DCO Quality As a Feedstock for Renewable Diesel
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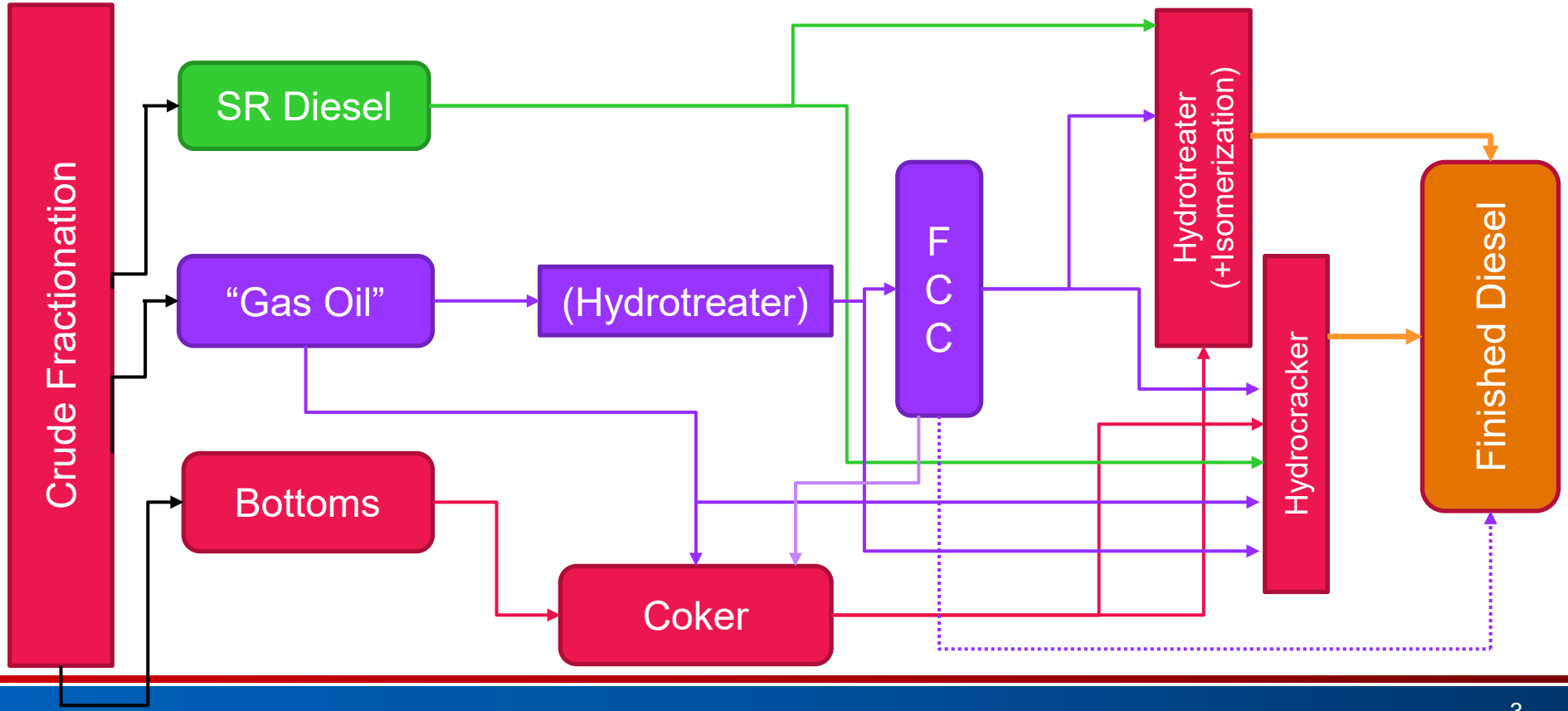
Marathon Petroleum - RAD

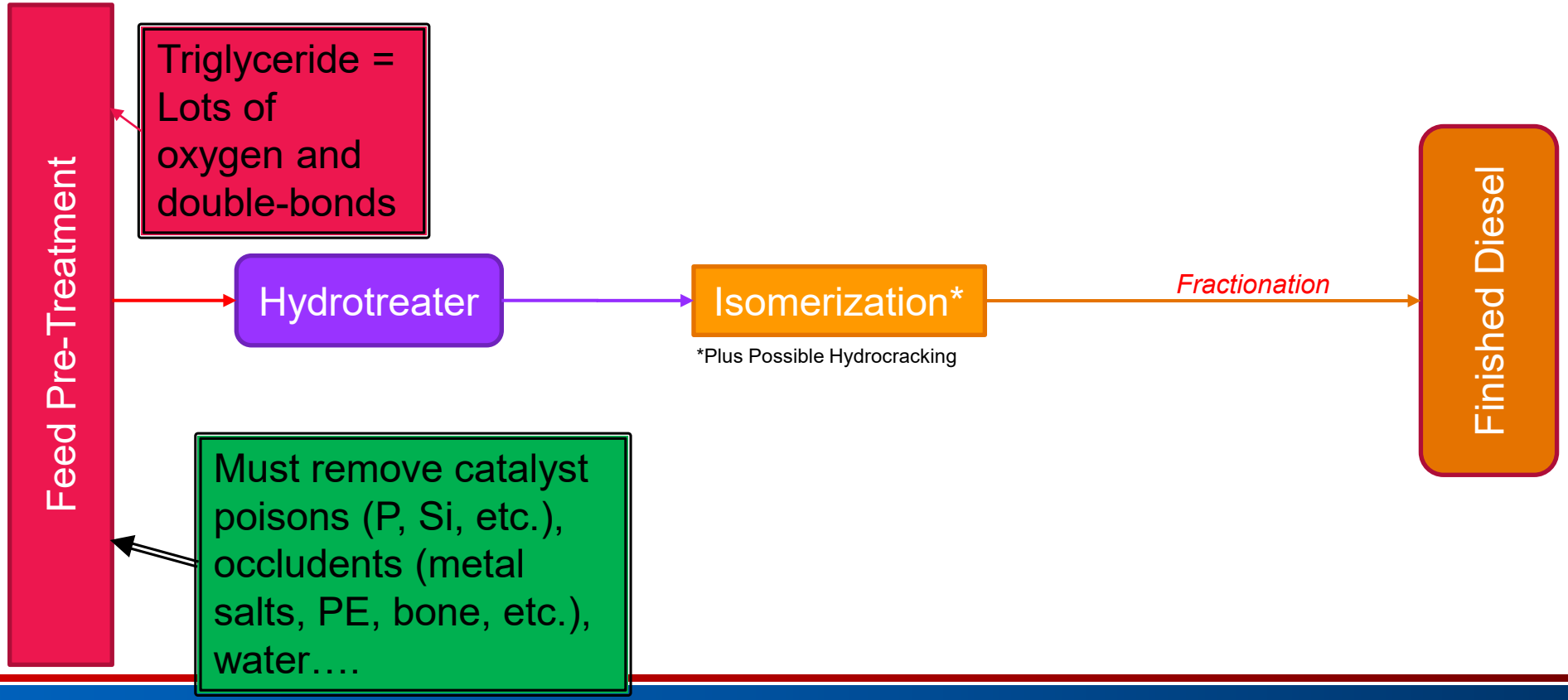
Marathon's RAD

- Refining, Analytical, and Development
- Technical Center located in Catlettsburg, KY
- Over 80 professionals, mostly B.S. Chemists, but also Chemistry Ph.Ds., Chemical Engineers, Mechanical Engineer
- Serve as the technical experts for refineries, pipeline, terminal, retail
- My Group: Reliability and Product Quality (R&PQ)
  - Fouling Mitigation
  - Spectroscopy (Chemometrics), including process applications
  - Additives, both process- and finished-fuel
  - Knock Engines
  - Fuels Quality

Production of Petroleum Diesel



Production of Renewable Diesel

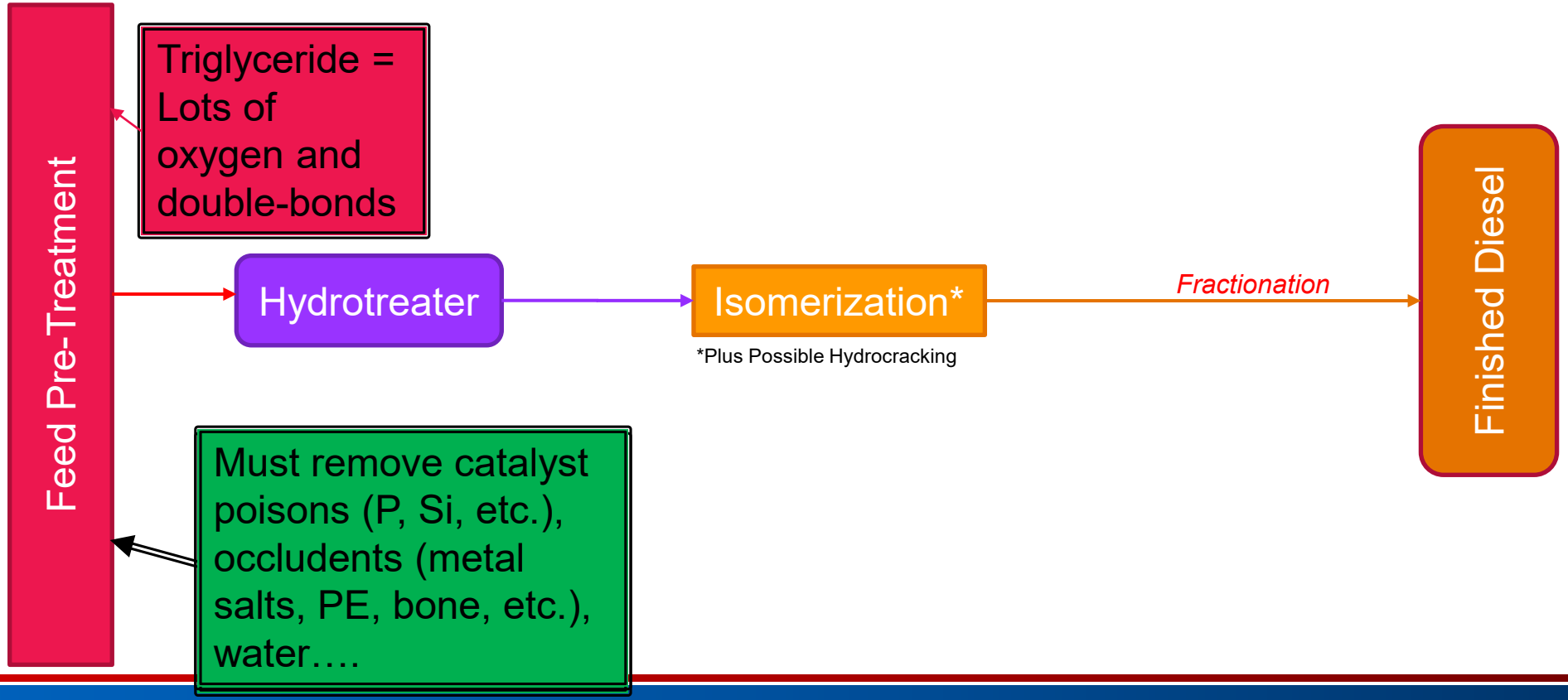


Pre-Treatment of Triglyceride

Not all are created equal

- Some Proprietary Technology
- Remove
  - Inorganic salts (e.g., NaCl)
  - Insoluble material
    - Polyethylene
    - Rust
    - Clays, sand, etc.
  - Water
  - “Silicon” and “Phosphorus”
  - Trace metals
- Reduce acid content

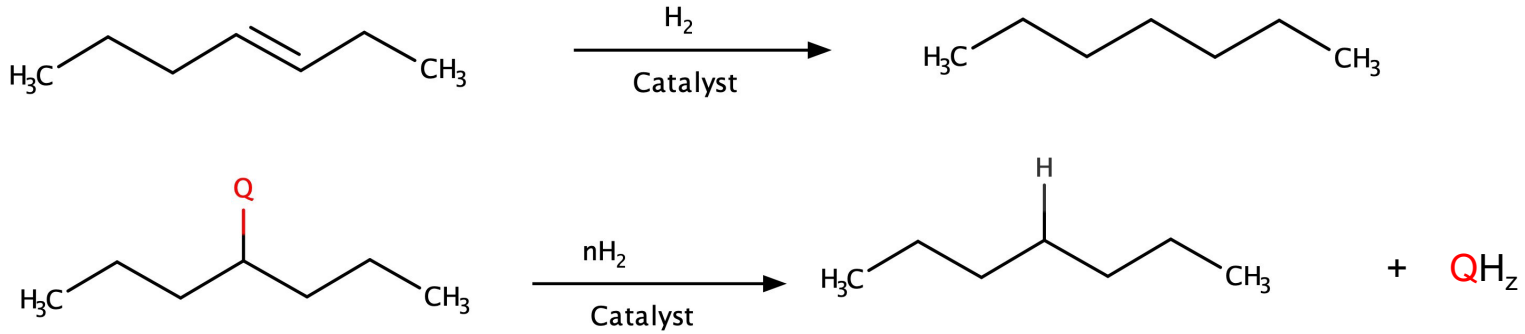
Production of Renewable Diesel



Most Important Process(es) for RD Production

Hydrotreating

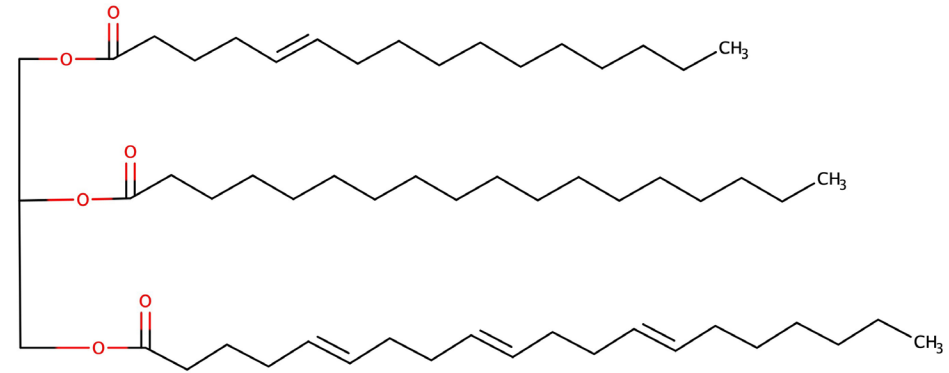
- Hydrotreating: removes atomic “contaminants” from organics, replaces with hydrogen
  - Sulfur, Nitrogen, Oxygen, Halogens
  - Double bonds/unsaturations/olefins and aromatics
  - Metals, P, Si (but contaminates catalyst)
- When replacing hetero-atom, makes H_2S, NH_3, H_2O, etc…

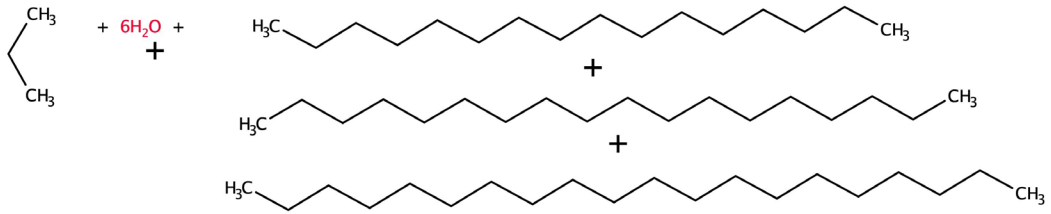


Producing RD

After just hydrotreating

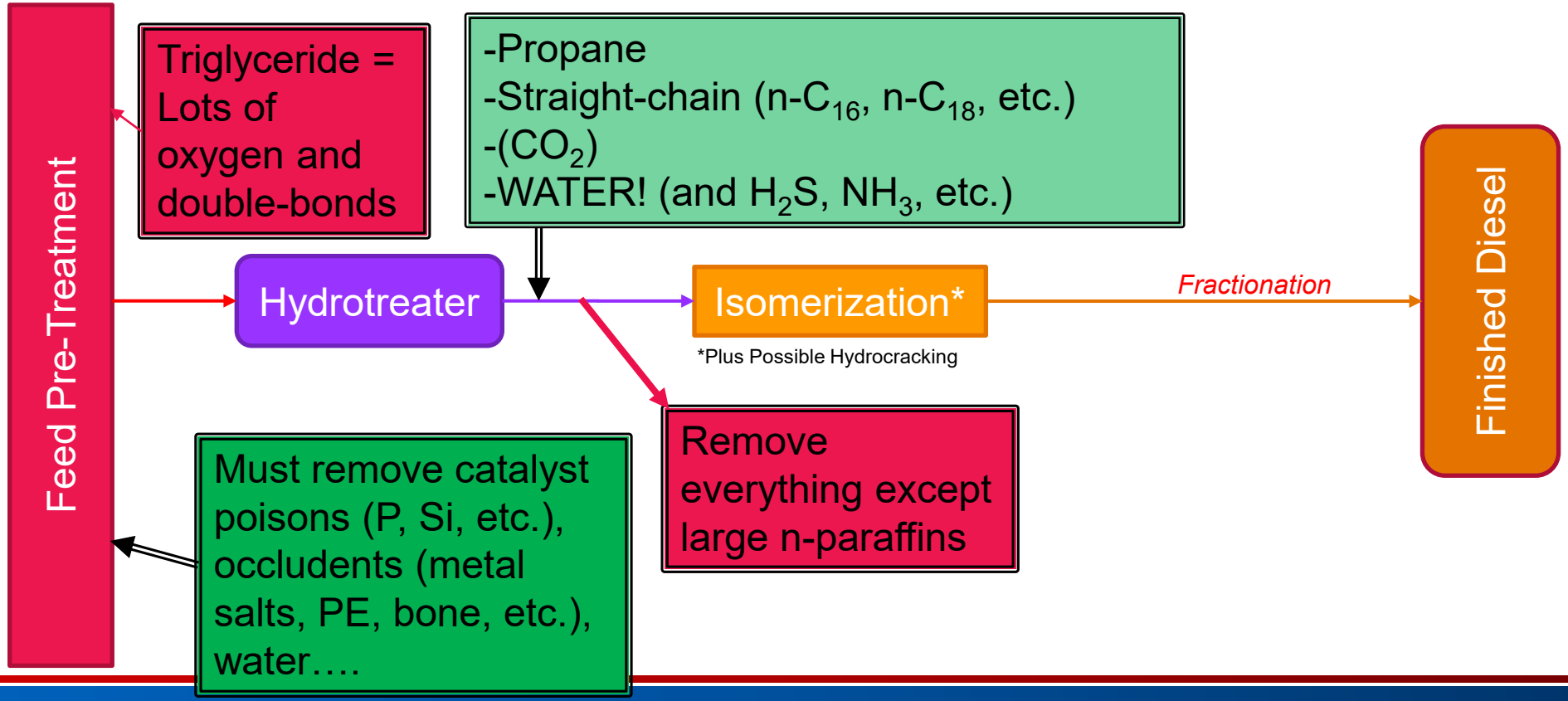
- Primarily nC_{16}, nC_{18}, nC_{20}, propane, and water
- Some side reactions produce CO_2 and odd-numbered n-paraffins (nC_{15}, nC_{17}, etc.





Approx: every 9 gallons of RD, 1 gallon water

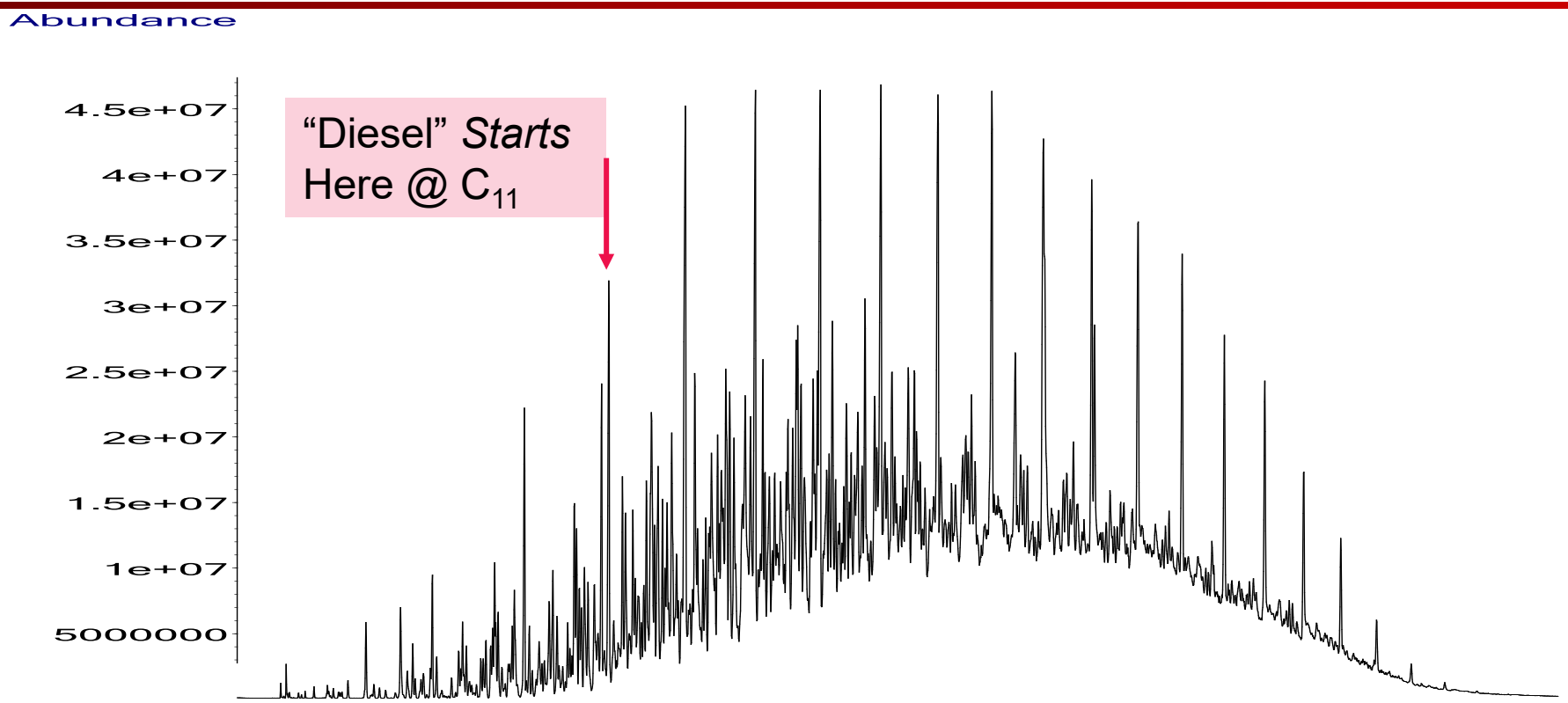
Production of Renewable Diesel



Hydrotreating: Why stop there?

- n-hexadecane melting point = 65 °F
- n-octadecane melting point = 84 °F
- n-icosane melting point = 98 °F

Typical Petroleum Diesel



Hydrotreating: Why stop there?

- n-hexadecane melting point = 65 °F
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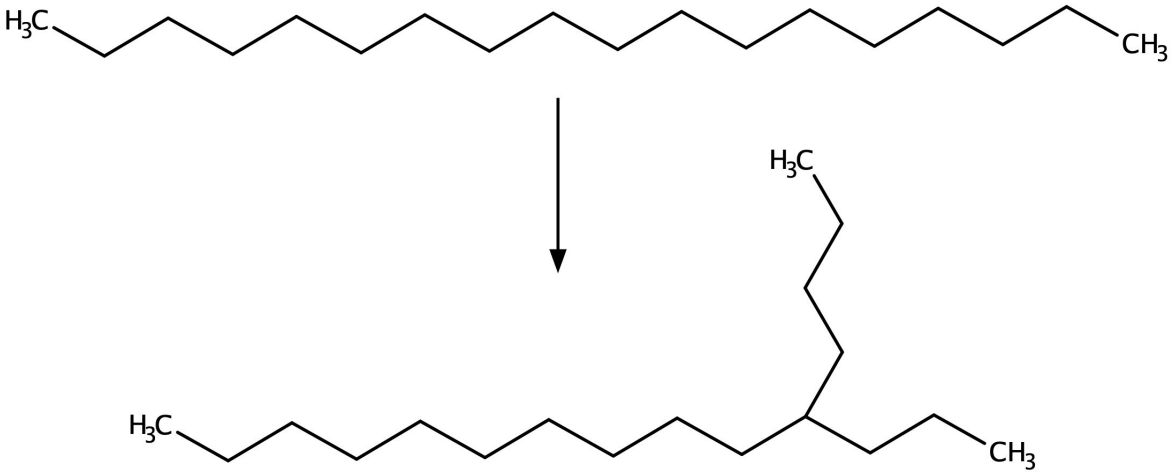
n-octadecane –> 3-ethyl hexadecane (melting point = 41 °F)

$C_{18}H_{38}$ $C_{18}H_{38}$

Most Important Process(es) for RD Production

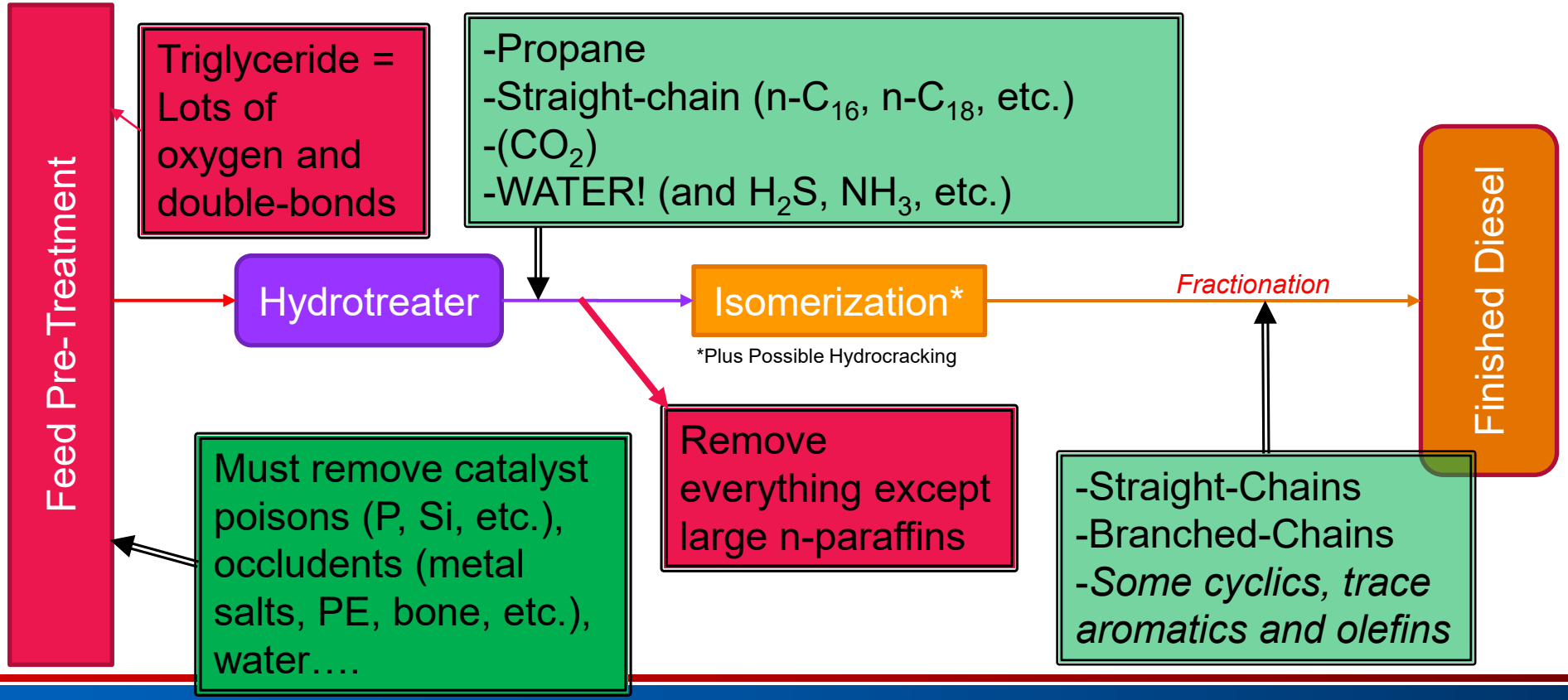
Isomerization (a.k.a. De-waxing)

- Increases amount of branching



n-paraffin –> iso-paraffin

Production of Renewable Diesel

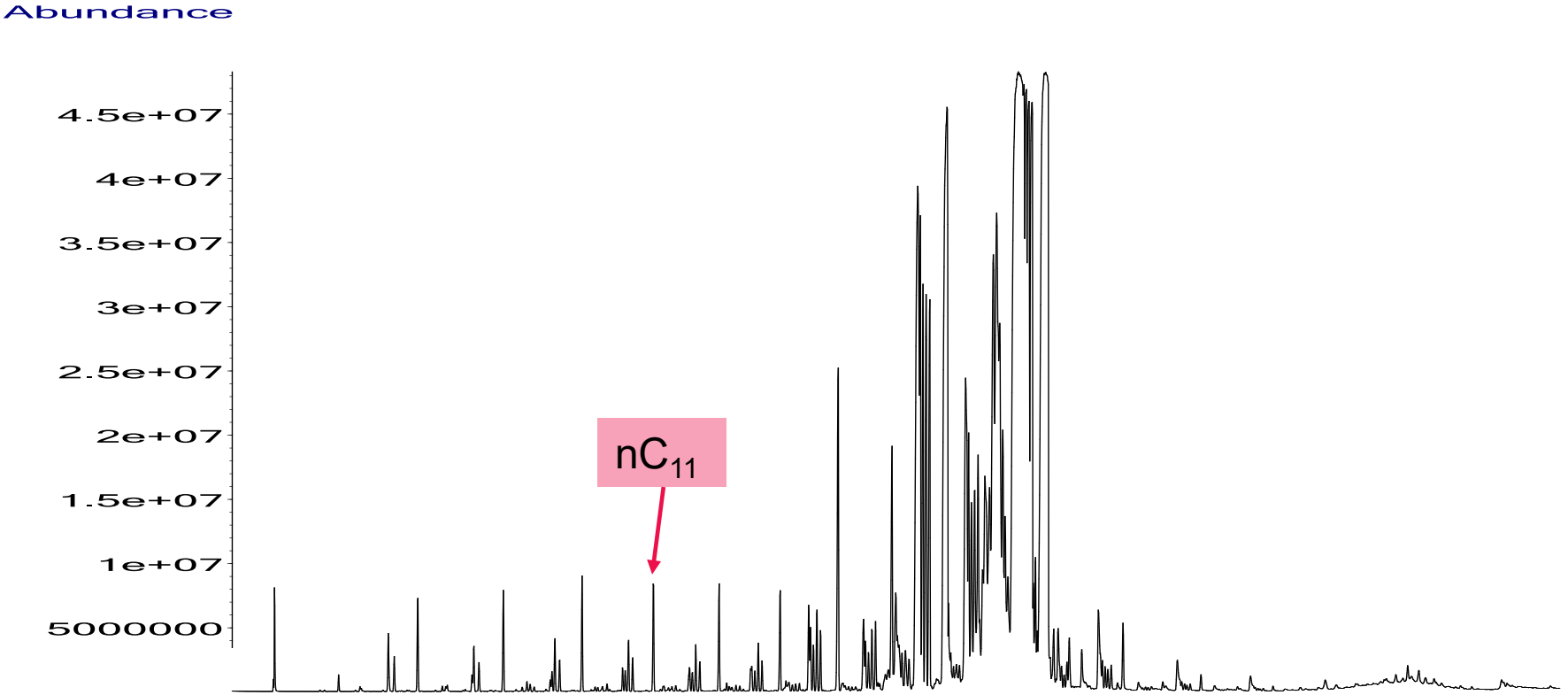


Most Important Process(es) for RD Production

Hydrocracking

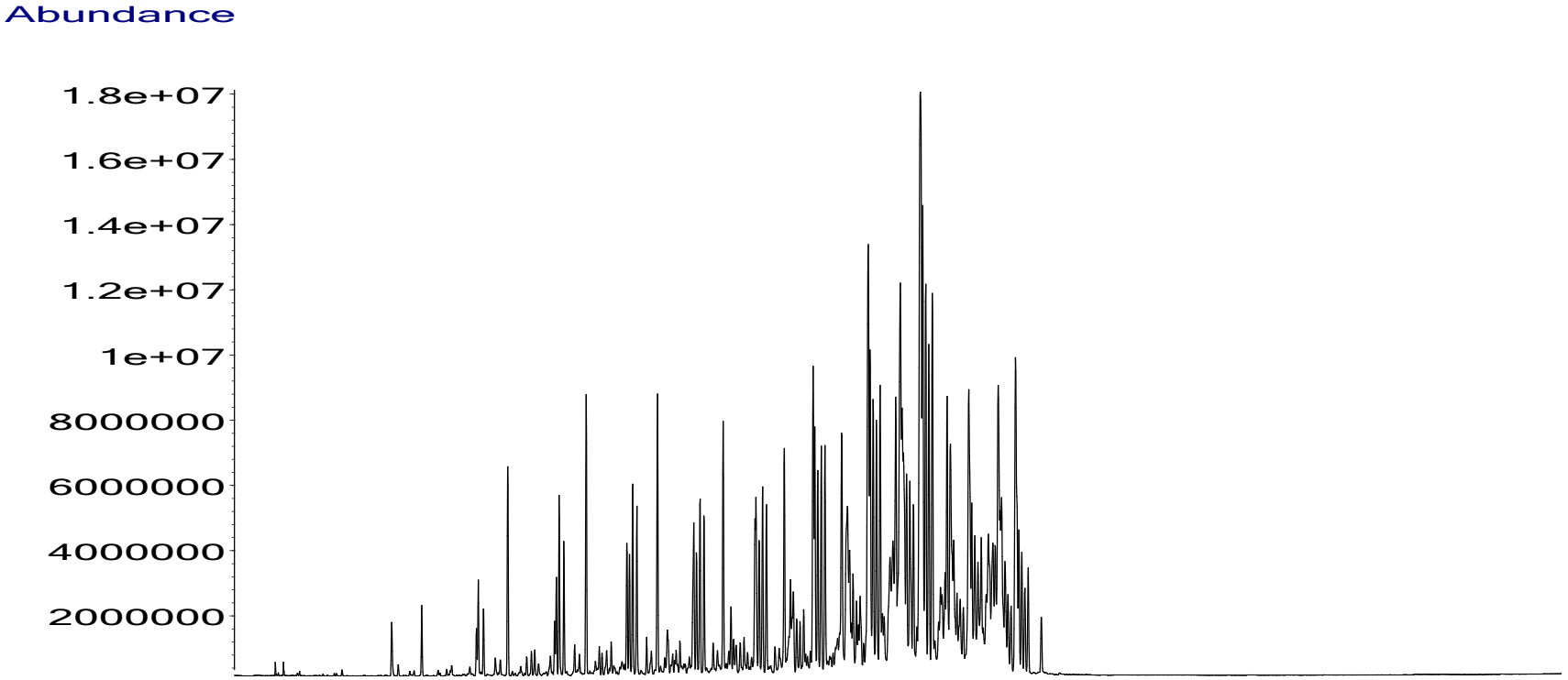
- Everything hydrotreating, plus breaks molecule into two, fills valence with hydrogen

Renewable Diesel
Lightly Isomerized



Renewable Diesel

Heavily Isomerized



Major Contaminants and Their Effects

(if not totally removed by pre-treatment)

- Salts (from FFA neutralization)
  - Can hydrolyze if there is water present to form HCl, which attacks metal
  - Will block the pores in the catalyst beds, causing an increase in dP (differential pressure) across the bed
- Other Insolubles such as rust, poly-ethylene
  - Size dependent: occlude pre-filters or occlude catalyst pores
- Silicon
  - Inorganic (sand): either occludes filters or catalyst pores.
    - Increases fouling or decreases throughput
  - Siloxane/Silicone, such as poly-(di-methyl siloxane). As an anti-foam or de-mulsifier
    - Permanently attaches to catalyst, decreasing the number of active-sites and thus the life of the catalyst

Major Contaminants and Their Effects

(if not totally removed by pre-treatment)

- Phosphorus (as phospho-lipids)
  - Permanently attaches to catalyst, decreasing the number of active-sites and thus the life of the catalyst
  - Increases coking
- Free-fatty acids (measured as TAN, Total Acid Number)
  - Corrodes metallurgy
- Solubilized metals
  - Similar to Phosphorus effects
- Unknown/Unforeseen contaminants
  - Organic moieties that quickly occlude filters, pump screens
  - Rail car lining failures

Does a few ppm really matter?

- Assume 5 wt ppm Si in feed that isn't removed.
  - 10,000 bbl/day (420,000 gal/day) feed
  - Approx. 3.15M lbs
  - @5 ppm Si = 15.75 lbs Si/day
  - Over 1 year→ 5,750 lbs Si

Other Issues

- Backhauling
  - No fossil fuels, solvents, polymers, or anything petroleum-derived! ^{14}C testing
    - Must be well-drained – contact your client for approval of priors and cleaning process
- USUALLY, a single excursion from a “spec” is not detrimental: effects are cumulative

Typical Feedstock Test Methods

- Standardized on many ASTM methods where possible
  - Existing equipment
  - More robust round-robin program
  - Internally compared to many AOCs methods
- *Metals – ASTM D5185 – ICP-AES
- *Silicon – ASTM D5186 or X-ray fluorescence
  - Analyze before and after filtration to discern inorganic (sand) from silicone/siloxanes
- *Phosphorus – ASTM D5185 – ICP-AES
- Insoluble matter – ISO 663 – filtration
- Chlorine – D7536 – X-ray fluorescence
  - Analyze before and after water wash to differentiate inorganic and organic chlorine
- *FFA – AOCS Ce1h-05/Ca 5a-40 – GLC
- *TAN – ASTM D664 Method B – Titration; AOCS Te 1a-64
- Polyethylene – Ca 16-75

Typical Feedstock Test Methods

Not necessarily contaminants, but good to know

- Iodine Value – ISO 3961; AOCS Cd 1d-92
  - Good to know for hydrogen consumption
- Pour Point – ASTM D97 – “tip method” others that rely on pulsed air not as reliable. Good to know when blending various sources
- Stability (OSI) – Cd 12b-92 some feedstocks have polymerization issues
- Nitrogen – ASTM D5762 – horizontal boat inlet combustion
- Water – Karl Fischer – We don’t like paying for water ☺

Thank you!

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