Hydrogen Generation for Refineries

DOE Phase II SBIR

Dr. Girish Srinivas P.I.

gsrinivas@tda.com
303-940-2321

Dr. Steven Gebhard, P.E.
Dr. Robert Copeland
Mr. Jeff Martin

TDA Research Inc.
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
  - Contractor 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 (Phase II)
    - $100,000 (Phase 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

This presentation does not contain any proprietary, confidential, or otherwise restricted information.
This presentation does not contain any proprietary, confidential, or otherwise restricted information
Relevance: Processing Heavy Crudes

- 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

- 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

<table>
<thead>
<tr>
<th>Residuum type</th>
<th>°API</th>
<th>Sulfur (wt%)</th>
<th>Carbon residue (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>
Example: H₂ 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 (MMSCFDD)</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>
<tr>
<td><strong>Additional Hydrogen Supplied</strong></td>
<td><strong>H₂ shortage</strong></td>
<td>23 (supplied)</td>
</tr>
</tbody>
</table>

Source: AIChE petroleum refining CD

- A 100,000 bbl/day refinery that has hydrocracking is typically short about 23 million standard ft³/day of H₂

- TDA process can be used to generate the extra hydrogen from bottom of the barrel vacuum residuum

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Hydrogen Prices

Target market

- 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

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<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 H₂ 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
- Online gas analyzer
- Gas manifold & MFCs
- Pressure control valve
- Fire resistant curtains
- Furnace and Reactor
- Oil and PetCoke Slurry Injection
- Process control electronics
- Boiler Furnace and coil
- ISCO high pressure syringe pumps for oil, water and petcoke slurry
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 ≈ 1.68

<table>
<thead>
<tr>
<th>Elemental analysis</th>
<th>1.68 H:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis: 100 grams Oil</td>
<td></td>
</tr>
<tr>
<td></td>
<td>#1</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>86.58</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>12.04</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.11</td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>0.58</td>
</tr>
<tr>
<td>Sulfur (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)
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

This presentation does not contain any proprietary, confidential, or otherwise restricted information
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 $\cong 1.71$

<table>
<thead>
<tr>
<th>Elemental Analysis</th>
<th>1.71 C/H ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Basis: 100 grams Oil</strong></td>
<td></td>
</tr>
<tr>
<td>#1</td>
<td>#2</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%
• H₂ 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)

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>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>

- 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

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

“Extra Heavy VTB”

Solid at room temperature
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%
- \( H_2 \) 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
  - \( \sim 1:1 \) \( \text{C}_{11} \) and \( \text{C}_{12} \) alkanes (paraffins)
  - Demonstrates using TDA’s *HyRes* process to generate hydrogen from middle distillates
  - Very easy feedstock for hydrogen generation using *HyRes*
H₂ Generation from Norpar 12
(simulates steam naphtha reforming)

2.15 ≤ H:C ≤ 2.18
Steam/carbon = 1.76

• 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% $H_2$ 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 \( H_2 \) 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
Summary - Continued

- **Renewable Hydrogen**
  - *HyRes* can be used to generate renewable H\textsubscript{2} 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