Successful Upgrading of Estonian Shale Oil Via Hydrotreating

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AS Narva Ölitehas

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Senior Consultant  
Jacobs Consultancy
Presentation Topics

- Introduction
  - Brief Introduction To Eesti Energia / Narva Õlitechas
  - ‘Drivers’ Leading To Shale Oil Pilot Testing Program
- Questions Addressed By Pilot Plant Testing
- Technical Results From Hydrotreating Pilot Plant
- Product Value Enhancement
- Forward Plans Of Eesti Energia / Narva Õlitechas
Business Mix Of Eesti Energia

- Oil Shale Mining: 240,000 TPA Rated (1.5 million bbl/yr)
- Generation Oil & Power: 2,603 MW(e) + 1,081 MW(heat)
- Transmission: 100% owned subsidiary
- Distribution: 100% owned subsidiary
- Supply & Trading
- Annual Production: ~ 14 million tons
- Covers Whole Of Estonia: 5,000 km network
- Covers 92% Of Estonia Population
- 500,000 Customers
- Export Power Sales: Latvia, Lithuania, Finland
The Narva Oil Factory, established in 1980, has almost 30 years of operating expertise
‘Drivers’ For Upgrading
Estonian Shale Oil Liquids

• Oil Shale Is A Major Natural Resource Of Estonia

• Narva Ōlitehas Is Already Processing Estonian Oil Shale Rock In Its Two Commercial TSK-140 Retorts [TSK = Recirculating Solid Heat Carrier Retort]

• Eesti Energia---Through AS Narva Ōlitehas---Is Planning A Major Expansion To Its Oil Shale Retorting Operations
Expanding TSK Retorting Plant AS Narva Ölitehas

- Mined Estonian Oil Shale Rock
- TSK-140 Retort Train #1
- TSK-140 Retort Train #2
- Additional TSK-280 Retort Trains
- Fully Combusted Residual Ash [With Captured SO2]
- As Aqueous Slurry To Inventorying Along With Water Decanting & Recycle
- Dusty Vapour Gas Mix
- Dusty Extra Heavy Shale Oil
- Shale Gasoline
- Shale Light Fuel Oil
- Shale Heavy Fuel Oil
- Sour Semi-Coke Gas
- Condensation Train #1
- Condensation Train #2
- Additional New Concept Condensation Trains
Narva TSK Retorting Plant By 2016

- TSK 280 design ready by May 2009
- Operational 2011/2012
- 30,000 BPSD Shale Oil Liquids By 2016
‘Drivers’ For Upgrading Estonian Shale Oil Liquids

- Market Resistance Encountered For Current Products:
  - Shale Gasoline
  - Shale Light Fuel Oil
  - Shale Heavy Fuel Oil

- Market Resistance = Discounting

- Unconventional Qualities Are Holding Down Interest And Sales
## Team Effort
### Shale Oil Pilot Plant Tests

<table>
<thead>
<tr>
<th>Company</th>
<th>Role</th>
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<tbody>
<tr>
<td><strong>Eesti Energia AS</strong> (Tallinn, Estonia)</td>
<td>Sponsor &amp; Owner</td>
</tr>
<tr>
<td><strong>AS Narva Õlitehas</strong> (Narva, Estonia)</td>
<td>Operator Of TSK Retorts</td>
</tr>
<tr>
<td></td>
<td>Shale Oil Producer / Supplier</td>
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<tr>
<td><strong>Jacobs Consultancy</strong> (Houston/London)</td>
<td>Program Planning, Organizing,</td>
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<td>Monitoring &amp; Results</td>
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<tr>
<td><strong>Intertek PARC</strong> (Pittsburgh, PA, USA)</td>
<td>HTU Pilot Plant Facility</td>
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<td>Operations</td>
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<td><strong>Haldor Topsoe</strong> (Lyngby, Denmark)</td>
<td>Hydrotreating Catalyst Supplier</td>
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Key Questions Addressed By Hydrotreating Test Program

• Can Estonian Shale Oil Liquids Be Upgraded Via Refinery-Type Distillate Hydrotreaters?

• Will Hydrotreated Products Be Attractive To European Union Refiners?
The Quality Problem
Naphtha-Distillates-VGO  Σ C5 to 565°C

<table>
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<tr>
<th>Quality</th>
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<th>Brent Crude Naphtha-Distillates-VGO</th>
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<tr>
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# The Quality Problem

**Naphtha-Distillates-VGO \( \Sigma C5 \) to 565°C**

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Heteroatom Oxygen Species
Estonian Raw Shale Oil Liquids

PHENOL
\[
\text{OH} \\
\text{C} = \text{O} \\
\text{H}
\]

m-CRESOL
\[
\text{OH} \\
\text{CH}_3
\]

m-XYLENOL
\[
\text{OH} \\
\text{CH}_3 \\
\text{CH}_3
\]

RESORCINOL
\[
\text{OH} \\
\text{OH}
\]

p-METHYL RESORCINOL
\[
\text{OH} \\
\text{CH}_3 \\
\text{OH}
\]

‘PHENOLIC PNA’
\[
\text{CH}_3 \\
\text{CH}_3
\]

‘ALDEHYDES / KETONES’

‘HIGHER ALCOHOLS’
\[
\text{R-C-OH} \\
\text{H-C-H}
\]

‘AROMATIC ETHERS’
\[
\text{CH}_2\text{-O-CH}_2\text{-R}
\]
Quality Challenges
Estonian Raw Shale Oil Liquids

- Very Aromatic & Unsaturated
- Uniquely High Content Of Organic Oxygen In All Fractions
  - Total Oxygen = 6.0-6.5 wt%
- Hydrogen Deficient
- As Quirks:
  - Shale Heavy Fuel Oil Is Low In Sulphur [S ~ 0.6 wt%]
  - Shale Gasoline Is Extreme In Sulphur, Nitrogen, Oxygen
    - Sulphur = 14,000 wppm
    - Nitrogen = 600 wppm
    - Oxygen = 76,000 wppm
    - Bromine Number = ~ 60 g Br2/100 g oil
Proposed Solution To Quality Challenges
- TSK Retort Plant Expansion
- New Shale Oil Upgrader Plant

Diagram showing the flow of processes:
- ASU Oxygen
- Sour Shale Off-Gas
- Gas POX Hydrogen Plant
- Sweet Fuel Gas
- High-Purity Hydrogen
- Sales Naphtha
- Low-Sulphur Diesel Gas Oil
- Low-Sulphur Vacuum Gas Oil
- Recycle VGO
- Sulphur Block
- Sulphur
Technical Objectives
HTU Pilot Plant Program

- **Prove** Estonian Shale Oil Liquids Can Be Upgraded Using *Refinery-Type* Hydrotreaters And Catalysts, *Despite*:
  - Extremely high organic oxygen content
  - Uncertainty whether poly-nuclear aromatic cores in shale oil will hydrogenate easily

- **Characterize** Derivative Oil Liquids
  - How Much Do Qualities Improve?

- **Verify** Chemical Hydrogen Requirements
## Key Results

### Kinetic Performance HTU Pilot Plant

- Hydro-De-Sulfurization = > 98%
- Hydro-De-Nitrification = ~ 90%
- Hydro-De-Oxygenation = ~ 96%
- Bromine Number Reduction = > 98%
- Selectivity ~ 94.5 wt % C5+  
  ~ 107 vol % C5+
- △ API Uplift  
  [Shale Oil Composite]  
  +20° △  
  [ 15° → 35° ]
- Chemical Hydrogen  
  ~ 3.4 wt%  
  2160± SCF per barrel
Changes Found Across Shale Oil Hydrotreater

- Specific Gravity = 0.966 → 0.865
- Organic Sulphur = 0.8 wt% → 0.015 wt%
- Organic Oxygen = 6.1 wt% → 0.3 wt%

TBP Distillation Curves --- Before And After
Before And After

Raw Shale Oil  Hydrotreated Shale Oil
After Quality Comparison
Naphtha-Distillates-VGO  Σ C5 to 565°C

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<tr>
<th>Quality</th>
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<th>Hydrotreated Shale Composite</th>
<th>Brent Naphtha-Distillate-VGO</th>
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<tr>
<td>Volume Balance Percent</td>
<td>100 %</td>
<td>107± %</td>
<td>-</td>
</tr>
<tr>
<td>API Gravity °API</td>
<td>15°</td>
<td>35°</td>
<td>42°</td>
</tr>
<tr>
<td>Sulphur Wt%</td>
<td>0.8</td>
<td>0.015</td>
<td>0.3</td>
</tr>
<tr>
<td>Nitrogen Wt%</td>
<td>0.25</td>
<td>0.025</td>
<td>0.045</td>
</tr>
<tr>
<td>Oxygen Wt%</td>
<td>6.1</td>
<td>0.3</td>
<td>0.15</td>
</tr>
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<td>Hydrogen Wt%</td>
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<td>12.9+</td>
<td>13.3</td>
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<td>45</td>
<td>1</td>
<td>&lt; 2</td>
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<td>11.7±</td>
<td>11.9±</td>
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Conclusions

• Operating Pressure Must Be Similar To Diesel Hydrotreater Units Making Ultra Low Sulphur Diesel Gas Oils:
  ▪ To deal with high oxygen + nitrogen+ sulphur in front end
  ▪ To gain marketability via hydrogenation of PNA cores

• Haldor Topsoe Catalyst Performed Very Well
  ▪ No indications of deactivation
  ▪ But only short duration tests

• High Percentages Of Organic Oxygen Can Be Removed

• Hydrotreated Oil Liquids Become Similar To Crude Oil Cuts
Challenges And Lessons Learned

• Shale Heavy Fuel Oil Is Subject To ‘Aging’ and ‘Chronic Coking’. Commercial HTU Must Mitigate Via:
  
  ▪ Direct transfer from TSK Retort Trains
  ▪ Latest generation oil feed filtration
  ▪ Hydrogen spiking as soon as possible
  ▪ Liquid phase dilution within HTU reactor

• Diluent Oil Must Boil In Vacuum Gas Oil Range
  
  ▪ Diluent oil is essential to control ΔT rises in reactor
  ▪ ULS diesel gas oil proved too volatile
Product Value Enhancement

- Very Large Uplifts In API Gravity And Cetane Index Occur In Diesel Gas Oil Fraction. Hypotheses On Why:
  - Release Of Polar Compaction From Oxygen Species
  - Intentional Hydrogenation Of Poly-Nuclear Aromatics
- Large Volumetric Expansions Found. This Offsets ‘Mass Loss’ From Removing Hetero-atoms [Organic S / N / O]
- Modeling Work Vis-A-Vis European Union Refineries Indicates All Three ‘Hydrotreated Shale Products’ Should Sell At Prices Similar To Marker Brent Crude
Commercial-Scale Bulk Shale Oil Hydrotreater Unit

- High-Purity Make Up Hydrogen
- Shale Gasoline
- Shale Light Fuel Oil
- Shale Heavy Fuel Oil
- Optional Purchased Vacuum Gas Oil Co-Processing
- Recycle HT Vacuum Gas Oil
- HT Shale Naphtha
- HT Shale Light Gas Oil
- HT Shale Vacuum Gas Oil
- Wash Water & Sour Water
- Lean Amine
- Rich Amine
- Sweet Fuel Gas
Forward Plans

• Update Strategic Plans For:
  ▪ New TSK Retorts & Condensation Trains
  ▪ Bulk Shale Oil Hydrotreater Unit
  ▪ Semi-Coke Gas POX Hydrogen Plant
  ▪ Sulphur Block

• Structure And Run Confirming HTU Pilot Plant Testing:
  ▪ Explore Catalyst Deactivation
  ▪ Develop Complete Assays For HT Shale Co-Products

• Prepare ‘Front End Engineering Design’

• Confirm ‘Capital Investments’
Acknowledgment

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- Lars Skyum

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Questions?