Petroleum Refining

• **INPUT:** Process Multiple Crude Compositions At Minimum Cost
• **OUTPUT:** Produce Slate Of Products That Provide The Most Profit For Current Market Conditions
• **CONVERSION:** Utilize Processes That Upgrade Value Of Petroleum Components
• **FULL CONVERSION REFINERY**
  – Change Less Valuable Fractions Into Higher Value Transportation Fuels
  – Process Heavier, Cheaper Crude Oil
  – Convert ~90% Of Crude Oil Into Fuels And Products
PETROLEUM REFINERY

Crude Oil →

LPG

Chemical Feedstock

Gasoline

Jet Fuel / Kerosene

Diesel

Fuel Oil

Lube / Specialty Oil

Byproducts

Coke

Sulfur

Ford, Bacon & Davis, LLC
Characteristics of Petroleum Processing

- **Molecular Weight**: Higher → Lower
- **Density**: Higher → Lower

- **LPG**
- **Vacuum Residue**
- **Atmospheric Resid**
- **Crude Oil**
- **Gas Oil**
- **Jet Fuel/Diesel**
- **Gasoline**
- **Coke**

**Average Carbon Number (Atoms per Molecule)**

- **Cracking**
- **Hydrogenation**

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Crude Oil → Crude Distillation → Conversion → Product Finishing → Byproduct Recovery

- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil
- Lube / Specialty Oil
- Byproducts
<table>
<thead>
<tr>
<th>Crude Distillation</th>
<th>Middle Distillates</th>
<th>Product Finishing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td>Naphtha</td>
<td>LPG</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical Feedstock</td>
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<tr>
<td></td>
<td></td>
<td>Gasoline</td>
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<tr>
<td></td>
<td></td>
<td>Jet Fuel / Kerosene</td>
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<td></td>
<td></td>
<td>Diesel</td>
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<td></td>
<td></td>
<td>Fuel Oil</td>
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<tr>
<td></td>
<td></td>
<td>Lube / Specialty Oil</td>
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<td></td>
<td></td>
<td>Byproducts</td>
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<td></td>
<td>Gas Oils</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>Residuals</td>
<td></td>
</tr>
</tbody>
</table>

Byproduct Recovery
1 BARREL

CRUDE
$60 / BBL (BRENT)

1 BARREL

GASOLINE
$87 / BBL

JET FUEL
$90 / BBL

DIESEL
$92 / BBL
1 BARREL CRUDE = 1.1 BARREL PRODUCT
Crude Oil
• Crude Oil Is A Complex Mixture Of Hydrocarbons Generated By Nature
• Light Crudes Have Lower Boiling Point Components With More Value As Products
• Sweet Crudes Have Lower Sulfur Concentrations
  – Less Expensive Materials Of Construction
  – Less Sulfur Handling Requirements
• Light, Sweet Crudes Are Becoming More Scarce And More Expensive
• Heavier Crudes Have Higher Boiling Point Components With Less Value As Products
• Heavier Crudes Require More Refinery Process Steps To Convert To Lower Boiling Point Components Of Higher Value
• Sour Crudes Have Higher Sulfur Concentrations
  – More Expensive Materials Of Construction
  – More Sulfur Handling Requirements
• Heavy, Sour Crudes Are More Available And Less Expensive Than Light, Sweet Crudes
• **Crude Assay** Is Used To Define Specific Properties That Impact Refining

• Crude Oil Properties Include:
  – Boiling Point Curve
  – API Gravity
  – Sulfur Content
  – Nitrogen Content
  – Metals (Nickel/Vanadium)
  – Conradson Carbon Residue (CCR)
  – PONA Analysis
    (Paraffins/Olefins/Naphthenes/Aromatics)
  – Viscosity Curve
• API Gravity Is A Measure Of Crude Oil Density

• Higher API Gravity = Lower Density

• Lower API Gravity = Higher Density

• **Light Crudes** Are Greater Than 40° API

• **Medium Crudes** Are 20° To 40° API

• **Heavy Crudes** Are Less Than 20° API
Light Sweet Crude

- Crude Oil
  - Light Sweet Crude Oil
    - Oso (Nigerian)
      - 47.4° API
      - 0.046 % Sulfur
    - Total
      - 81.49 %
  - Byproducts
  - LPG
  - Chemical Feedstock
  - Gasoline
  - Jet Fuel / Kerosene
  - Diesel
  - Fuel Oil
  - Lube / Specialty Oil
  - Total
    - 81.49 %
Medium Sweet Crude

Crude Oil

Medium Sweet Crude Oil
- Brent (North Sea)
  - 38.5°API
  - 0.43 % Sulfur

Total
- 61.8 %

Byproducts
- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil
- Lube / Specialty Oil

Byproducts
- 3.4 %
- 28.8 %
- 14.9 %
- 14.7 %

Ford, Bacon & Davis, LLC
Medium Sour Crude

“Medium” Sour Crude Oil
Maya (Mexico)
22.2°API
3.3 % Sulfur

Total 40.8 %

1.1 % LPG
15.6 % Chemical Feedstock
11.4 % Gasoline
12.7 % Jet Fuel / Kerosene
12.7 % Diesel
11.4 % Fuel Oil
11.4 % Lube / Specialty Oil
1.1 % Byproducts

Crude Oil
<table>
<thead>
<tr>
<th>Product</th>
<th>Percentage</th>
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<tbody>
<tr>
<td>Heavy Sour Crude Oil</td>
<td>16.0° API</td>
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<tr>
<td>LPG</td>
<td>0.61 %</td>
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<tr>
<td>Chemical Feedstock</td>
<td>8.55 %</td>
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<tr>
<td>Gasoline</td>
<td>8.64 %</td>
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<tr>
<td>Jet Fuel / Kerosene</td>
<td>15.50 %</td>
</tr>
<tr>
<td>Diesel</td>
<td></td>
</tr>
<tr>
<td>Fuel Oil</td>
<td></td>
</tr>
<tr>
<td>Lube / Specialty Oil</td>
<td></td>
</tr>
<tr>
<td>Byproducts</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>33.30 %</td>
</tr>
</tbody>
</table>
Crude Distillation
Crude Distillation

Crude Oil

- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil
- Lube / Specialty Oil
- Byproducts

Conversion

Byproduct Recovery

Light Ends
- Naphtha

Middle Distillates
- Gas Oils

Residuals
- Crude Distillation

Crude Oil
History Of Crude Distillation

Batch Still
Late 1800’s

Continuous Bench Still
Early 1900’s
Pipe Continuous Still
Early 1900’s

Trumble Process
Crude Distillation

Crude Unit
- Light Ends
- Naphtha
- Distillate
- Residual

Crude/Vac
- Preheat and Desalter
- Separates Lighter Crude Components
- Atmospheric Tower
- Separates Heavier Crude Components
- AGO
- ATB

Pipestill
- Off Gas
- Straight-Run Naphtha
- Straight-Run Kerosene
- Straight-Run Diesel
- AGO
- Lube / Specialty Oil
- Byproducts
- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil

Byproducts
- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil

Ford, Bacon & Davis, LLC
Lower Boiling Temperature
Lower Molecular Weight

Higher Boiling Temperature
Higher Molecular Weight
Conversion
**Crude Distillation**

- **Crude Oil** → **Conversion** → **Product Finishing** → **Byproduct Recovery**

**Crude Distillation**:
- Light Ends
- Naphtha
- Distillate
- Gas Oil
- Residual

**Conversion**:
- Off Gas
- SR Naphtha
- SR Kero
- SR Diesel
-AGO
- LVGO
- HVGO
- Vac Btms

**Product Finishing**:
- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil
- Lube / Specialty Oil
- Byproducts

**Byproduct Recovery**
Conversion

Crude Distillation

- Light Ends
- Naphtha
- Distillate
- Gas Oil
- Residual

Conversion

- Off Gas
- SR Naphtha
- SR Kero
- SR Diesel
- AGO
- LVGO
- HVGO
- Vac Btms

Product Finishing

- Alkylation
- Hydrocracker
- FCCU
- Delayed Coker

Byproduct Recovery

- LPG
- Chemical Feedstock
- Gasoline
- Jet Fuel / Kerosene
- Diesel
- Fuel Oil
- Lube / Specialty Oil
- Byproducts

Ford, Bacon & Davis, LLC
Fluidized Catalytic Cracking (FCC) Reaction - Regeneration

- Light Ends
- Naphtha
- Middle Distillates
- Gas Oils
- Residuals

Byproduct Recovery

- Riser
- Reactor
- Regenerator

- AGO
- LVGO
- HVGO
- Other Gas Oil

- FCC Wet Gas
- Fractionator Overhead
- Heavy Cat Naphtha (HCN)
- Light Cycle Oil (LCO)
- Clarified Slurry Oil (CSO)
- (Decant Oil)
FCC Unit

- Reactor
- Regenerator
- Main Fractionator
Alkylation

- Feed Preparation
- Reactors
- Fractionation

- Isobutane
- FCC C4’s
- FCC C5’s
- FCC C3’s

- Recycle Isobutane
- Propane
- N-Butane
- Alkylate
ALKYLATION-UNIT FLOW DIAGRAM

Olefin feed

Coalescer drum

Water

Isobutane drum

Settler

HF

Normal butane

Depropanizer

Depropanizer receiver drum

HF stripper

Propane

HF

Alkylate

Isobutane from isomerization

Olefin feed drier

Isobutane

Reactor

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**Alkylation**

The process flow diagram illustrates the alkylation reaction involving the following components:

- **Spent Acid**
- **Fresh Acid**
- **OLEFIN AND ISOBUTANE**
- **CONTACTOR REACTORS**
- **ACID SETTLERS**
- **SUCTION TRAP**
- **FLASH DRUM**
- **Refrigerant Recycle**
- **To Feed/Effluent Exchangers**
- **To Refrigeration Section**
- **From Refrigeration Section**

**Equations for Alkylation:***

- **Isobutene + Isobutane → 2,2,4-Trimethylpentane**
  
- **Propene + Isobutane → 2,2-Dimethylpentane**

**DuPont STRATCO**
Full Conversion

Hydrocracker Naphtha = Hydrocrackate

Diagram:
- Hydrogen
- AGO
- Coker GO
- HVGO/LVGO
- Recycle Compressor
- HDS/HDN Reactors
- Hydrocrkg Reactors
- Separators
- Fractionation
- Fuel Gas
  - HCU LPG
  - Lt Naphtha
  - Hvy Naphtha
  - Lt Distillate
  - HCU Diesel

Unconverted Oil
Partial Conversion

Hydrogen
AGO
Coker GO
HVGO/LVGO

Recycle Compressor

HDS/HDN Reactors

Hydrcrkg Reactors

Separators

Fractionation

Fuel Gas
HCU LPG
Lt Naphtha
Hvy Naphtha
Lt Distillate
HCU Diesel
FCC Feed

Hydrocracker Naphtha = Hydrocrackate
Delayed Coking

Byproduct Recovery

Heater

Vacuum Btms

Coke Drums

Main Fractionator

Coker Gas Plant

Coker Gas

Fuel Gas

Coker LPG

Coker Naphtha

Coker Distillate

(Coker Diesel)

Coker Gas Oil

Petroleum Coke

Recycle
Product Finishing
• **Light Ends** – Fuel Gas

• **Naphtha** – Gasoline

• **Distillates** – Kerosene, Jet Fuel, Diesel

• **Gas Oils** – Pre-/Post- Hydrotreating Before Converting to Gasoline (FCCU) Or Diesel (Hydrocracking)
Light Ends Processing

**Saturate Gas Plant**

- **From Multiple Refinery Sources**
  - LPG
  - Absorber–Deethanizer
  - LPG

- **From Amine Regeneration**
  - Lean Oil
  - Sponge Absorber
  - Lean Amine

- **Amine Absorber**
  - Lean Amine
  - Fuel Gas
  - Rich Amine
  - To Amine Regeneration

- **Debutanizer**
  - Lt Naphtha
  - Isobutane
  - To Alkylation

- **Depropanizer**
  - Propane
  - To Sales

- **Deisobutanizer**
  - N-Butane
  - To Gasoline Blending Or Sales

- **To Sales**
- **To Refinery Heaters**
- **To Gasoline Blending**
- **Or Sales**

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Naphtha Processing

Crude Distillation
- Atmospheric Crude Tower
  - Straight Run
  - Light Hydrocrackate
  - Heavy Hydrocrackate
- Hydrocracker
  - Light Cat
  - Heavy Cat
- FCCU
- Delayed Coker
- Hydrotreaters
  - Wild

Conversion
- Naphtha
  - Critical Gasoline Specifications:
    - Octane
    - Sulfur
    - Reid Vapor Pressure

Product Finishing
- Coker
<table>
<thead>
<tr>
<th></th>
<th>Octane</th>
<th>Sulfur</th>
<th>RVP</th>
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</thead>
<tbody>
<tr>
<td>SR Naphtha</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Coker Naphtha</td>
<td>Medium</td>
<td>Very High</td>
<td>High</td>
</tr>
<tr>
<td>Wild Naphtha</td>
<td>Very Low</td>
<td>Very High</td>
<td>Very High</td>
</tr>
<tr>
<td>Lt Hydrocrackate</td>
<td>Medium</td>
<td>Very Low</td>
<td>High</td>
</tr>
<tr>
<td>Hvy Hydrocrackate</td>
<td>Medium</td>
<td>Very Low</td>
<td>Low</td>
</tr>
<tr>
<td>Lt Cat Naphtha</td>
<td>High</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Hvy Cat Naphtha</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Alkylate</td>
<td>Very High</td>
<td>None</td>
<td>Low</td>
</tr>
</tbody>
</table>
SR/Coker/Wild

**Stabilize** – Reduce RVP

**Hydrotreat** – Remove Sulfur and Olefins

**Split** – Separate Light And Heavy SR

**Reform** – Boost Heavy SR Octane

**Isomerize** – Boost Light SR Octane
SR/Coker/Wild

Stabilize – Reduce RVP

Hydrotreat – Remove Sulfur and Olefins

Split – Separate Light And Heavy SR

Reform – Boost Heavy SR Octane

Isomerize – Boost Light SR Octane
SR/Coker/Wild

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**Hydrotreat** – Remove Sulfur and Olefins

**Split** – Separate Light And Heavy SR

**Reform** – Boost Heavy SR Octane

**Isomerize** – Boost Light SR Octane

---

Ford, Bacon & Davis, LLC
 Lt Cat/Hvy Cat/Lt Coker

Remove Diolefins (Gum-Formers)  Split to Maximize Light Cat Naphtha Octane
Remove Mercaptans (Sulfur)     Hydrotreat But Minimize Olefin Saturation
                                  Stabilize To Decrease Gasoline RVP
Distillate Hydrotreater (DHT)

- **HDS Reactors**
  - SR Kerosene
  - SR Diesel
  - Coker Distillate
  - Lt Cycle Oil
  - Hydrogen

- **Recycle Compressor**

- **Fractionation**
  - Wild Naphtha
  - Kerosene
  - ULSD

- **Fuel Gas**
Gas Oil Hydrotreater (GOHT)

Hydrotreating Gas Oil Before FCCU Avoids Hydrotreating Separate FCCU Products
Byproduct Recovery
Claus Sulfur Unit

- Sour Water Stripper Gas
- Burner/Waste Heat Boiler
- Air
- Condenser 1
- Condenser 2
- Condenser 3
- Condenser 4
- Tail Gas

Sulfur
Sulfur
Sulfur
Sulfur
Tail Gas Treatment

REACTION
PREHEATING
TAIL GAS FROM SRU

REATION (SO2 CONVERSION TO H2S)

PROCESS GAS QUENCH COOLING

H2S ABSORPTION

SOLVENT REGENERATION

LEAN SOLVENT

RICH SOLVENT

BFW

HP STEAM

ACID GAS TO SRU

TREATED TAIL GAS TO ATMOS

INCINERATION/ WASTE HEAT RECOVERY

LEAN SOLVENT

RICH SOLVENT

BFW

HP STEAM

ACID GAS TO SRU

TREATED TAIL GAS TO ATMOS

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61
• Petroleum Refinery Converts Crude Oil To Fuels and Chemical Feedstocks
• Molecules In Crude Oil Are Converted To High Value Products Through Refinery Conversion And Product Finishing Steps
• Removing Sulfur From Refinery Products Is Critical in Meeting Environmental Requirements (Tier 3 = 10 ppmw)