
- Other feedstocks of interest to DOE
- Preliminary design of continuous system, process simulation, economics
- Teaming with a major industrial gas supplier as a partner
- TDA has a patent application on file covering the process
Summary

• **Hydrogen for Refineries**
  - *HyRes* can be used to generate hydrogen from middle distillates (viable alternative for naphtha steam reforming)
  - *HyRes* can be used to generate hydrogen from refinery residuum feedstocks (e.g. ATB and VTB) at $4/1000 CF
  - Catalyst is regenerated between reforming cycles by burning off coke and sulfur in air before they can deactivate the catalyst
  - No catalyst deactivation (well over 500 hours of laboratory testing with assorted heavy refinery feedstocks)
  - Gives refiners an alternative to coking or asphalt production from bottom of the barrel fractions
  - Can generate H₂ from bitumen for syncrude production
  - No oxygen separation plant is needed and no nitrogen ends up in the syngas because steam reforming and catalyst regeneration are done in separate vessels
Renewable Hydrogen

- HyRes can be used to generate renewable H₂ from raw, whole biomass fast pyrolysis oil
- Can operate at steam/carbon ratios of 1 - 2
- HyRes system is much simpler than a gasifier
- HyRes process is much less expensive than a gasifier
- HyRes better suited to small distributed plants compared to a gasifier