

Successful Upgrading of Estonian Shale Oil Via Hydrotreating

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Presentation Topics

- **Introduction**
 - **Brief Introduction To Eesti Energia / Narva Õlitehas**
 - **'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 Õlitehas**

Business Mix Of Eesti Energia



- Annual Production: ~ 14 million tons

- Shale Oil Retorts: 240,000 TPA Rated
(1.5 million bbl/yr)

- Power Plants: 2,603 MW(e)+ 1,081MW(heat)

- Covers Whole Of Estonia: 5,000 km network

- Covers 92% Of Estonia Population

- 500,000 Customers

- Export Power Sales:
Latvia, Lithuania, Finland

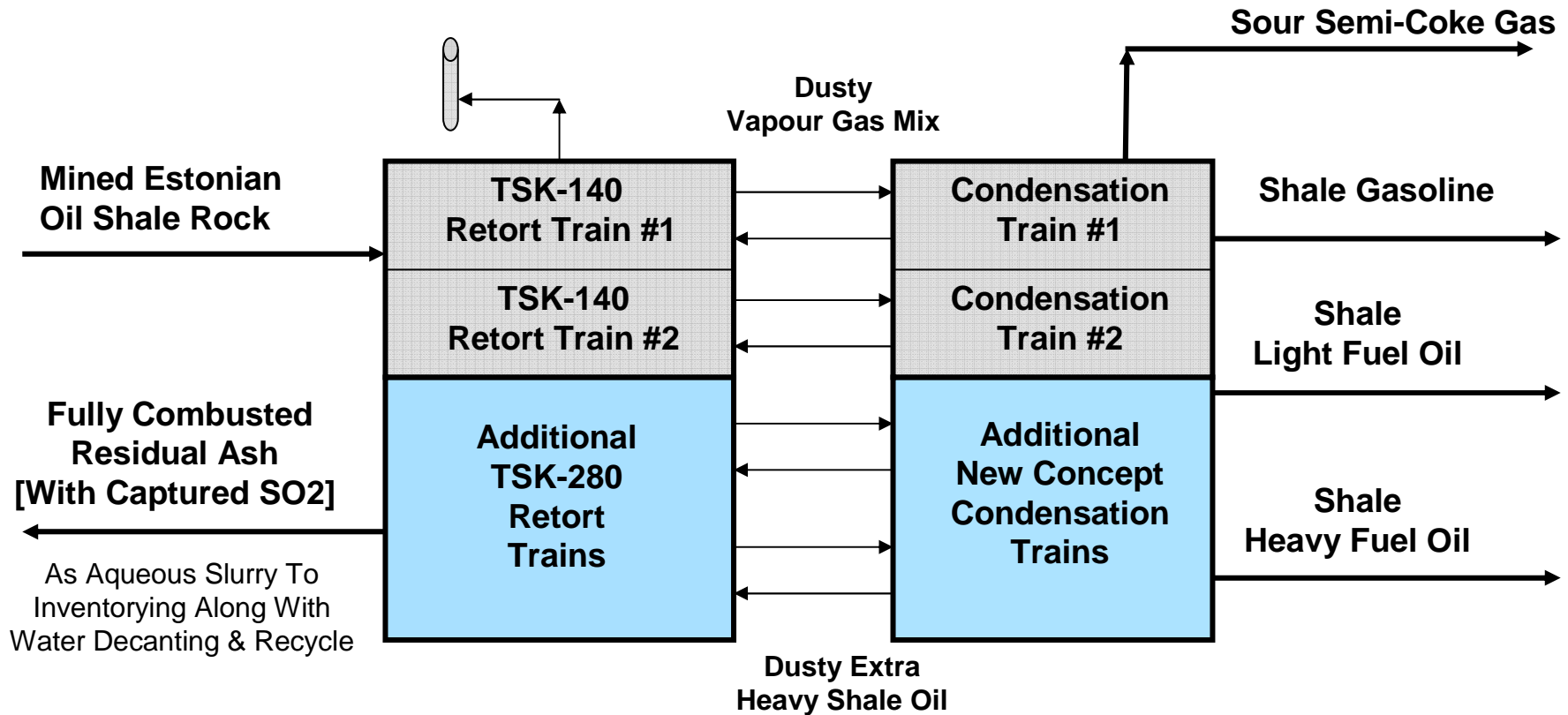


The Narva Oil Factory, established in 1980, has almost 30 years of operating expertise

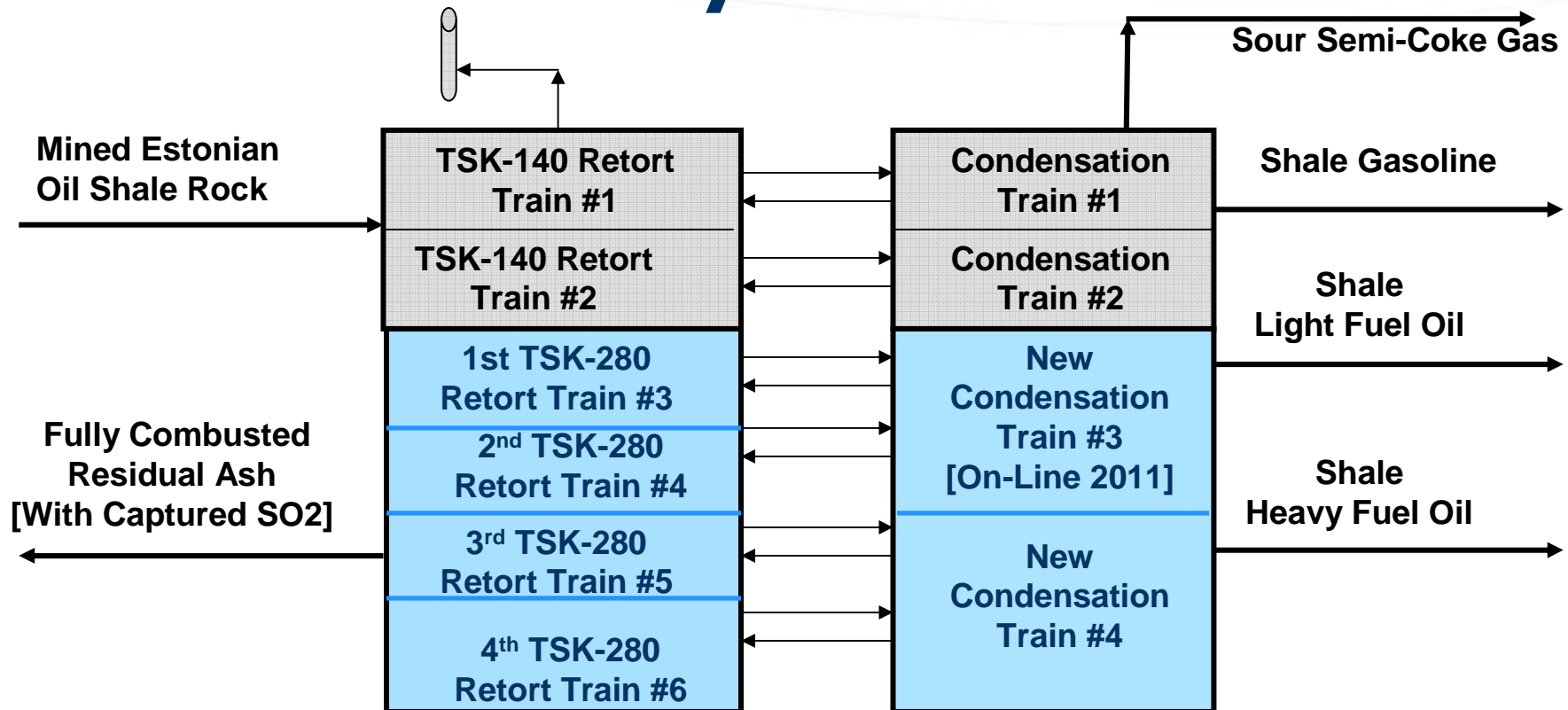
'Drivers' For Upgrading Estonian Shale Oil Liquids

- **Oil Shale Is A Major Natural Resource Of Estonia**
- **Narva Õlitehas 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 Õlitehas---Is Planning A Major Expansion To Its Oil Shale Retorting Operations**

Expanding TSK Retorting Plant AS Narva Õlitehas



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

- **Eesti Energia AS**
(Tallinn, Estonia)

Sponsor & Owner

- **AS Narva Õlitehas**
(Narva, Estonia)

Operator Of TSK Retorts
Shale Oil Producer / Supplier

- **Jacobs Consultancy**
(Houston/London)

Program Planning, Organizing,
Monitoring & Results

- **Intertek PARC**
(Pittsburgh, PA, USA)

HTU Pilot Plant Facility
Operations

- **Haldor Topsoe**
(Lyngby, Denmark)

Hydrotreating Catalyst Supplier

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

Quality		Raw Estonian Composite Shale Oil	Brent Crude Naphtha-Distillates-VGO
API Gravity	°API	15°	42°
Sulphur	Wt%	0.8	0.3
Nitrogen	Wt%	0.25	0.045
Oxygen	Wt%	6.1	< 0.15
Hydrogen	Wt%	9.8	13.3
Cetane In Diesel Cut	CI(D976)	~ 28	~ 49
Bromine Number	`g Br ₂ /100g	~ 45	< 2
UOP/Watson K	-	10.5±	11.9±

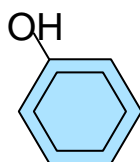
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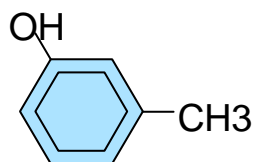
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Heteroatom Oxygen Species Estonian Raw Shale Oil Liquids

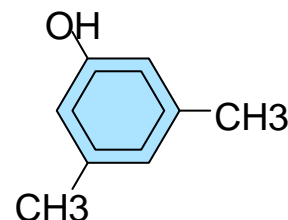
PHENOL



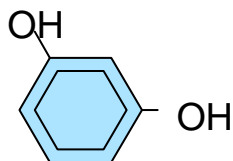
m-CRESOL



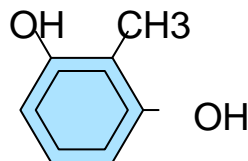
m-XYLENOL



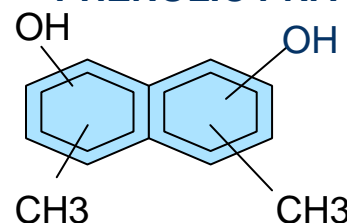
RESORCINOL



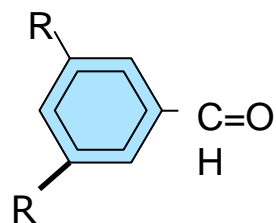
p-METHYL
RESORCINOL



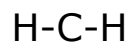
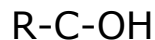
'PHENOLIC PNA'



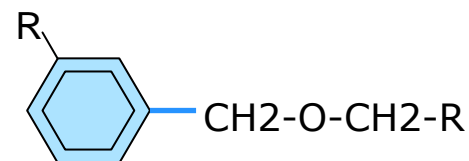
'ALDEHYDES /
KETONES'



'HIGHER ALCOHOLS'



'AROMATIC ETHERS'



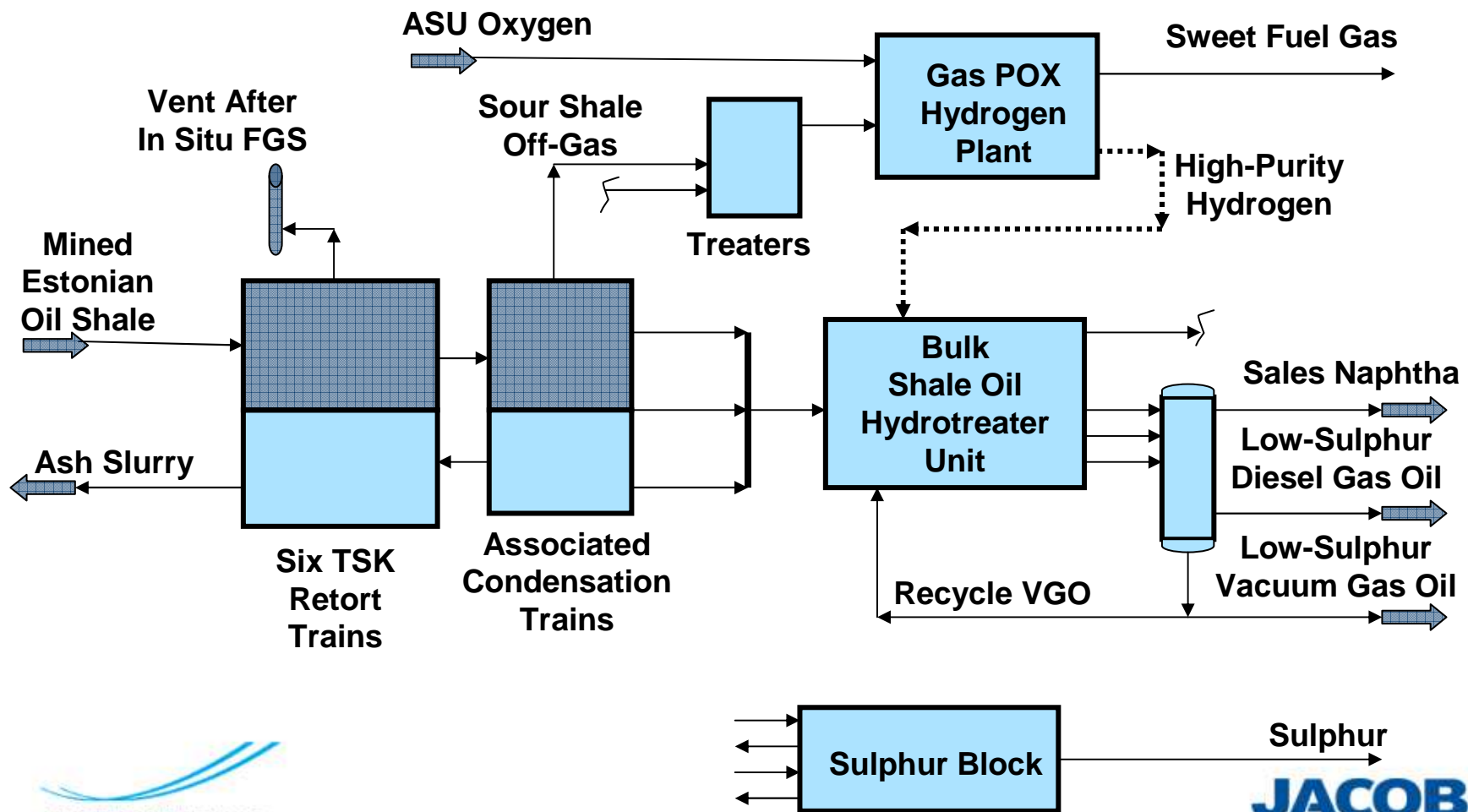
Quality Challenges Estonian Raw Shale Oil Liquids

- **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 Br ₂ /100 g oil

Proposed Solution To Quality Challenges

- TSK Retort Plant Expansion
- New Shale Oil Upgrader Plant



Technical Objectives

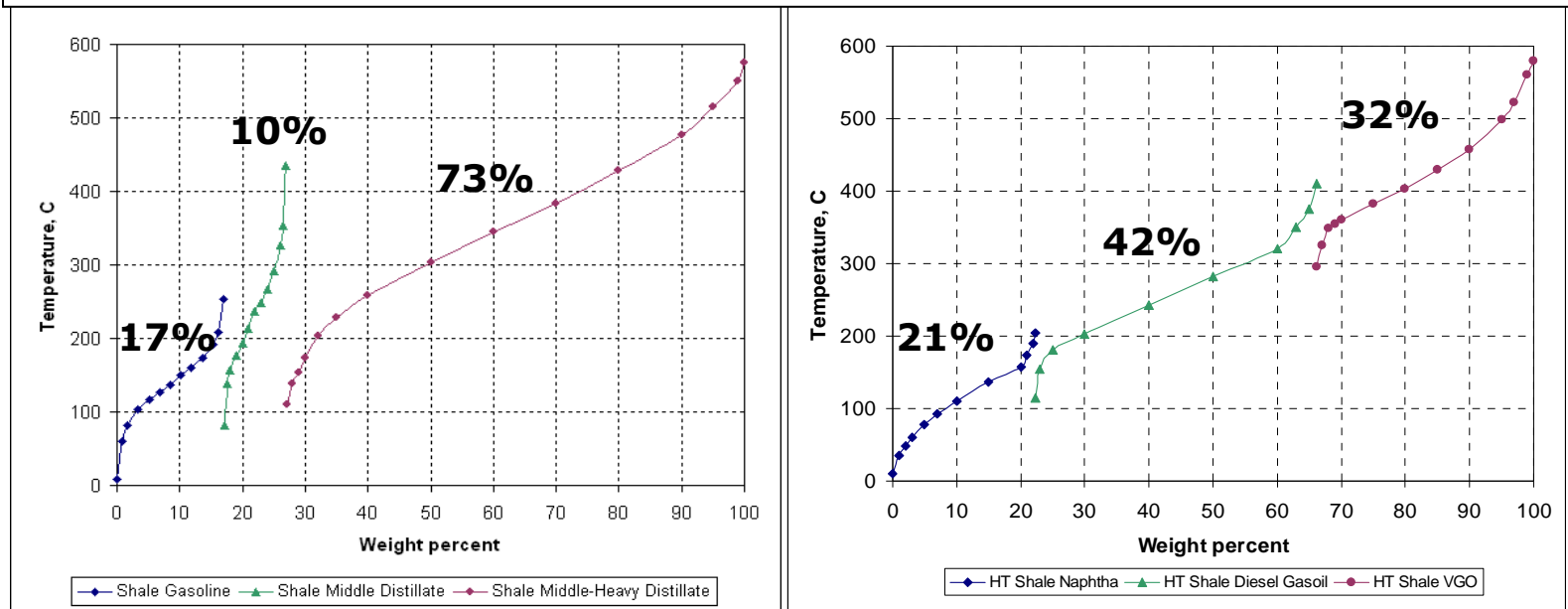
HTU Pilot Plant Program

- 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

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

Quality		Raw Shale Composite	Hydrotreated Shale Composite	Brent Naphtha-Distillate-VGO
Volume Balance	Percent	100 %	107± %	-
API Gravity	°API	15°	35°	42°
Sulphur	Wt%	0.8	0.015	0.3
Nitrogen	Wt%	0.25	0.025	0.045
Oxygen	Wt%	6.1	0.3	0.15
Hydrogen	Wt%	9.8	12.9+	13.3
Cetane In Diesel	CI(D976)	~ 28	~ 47	~ 49
Bromine No.	`g Br2	45	1	< 2
UOP/Watson K	-	10.5±	11.7±	11.9±

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**

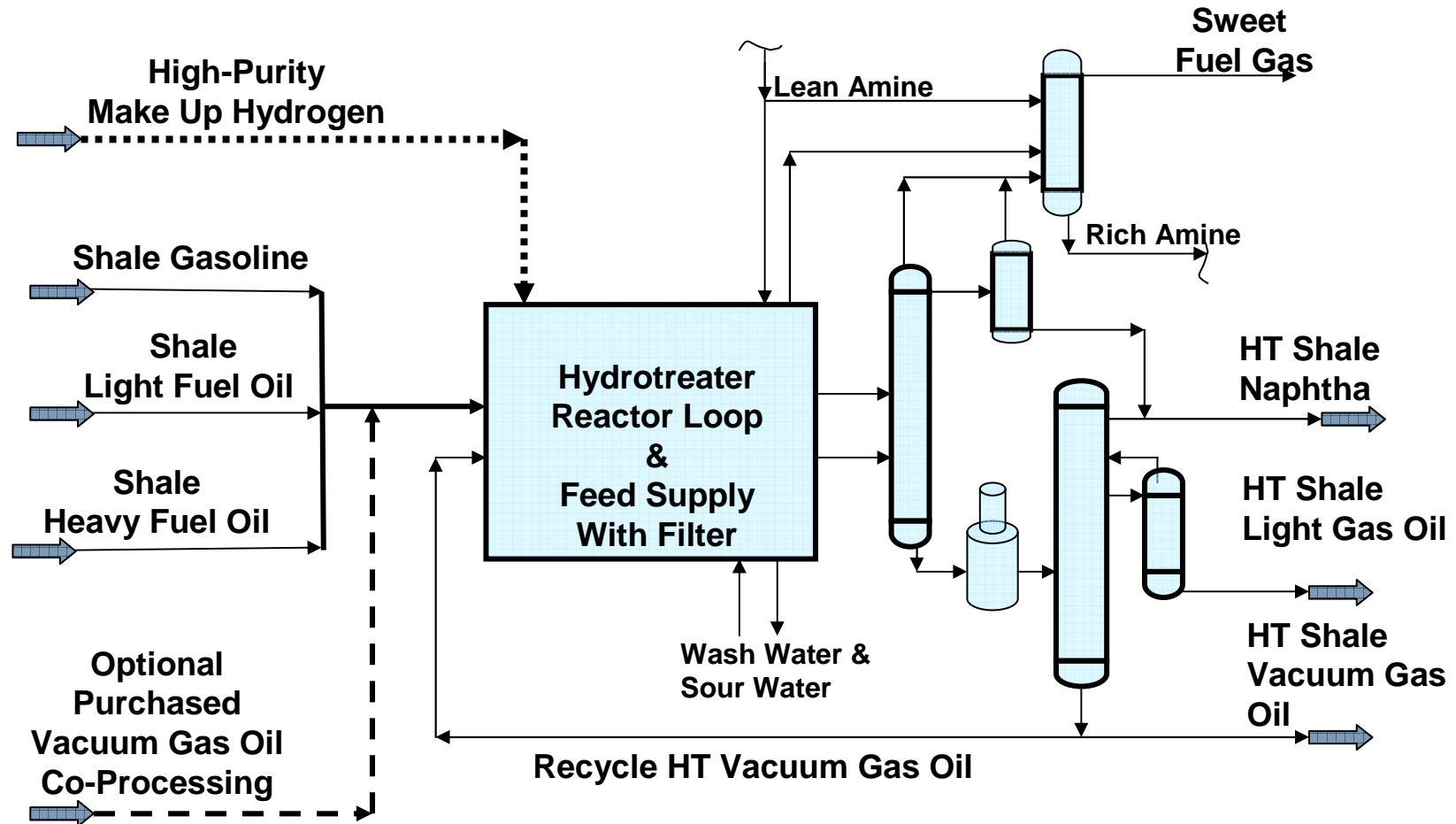
Challenges And Lessons Learned

- **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



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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Questions?