Options for Upgrading & Refining Fischer-Tropsch Liquids

- **Major factors affecting XtL product yields & properties**
  - Plant siting issues
  - Focus on transportation fuels

- **Comparison of petroleum & FT liquids**
  - Fluid composition & distillation
  - Refining options

- **Chemistries for refining FTLs**
  - Achieving product slate flexibility with XtL

- **Blending FT & petroleum liquids & biofuels**
  - Briefly discuss fuel properties

- **Closing thoughts**
Many factors can affect XtL product yields & properties

<table>
<thead>
<tr>
<th>Feed Type</th>
<th>Gasification Options</th>
<th>Xtl Plant Siting</th>
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<tbody>
<tr>
<td>Coal (rank)</td>
<td>POX vs. Reforming</td>
<td>Distance to refineries &amp; markets</td>
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<tr>
<td>Pet Coke &amp; Residuals</td>
<td>Temperature</td>
<td>Mode of feed &amp; product transport</td>
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<td>Biomass</td>
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<td>CO₂ Capture</td>
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<td>Feed Composition</td>
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<td>Ultimate Analysis</td>
<td>FT Conversion Options</td>
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<tr>
<td>H / C Ratio</td>
<td>Temperature</td>
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<tr>
<td>Oxygen</td>
<td>Catalyst (α, P/O)</td>
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<td>- Fluid-Bed</td>
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<td>- Slurry-Bed</td>
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Up-Stream

Down-Stream

Product End-Use

- Transportation - existing vs. future fuels
- SNG or Hydrogen
- Chemicals
- Combined Heat & Power
Siting Issues Affecting XtL Yields & Properties

**XtL Plant Siting**

- **On-Site Refining**
  - Refining & Blending within Dedicated FTLs Refinery
  - Batch-Shipments of Finished Fuel Blendstocks via Clean-Product Pipelines
  - Blending with Petroleum Fuels or Ethanol at Product Terminal

- **Across-The-Fence Refining**
  - Refining & Blending within Existing Petroleum Refinery
  - FTL Fractionation / Batch or Pooled Processing with Petroleum Intermediates

- **Remote Refining**
  - Partial Upgrading for Crude-Oil Pipeline Transport
  - Batch-Shipments of FT Syncrude
  - FTL Fractionation / Batch or Pooled Processing with Petroleum Intermediates
  - Shipment of FT Syncrude/Petroleum Mixture
  - Fractionation and Upgrading with Petroleum

**Inside XtL fence**

**Offsite**
## Assays for Petroleum & FT Liquids

### Graphs

- **Lo-S/Lgt Crude Oil**
- **Hi-S/Hvy Crude Oil**
- **Hi-S/VHvy Crude Oil**
- **Hi-T FTS**
- **Lo-T FTS**
- **FT Syncrude**

### Table

<table>
<thead>
<tr>
<th>Property</th>
<th>Lo-S/Lgt</th>
<th>Hi-S/Hvy</th>
<th>Hi-S/VHvy</th>
<th>Hi-T FTS</th>
<th>Lo-T FTS</th>
<th>FT Syncrude</th>
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Chemical Composition of Petroleum & FTL

**Virgin Crude Oil**
- paraffins: n-butane, isoctane (Octane)
- naphthenes: methyl cyclopentane, cyclohexane
- aromatics: benzene, alkyl benzene
- polyaromatics: naphthalene
- asphaltenes: during processing
- olefins: isobutylene, isoctene

**Raw FT Liquids**
- n-paraffins: n-octane, n-hexadecane (Cetane)
- α-olefins: 1-butene, 1-octene
- n-alcohols: 1-octanol
- during processing: isoparaffins, 1-methyl heptane
- Internal olefins: 2-butene, isoamylenes
- isoolefins: during processing
Petroleum Refining

%Distilled Off (ASTM D-86)
- 95% @ -38°C max
- 10% @ 50-70°C max
- 50% @ 77-121°C range
- 90% @ 185-190°C max
- EP @ 225°C max
- 10% @ 205°C max
- EP @ 300°C max
- 90% @ 282-338°C range

Premium Products
- LPG
- Jet Fuel
- Diesel Fuel

TBP Cut Points
- -42°C (C3-C4)
- 27-32°C (C5-C11)
- 166-193°C (C10-C15)
- 216-271°C (C15-C20)
- 321-343°C (>C20 & <C25-C50)
- 427-566°C (>C25-C50)

Processes:
- Hydrotreating
- Isomerization or Cat Reforming
- Alklation
- Cat Cracking or Hydrocracking
- Coking or Visbreaking
- Resid Hydroprocessing

Products:
- Fuel Gas
- Naphtha RGLs
- Heavy Gas Oil
- Diesel
- Kerosene
- Premium Products
- RFO
FT Liquids Refining

**Premium Products**

- **LPG**
  - 95% @ -38°C max
- **Gasoline**
  - 10% @ 50-70°C max
  - 50% @ 77-121°C range
  - 90% @ 185-190°C max
  - EP @ 225°C max
- **Jet Fuel**
  - 10% @ 205°C max
  - EP @ 300°C max
- **Diesel Fuel**
  - 90% @ 282-338°C range

**%Distilled Off**

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- 166-193°C (C10-C15)
- 216-271°C (C15-C20)
- 321-343°C (C20-C50)
- 427-566°C (>C50)

**FT Waxes**

**Special Naphthas**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization or Alkylation
- Olefin Metathesis

**Diesel**

- Cat Cracking or Hydrocracking
- Hydrotreating

**Kerosene**

- Cat Cracking or Hydrocracking
- Hydrotreating

**Naphtha**

- Cat Cracking or Hydrocracking
- Hydrotreating

**Naphtha RGLs**

- Cat Cracking or Hydrocracking
- Hydrotreating
- Isomerization or Cat Reforming

**Oligomerization or Alkylation**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization

**Olefin Metathesis**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization

**Isomerization & Dehydrogenation**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization

**Hydrotreating**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization

**Hydrocracking**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization

**Cat Reforming**

- Isomerization & Dehydrogenation
- Hydrotreating
- Isomerization or Cat Reforming
- Oligomerization
FT Light-Ends Work-Up

- **Paraffin Isomerization**
  \[ R \cdot CH_2 - CH_2 - CH_3 \xrightarrow{BM \text{ on acidic support}} R \cdot CH - CH_3 + \text{heat} \]

- **Dehyrogenation**
  \[ R \cdot CH_2 - CH_2 - R' \xrightarrow{CrA} R \cdot CH = CH - R' + H_2 \]

- **Olefin Isomerization I**
  \[ R \cdot CH_2 - CH = CH_2 \xrightarrow{Zeolite} R \cdot CH - CH - CH_3 \]

- **Olefin Isomerization II**
  \[ R \cdot CH = CH - CH_3 \xrightarrow{Zeolite} R \cdot C = CH_2 + \text{heat} \]

**Not typically found in pet refinery**
FT Light-Ends Work-Up
(continued)

- Alkylation
  isobutylene alkylation

- Catalytic Polymerization
  isobutylene dimerization

Not typically found in pet refinery
FT Naphtha & Distillates Work-Up

- **Hydrotreating** olefin saturation
  \[ R - CH_1 = CH_2 + H_2 \xrightarrow{BM \text{ on acidic support}} R - CH_2 - CH_3 + \text{heat} \]

- **Isomerization**
  \[ R - CH_2 - CH_2 - CH_3 \xrightarrow{NM \text{ on acidic support}} R - CH - CH_3 + \text{heat} \]

- **Catalytic Reforming**
  \[ R - C_6H_{13} + \text{heat} \xrightarrow{NM \text{ on acidic support}} 4H_2 + R - C_6H_5 [\text{aromatic}] \]

- **Olefin Metathesis I**
  \[ R_1 - CH = CH - R_2 + R_5 - CH = CH - R_6 \xrightarrow{W \text{ or Mo w/Pt}} R_1 - CH = CH - R_2 + R_5 - CH = CH - R_4 \]

\[ 4 < \text{CN} < 9 \quad \text{and} \quad 9 < \text{CN} < 18 \]

*Not typically found in pet refinery*
**FT Wax Work-Up**

- **Hydrocracking with olefin saturation**
  \[ R - CH_2 - CH_2 - CH_1 = CH_2 + H_2 \rightarrow RH + CH_3 - CH_2 - CH_3 + \text{heat} \]
  with NM or BM on acidic support

- **Hydrocracking with isomerization**
  \[ R' - CH_2 - CH_2 - CH_2 - R'' + H_2 \rightarrow R' - C - CH_3 + R'' H + \text{heat} \]
  with Zeolite

- **Catalytic Cracking**
  \[ R' - CH_2 - CH_2 - R'' + \text{heat} \rightarrow R' = CH_2 + R'' = CH_2 + H_2 \]

- **Olefin Metathesis II**
  \[ R_1 - CH = CH - R_2 + R_5 - CH = CH - R_6 \leftrightarrow R_1 - CH = CH - R_2 + R_5 - CH = CH - R_4 \]

Not typically found in pet refinery
Adjusting Gasoline-to-Distillate Ratio

**to Increase G/D**
- Minimize Wax-Make
  - raise FT Reactor Temp
- Alkylation or Cat Poly to Gasoline
- Wax Catalytic Cracking
- Wax / Distillate Hydrocracking
  - gasoline mode

**to Decrease G/D**
- Maximize Wax-Make
  - lower FT Reactor Temp
- Cat Poly to Kero or Diesel
- Wax Hydrocracking
- Olefin Metathesis I
  - Naphtha to Kero/Diesel
- Olefin Metathesis II
  - Wax to Kero/Diesel
Estimated Product Distributions from Upgrading & Refining FTLs

Maximum Gasoline
- Gasoline: 65%
- Distillate Fuels: 15%
- LPG: 20%

G/D = 4.2

Maximum Distillate Fuel
- Gasoline: 67%
- Distillate Fuels: 26%
- LPG: 7%

G/D = 0.4

Minimum Upgrading for Transport
- Gasoline: 25%
- LPG: 6%
- Heavy Gas Oil: 32%
- Distillate Fuels: 38%

The Current fuels market in U.S.
G/D = 0.91

Upgrading flexibility leads to higher utility for FT syncrude within petroleum refinery and thus higher premium.
Improving FT Gasoline Quality

- In general, FT Naphtha has low octane number
- However, it is of high quality in other respects
  - zero sulfur, benzene & aromatics
  - olefins can be saturated
- To increase octane:
  - alkylate & isomerize
  - blend with higher-octane petroleum blendstocks
- Catalytic reforming is least desirable option
  - produces aromatics
  - volume loss
  - n-paraffins are poor feedstocks for reforming
Closing Observations

- **Plant location & scale will strongly influence degree of FTL upgrading that will occur at XtL plant**
  - logistically complex - many options to consider
  - Small scale & remote location would seem to favor minimal FTL upgrading strategies
  - However, no studies have been done to quantify from an economic, environmental, or security perspective, when and where it might makes sense to upgrade and refine FT liquids
    - Alberta oil sands industry may be a “model” for XtL infrastructure development

- **Near term, distillate fuels will be focus of XtL**
  - FT naphtha production will be minimized and sold for other non-fuel applications, e.g. steam cracker feed to produce ethylene/propylene

- **Longer term, FT naphtha may need to be refined into gasoline**
  - Refining LP models can be used to help determine the optimum product slate for any given XtL development scenario
Closing Observations

- **Refining technologies exist to upgrade FTL to premium fuels – gasoline, jet & diesel fuels**
  - However, they may be configured and operated in ways quite different from current refining practice with naturally occurring petroleum crude oils
  - *e.g.* FT medium-heavy naphtha might be isomerized, something not considered viable for petroleum naphtha
  - And, are at various states of development and commercialization
  - Therefore, there are R&D opportunities in this arena

- **Continuing evolution of clean transportation fuels in U.S. and Europe favors XtL over other liquefaction technologies**
  - This is unlikely to change
  - FTLs can be produced from renewable biomass or blended with other biofuels
One Last Thought

To paraphrase Marcus Samuel, the founder of Shell:

“\textit{The mere production of oil* is almost its least value and its least interesting state. Markets have to be found}” --- circa. 1900

*can substitute ‘GTL’, ‘CTL’ or ‘BTL’ for ‘oil’

From \textit{The Prize} by Daniel Yergin, 1991 ---- *my interpretation
Options for Upgrading & Refining Fischer-Tropsch Liquids

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