
# Biomass 2013 – FCC Pilot Plant Results with Vegetable Oil and Pyrolysis Oil feeds

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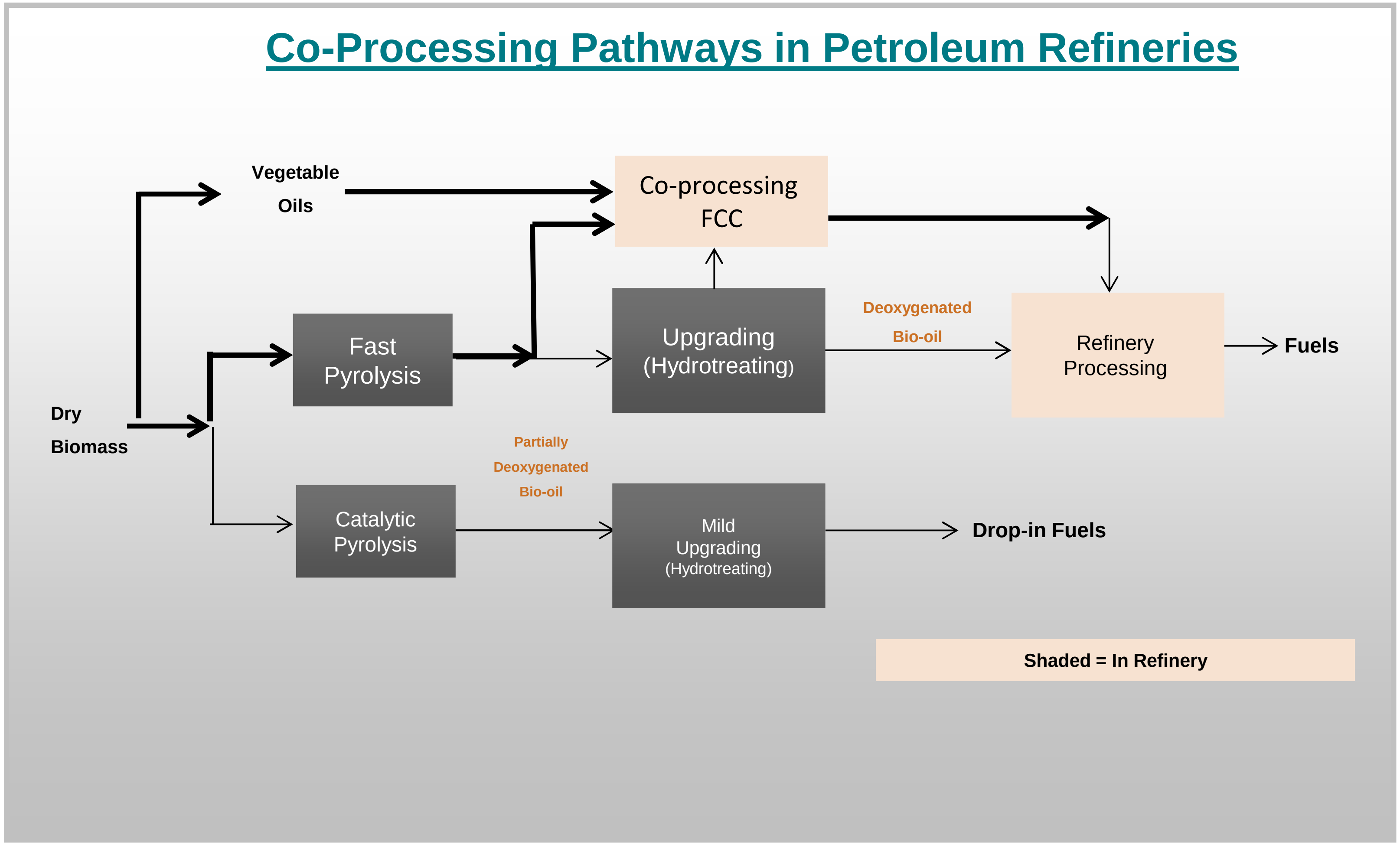
# Introduction

- **Refiners are under pressure to process bio-oils in petroleum refineries, with co-feed to the Fluid Catalytic Cracking (FCC) unit a favored option.**
- **The presentation gives data on two bio-oil FCC feed options.**

## Overview of Presentation

- **Options for co-processing bio-mass in petroleum refineries.**
- **Description of the Grace FCC unit pilot plant (DCR™).**
- **Performance comparison of the DCR to commercial FCC units.**
- **Results – Vegetable oil feed**
- **Results – Pyrolysis oil feed**
- **Conclusions**

# Bio-Mass Refining Options




**There are multiple pathways for co-processing biomass in refineries.**



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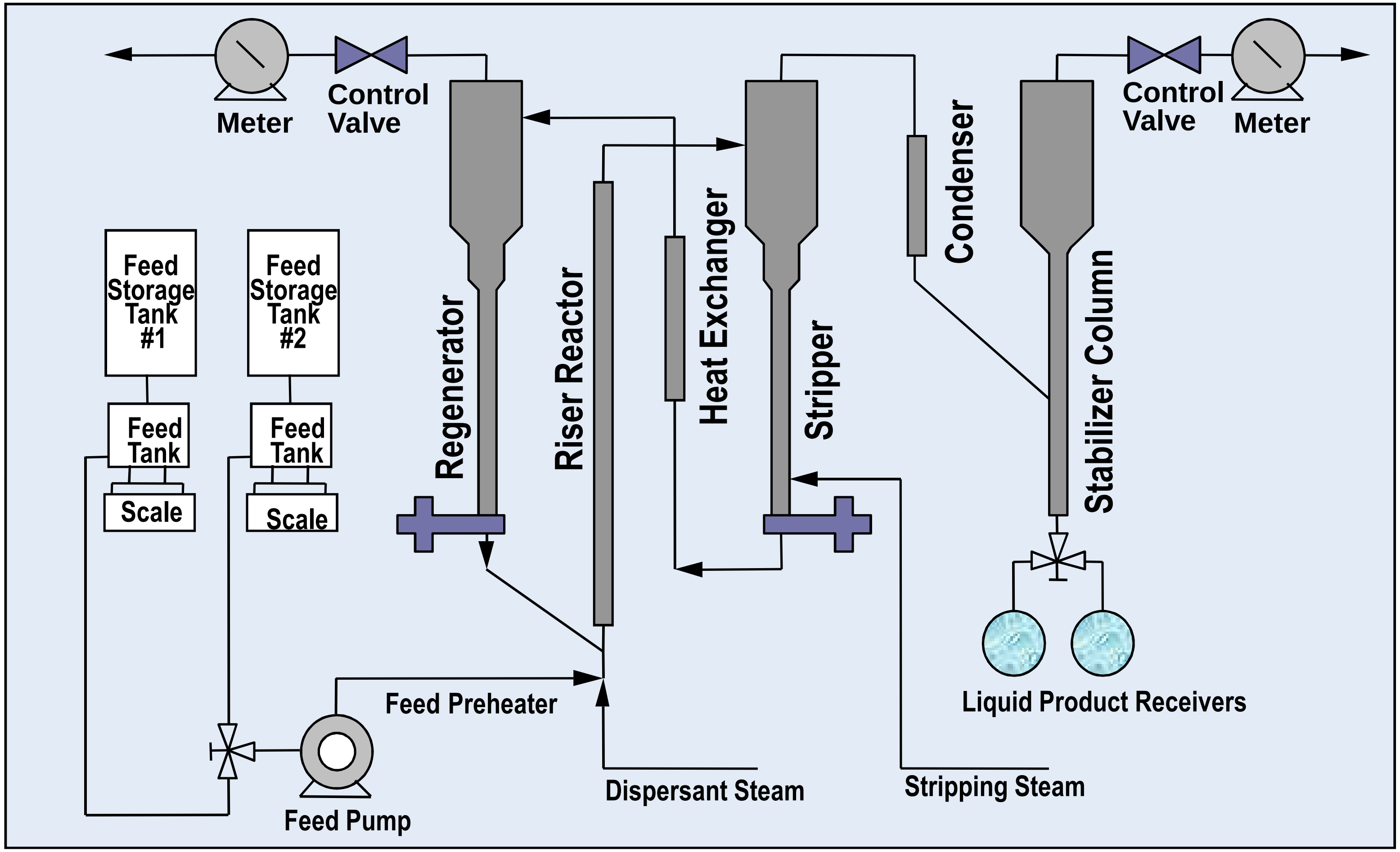
# Grace DCR™ Pilot Plant Schematic




**Continuous circulating riser.**

# Grace DCR™ Pilot Plant

**26 licensed DCR pilot units have been constructed throughout the world.**



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# DCR Comparison to Commercial FCCU- Gas Oil Feed

- **Commercial Ecat, feed, operating conditions used in DCR**

| | DCR | FCCU |
|---|---|---|
| Riser Temperature (°F) | 959 | 959 |
| C/O | 6.6 | 5.9 |
| Conversion (wt%) | 67.2 | 66.2 |
| | | |
| Yields (wt%) | | |
| Fuel Gas | 2.2 | 2.3 |
| LPG | 9.2 | 8.7 |
| Light Gasoline (C5–302°F) | 31.4 | 31.1 |
| RON | 93.3 | 93.1 |
| MON | 79.4 | 78.3 |
| Heavy Gasoline (302-365°F) | 7.2 | 6.4 |
| Naphtha (365-500°F) | 13.1 | 12.7 |
| LCO (500-644°F) | 11.3 | 13.3 |
| HCO (644°F+) | 21.4 | 20.4 |
| Coke | 3.9 | 4.5 |

**Close match to commercial yields.**

# Comparison of 100% Soybean Oil to a Mid-Continent VGO

- **A model case to understand how vegetable oil would change yields and process conditions**

| | Soybean Oil | Mid Continent VGO |
|---|---|---|
| API (°) | 21.6 | 24.7 |
| Sulfur, wt.% | 0.00 | 0.35 |
| **Oxygen, wt.%** | **10.5** | 0.0 |
| D2887 Distillation, °F | | |
| IBP | 702 | 527 |
| 5% | 1059 | 651 |
| 10% | 1069 | 691 |
| 30% | 1090 | 773 |
| 50% | 1102 | 848 |
| 70% | 1111 | 928 |
| 90% | 1183 | 1045 |
| 95% | 1232 | 1108 |
| FBP | 1301 | 1259 |

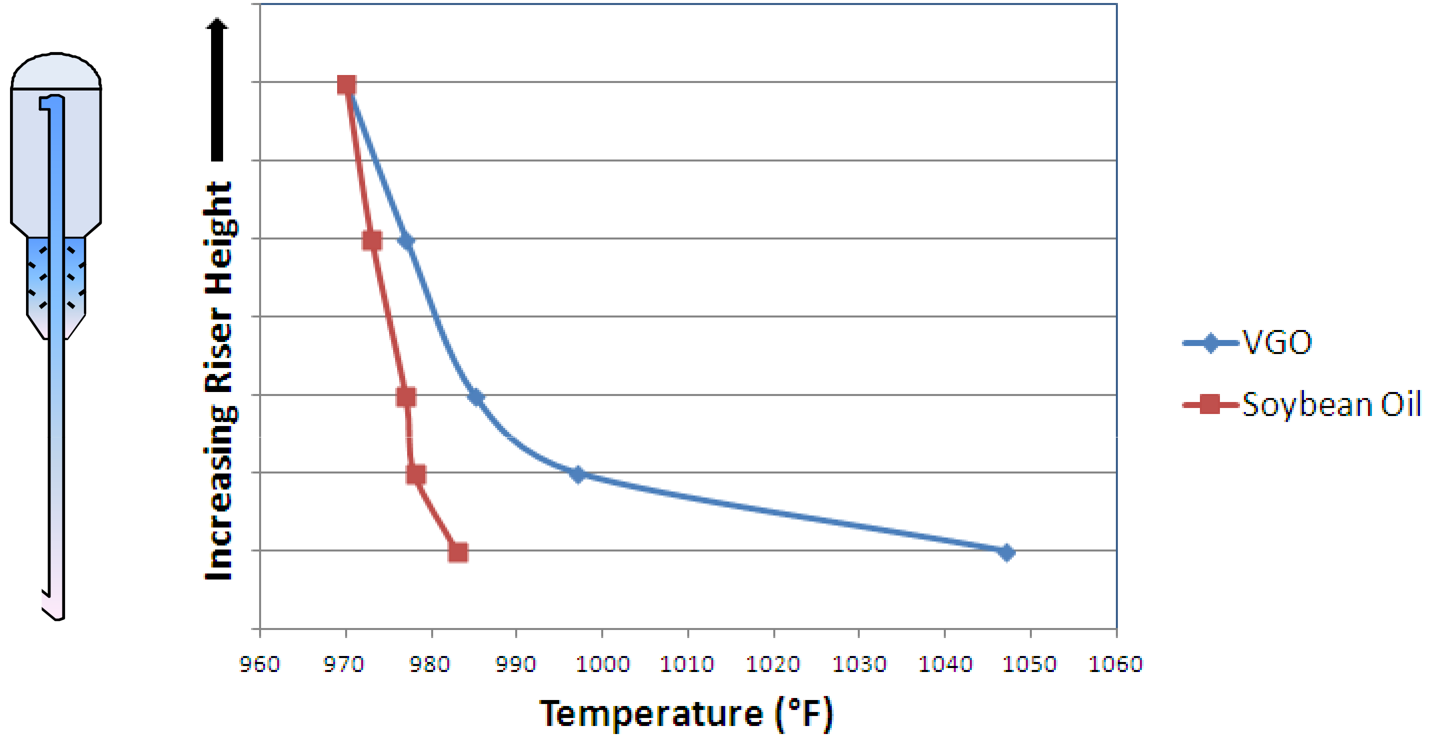
**Soybean oil is much different than VGO - 10 wt% oxygen.**

# Yields at Same Operating Conditions

| | 100% Soybean Oil | 100% VGO |
|---|---|---|
| Rx Exit Temp (°F) | 970 | 970 |
| Catalyst Temp (°F) | 1300 | 1300 |
| Feed Temp (°F) | 250 | 250 |
| Pressure (psig) | 25 | 25 |
| C/O Ratio | 6.7 | 9.3 |
| H2 Yield wt% | 0.04 | 0.02 |
| C1 + C2's wt% | 1.9 | 2.1 |
| Total C3 wt% | 4.3 | 6.7 |
| Total C4 wt% | 6.2 | 12.4 |
| **Gasoline (C5-430˚F) wt%** | **44.5** | **53.1** |
| G-Con RON EST | 90.9 | 90.2 |
| G-Con MON EST | 79.0 | 79.5 |
| **LCO (430-700°F) wt%** | **22.0** | **15.4** |
| Bottoms (700°F+) wt% | 3.9 | 4.9 |
| Coke wt% | 4.6 | 5.2 |
| Fuel Gas CO (wt%) | **1.2** | 0.0 |
| Fuel Gas $CO_2$ (wt%) | **0.9** | 0.0 |
| Fuel Gas $H_2O$ (wt%) (by difference) | **10.3** | 0.0 |

**Soybean oil produces less gasoline and more LCO than VGO.**

# Adiabatic Riser Temperature Profile




**Same preheat, catalyst temperature and riser outlet temperature.**

**Soybean oil has significantly lower heat of cracking than VGO!**

# Key Findings – Soybean Oil

- **Soybean oil cracking changes the riser temperature profile.**
  - Heat of cracking is only ~15% of conventional VGO.
- **Most of the oxygen reacts to form water.**
- **Product yield slate is different.**
  - Sharply lower gasoline.
  - Sharply higher LCO, lower bottoms.

**Soybean Oil could likely be processed in a commercial FCC unit.**

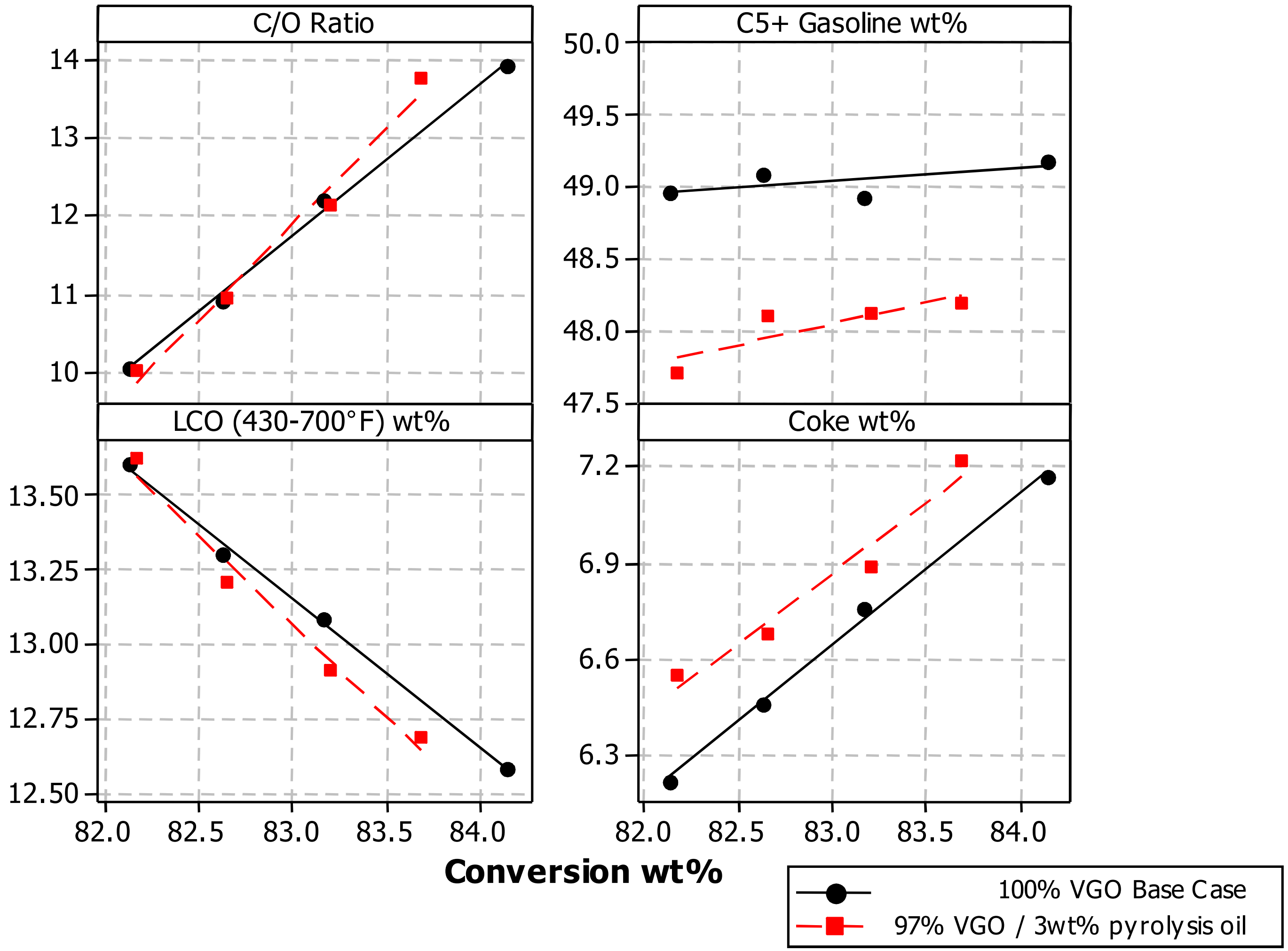
## Processing a Blend of Pyrolysis oil and VGO

- **A blend of 3wt% pine-derived pyrolysis oil and 97wt% mid-continent VGO was processed in the DCR.**
- **The pine-derived pyrolysis oil had the following properties.**

| | |
|---|---|
| Water content (wt%) | 23.0 |
| Carbon (as-is) (wt%) | 39.5 |
| Hydrogen (as-is) (wt%) | 7.5 |
| Oxygen (as-is) (wt%) (by difference) | 53.0 |
| Carbon (dry basis) (wt%) | 55.5 |
| Hydrogen (dry basis) (wt%) | 6.5 |
| **Oxygen (dry-basis) (wt%) (by difference)** | **38.0** |

**Properties are those of a typical pyrolysis liquid that has not been upgraded.**

# Yield Effects of Blending in 3 wt% Pyrolysis Oil




**Adding pyrolysis oil results in more coke, less gasoline and less LCO.**

# Interpolated Yields at Constant Conversion

| | 100% VGO | 3 wt% pine-based pyrolysis oil – 97 wt% VGO |
|---|---|---|
| Rx Exit Temp (°F) | 970 | 970 |
| Catalyst Temp (°F) | 1300 | 1300 |
| Pressure (psig) | 25 | 25 |
| Conversion wt% (100-LCO-bottoms) | 82.5 | 82.5 |
| C/O Ratio | 10.7 | 10.6 |
| H2 Yield wt% | 0.05 | 0.05 |
| C1 + C2's wt% | 3.1 | 3.2 |
| Total C3 wt% | 8.6 | 8.2 |
| Total C4 wt% | 15.1 | 14.4 |
| Gasoline (C5-430°F) wt% | 49.0 | 47.9 |
| G-Con RON EST | 93.6 | 94.5 |
| G-Con MON EST | 82.5 | 83.1 |
| LCO (430-700°F) wt% | 13.4 | 13.3 |
| Bottoms (700°F+) wt% | 4.1 | 4.2 |
| Coke wt% | 6.40 | 6.65 |
| **Fuel Gas CO (wt%)** | 0 | **0.55** |
| **Fuel Gas $CO_2$ (wt%)** | 0 | **0.09** |
| **Fuel Gas $H_2O$ (wt%) (by difference)** | 0 | **1.27** |

**A majority of the pyrolysis oil formed $H_2O$, CO and $CO_2$ in the product gas.**



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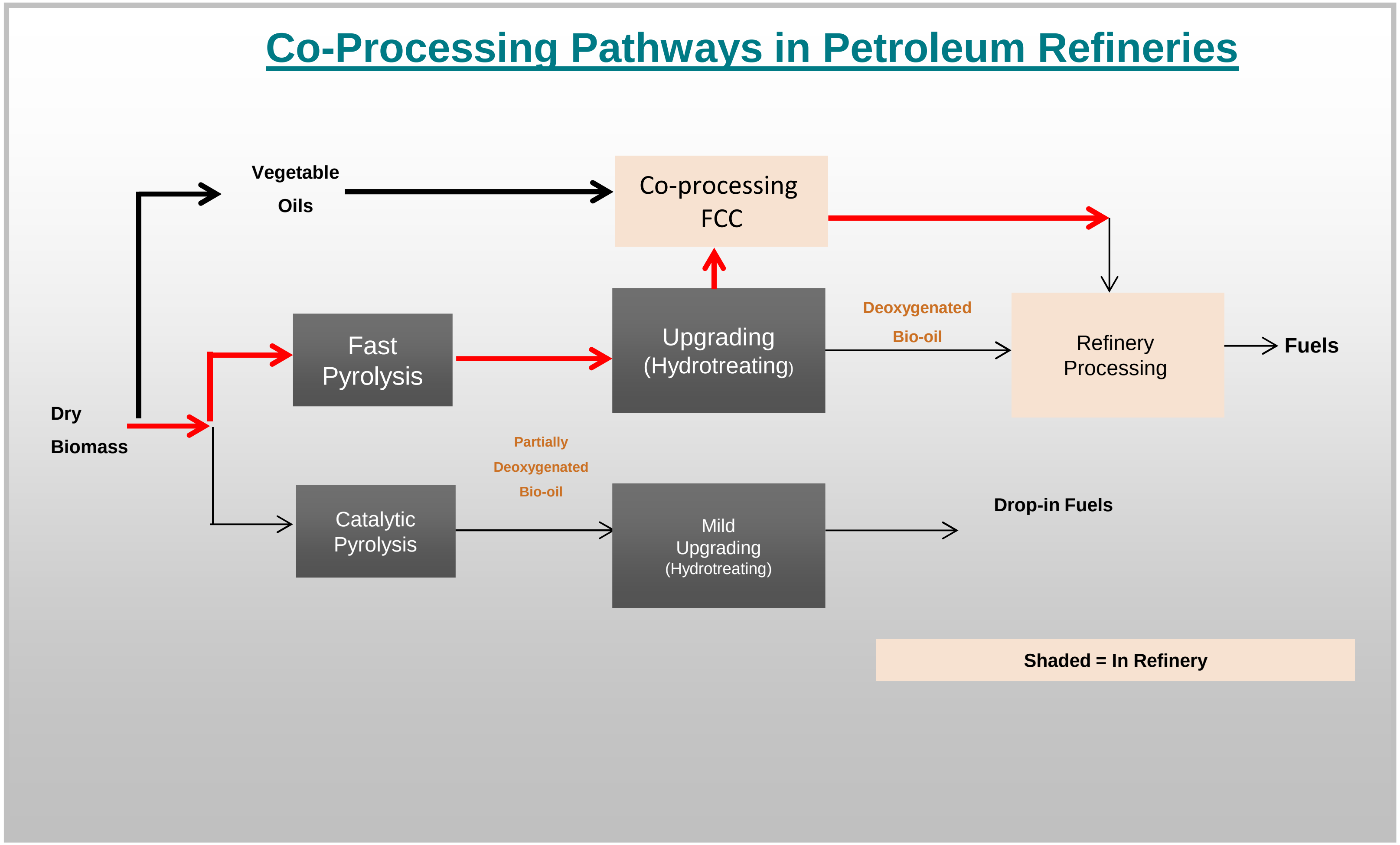
## Key Findings from Co-Processing Pyrolysis Oil

- **Even small amounts (3 wt%) of pyrolysis oil result in significant yield shifts.**
  - **A majority of the pyrolysis oil converts to $H_2O$, CO and $CO_2$.**
  - Incremental yields of coke and bottoms are also very high.
  - Gasoline and LCO decrease.
- **Economics will likely preclude co-processing raw pyrolysis oil in an FCC.**

**Processing of raw pyrolysis oils in FCC will be very difficult.**

# Likely Processing Pathway for Bio-Mass via Pyrolysis




**Pyrolysis Oils will require upgrading (hydrotreating) prior to processing in FCC**



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# Conclusions

- **Bio-oils vary greatly in quality, and their ability to be co-fed to commercial FCC units varies accordingly.**
  - Vegetable oils can likely be processed easily.
  - Raw pyrolysis oils will be a major challenge.  They will need to be hydrotreated prior to processing in FCC.
- **The oxygen content of bio-oils can be expected to fully react in an FCC unit and will form mostly $H_2O$, with some CO and $CO_2$.**
- **Low oxygen feeds such as vegetable oil could be directly processed in FCC without pretreatment, but may still require some refinery adjustments due to their different product yield slate.**

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**For additional information, please visit www.grace.com or contact:**

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