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Recycle and Catalytic Strategies for Maximum FCC Light Cycle Oil Operations

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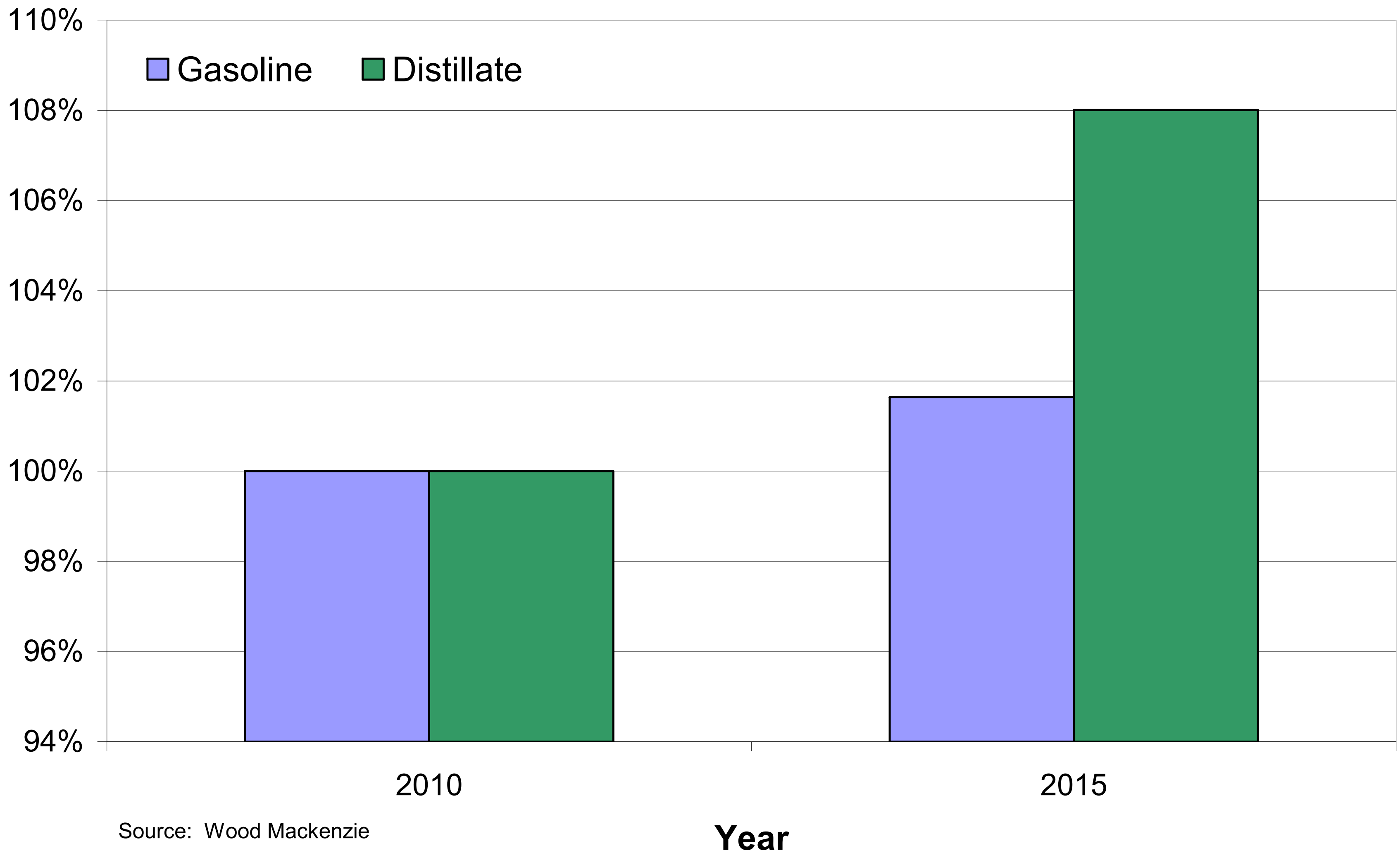
North America Refined Gasoline and Distillate Demand

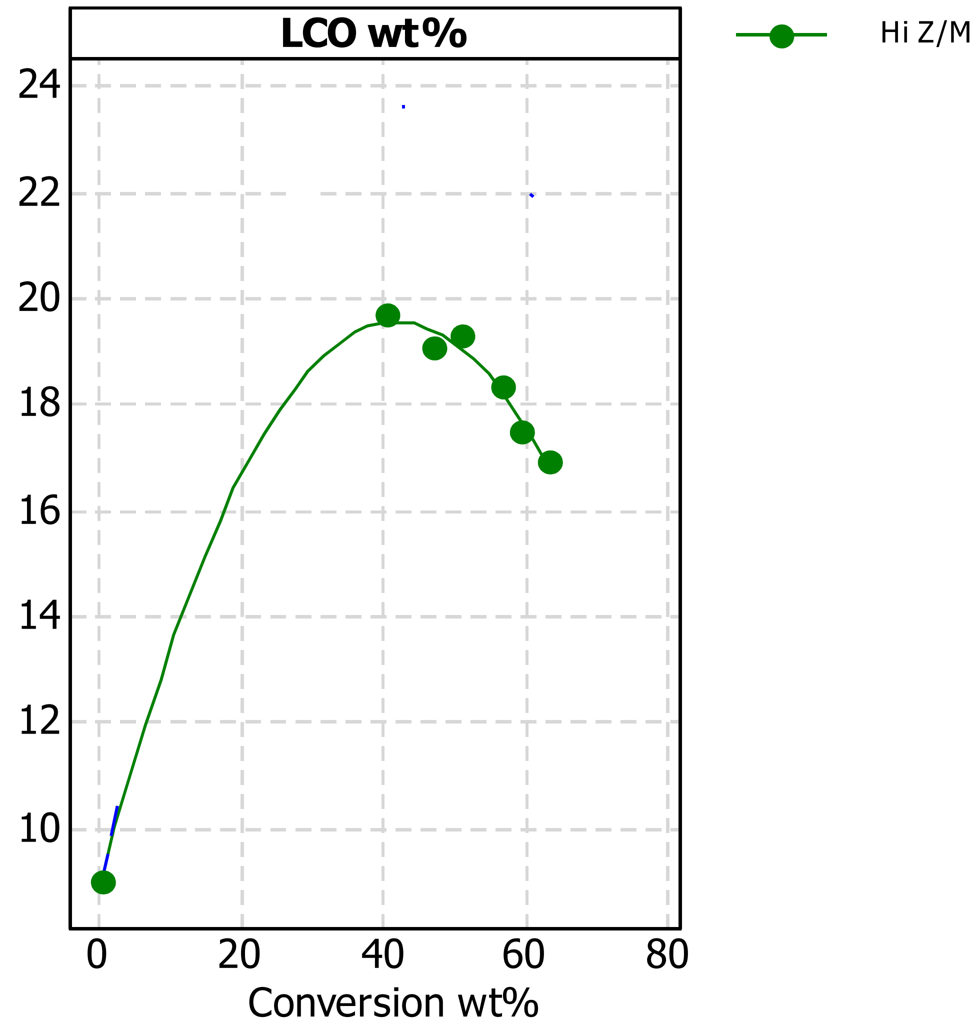


Source: Wood Mackenzie

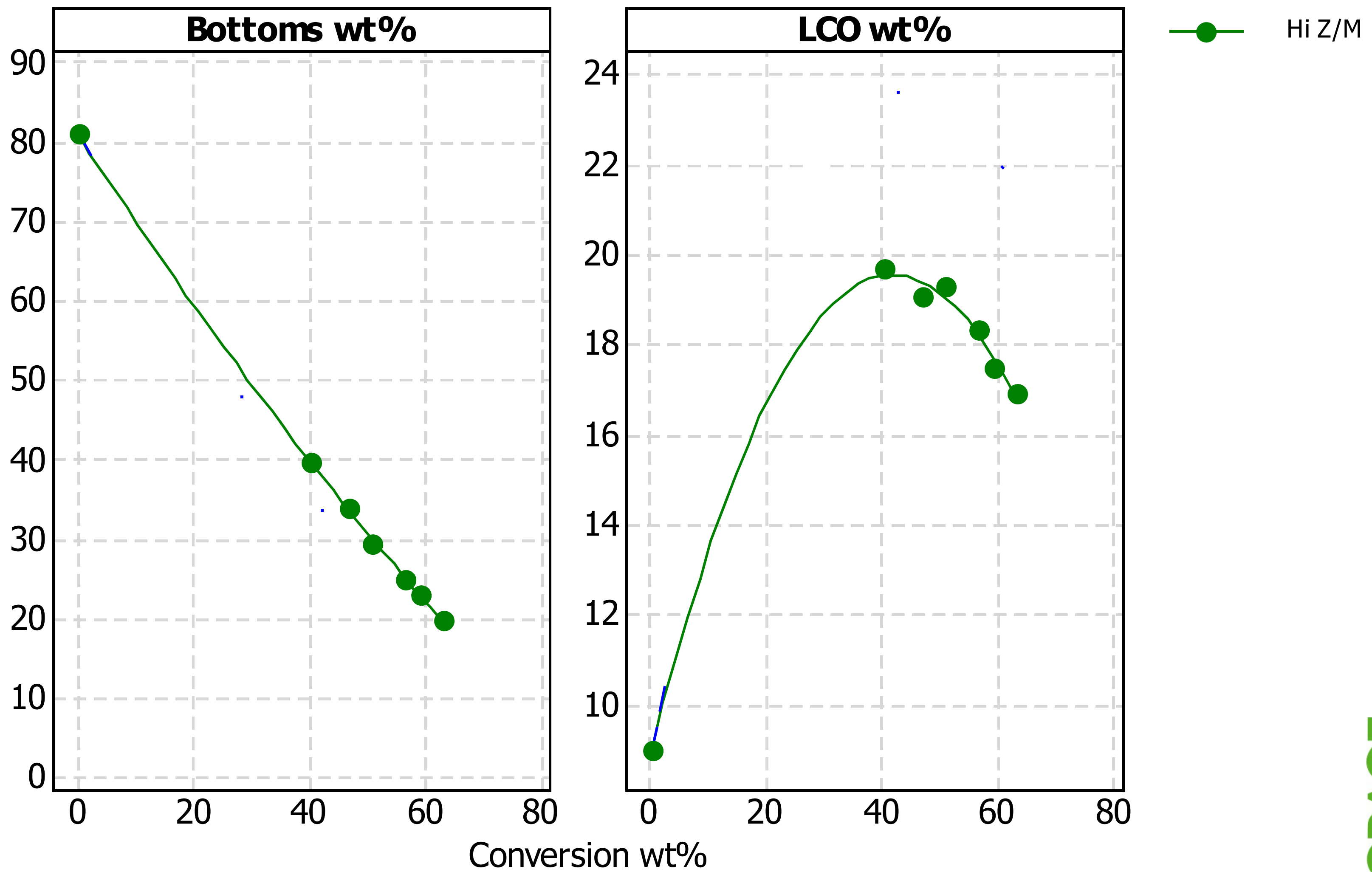
Distillate demand growth is expected to exceed Gasoline

LCO Selectivity

LCO is an Intermediate Product

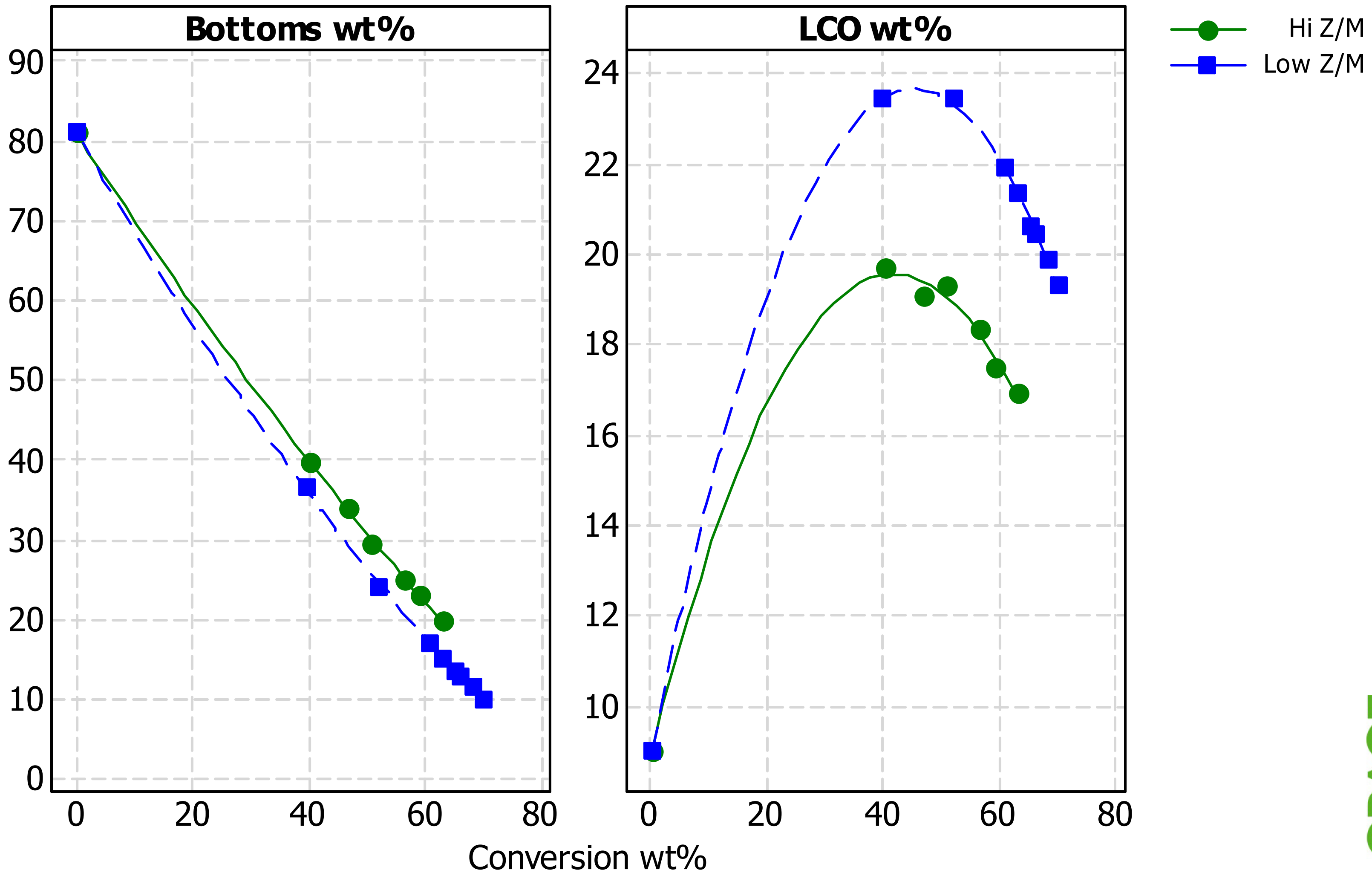


LCO and Bottoms Selectivity



LCO and Bottoms Selectivity

Is the Maximum LCO Point Optimal?



Maximum LCO Optimization Strategies

- **Reduce gasoline endpoint and maximize LCO endpoint**
- **Feedstock**
  - Removal of diesel range material from the FCC feedstock
  - FCC feed hydrotreating severity optimization
  - Residual feedstock optimization
- **Operating Conditions**
  - Lower reactor temperature
  - Higher feed temperature
  - Lower equilibrium catalyst activity

Additional Bottoms Results!

Maximum LCO Optimization Strategies

- **Catalyst Optimization**
  - Increased bottoms conversion
  - Lower zeolite and higher matrix surface area
  - Lower Activity
  - Maintain C_3+ liquid yield and gasoline octane

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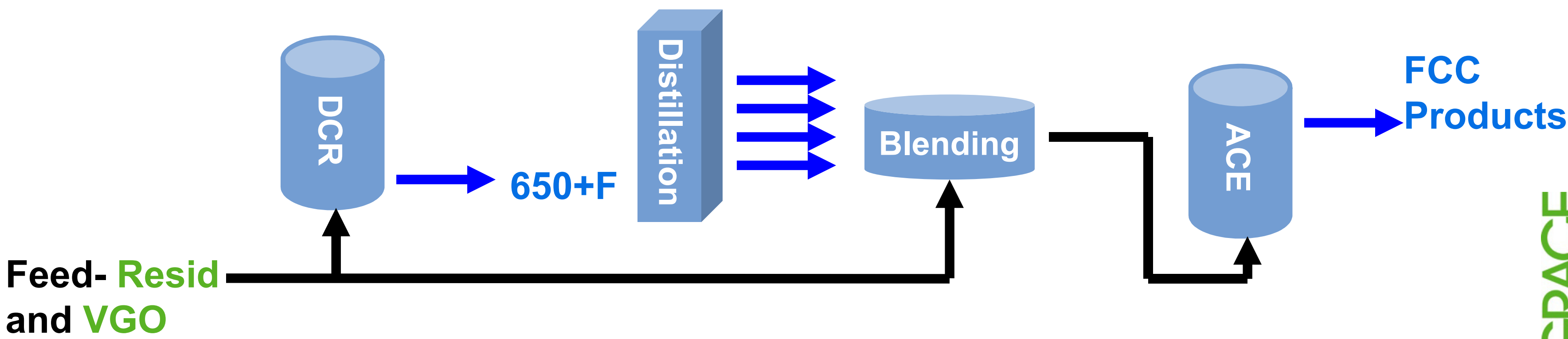
Recycle

- **To fully maximize LCO, recycle is required to maintain bottoms yield as conversion is reduced.**
- **Which recycle stream is best to recycle?**
  - Heavy cycle oil or bottoms?
  - Which specific boiling range is optimal?
  - Does the feedstock type play a role?

Lab Simulation of Recycling Operation

- **A two-pass Davison Circulating Riser (DCR) +ACE scheme was adopted to simulate the recycling operation in a commercial unit.**
  - DCR was used to generate 650+°F material over a conversion range of 75 to 54 wt% with a **Resid** and **VGO** feedstock.
  - 650+°F stream was distilled into desired bottom cuts.
  - Bottoms cuts were blended with original resid feed.
  - ACE used original feeds together with recycle streams.
  - Grace's MIDAS® premium bottoms cracking catalyst was used.



Riser Pilot Plant (DCR) Used to Generate Recycle Streams

- **Recycle streams at 54% conversion distilled to:**
  - 650°F to 750°F
  - 650°F to 800°F
  - 650°F to 850°F
  - 650°F+
  - 750°F+
  - 800°F+
  - 850°F+
- **Recycle streams at 54%, 58%, 68%, & 75% conversions distilled to:**
  - 650°F to 750°F
- **Quantity of each recycle stream measured from 1st pass cracking**
- **Properties of each recycle stream**

Incremental Yields of 650-750°F Recycle Streams

Boiling Range	VGO	650-750°F from VGO	Resid	650-750°F from Resid
Recycle Ratio, wt%	0	10.5	0	7.3
Cat-to-Oil Ratio	3.29	3.49	3.43	4.80
Dry Gas, wt%	0.70	0.73	1.08	1.13
LPG, wt%	8.39	8.89	7.96	13.34
C5+ Gasoline, wt%	44.01	43.58	40.63	39.79
LCO, wt%	26.04	26.32	24.72	36.97
Bottoms, wt%	18.96	18.68	20.28	8.03
Coke, wt%	1.90	1.81	5.59	5.45

?

- 650-750°F fractions from VGO made about the same LCO and bottoms as fresh VGO.
- 650-750°F fractions from Resid made much more LCO, less bottoms and additional LPG than fresh Resid.

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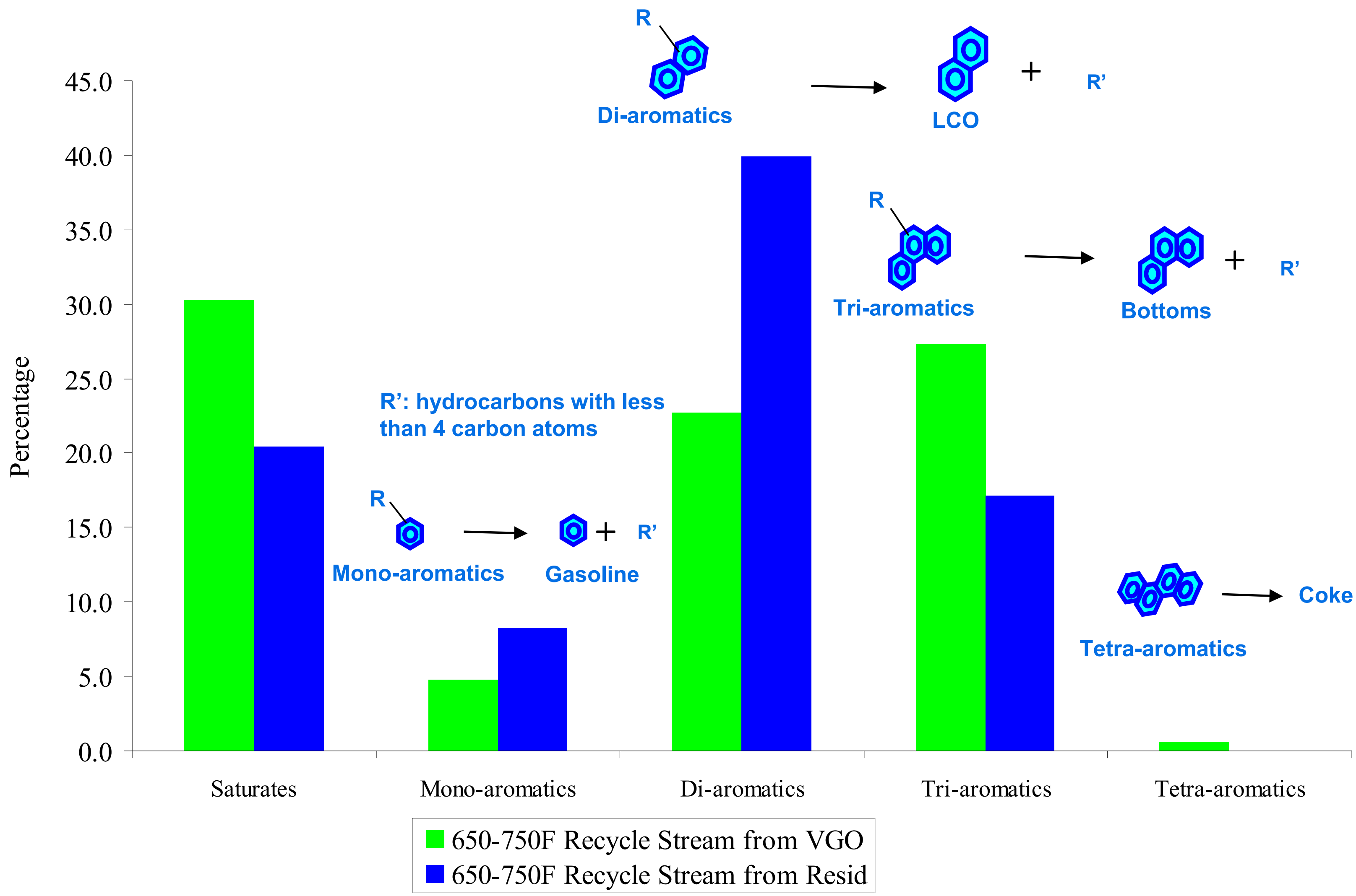
Cracking Path of Hydrocarbon Molecules



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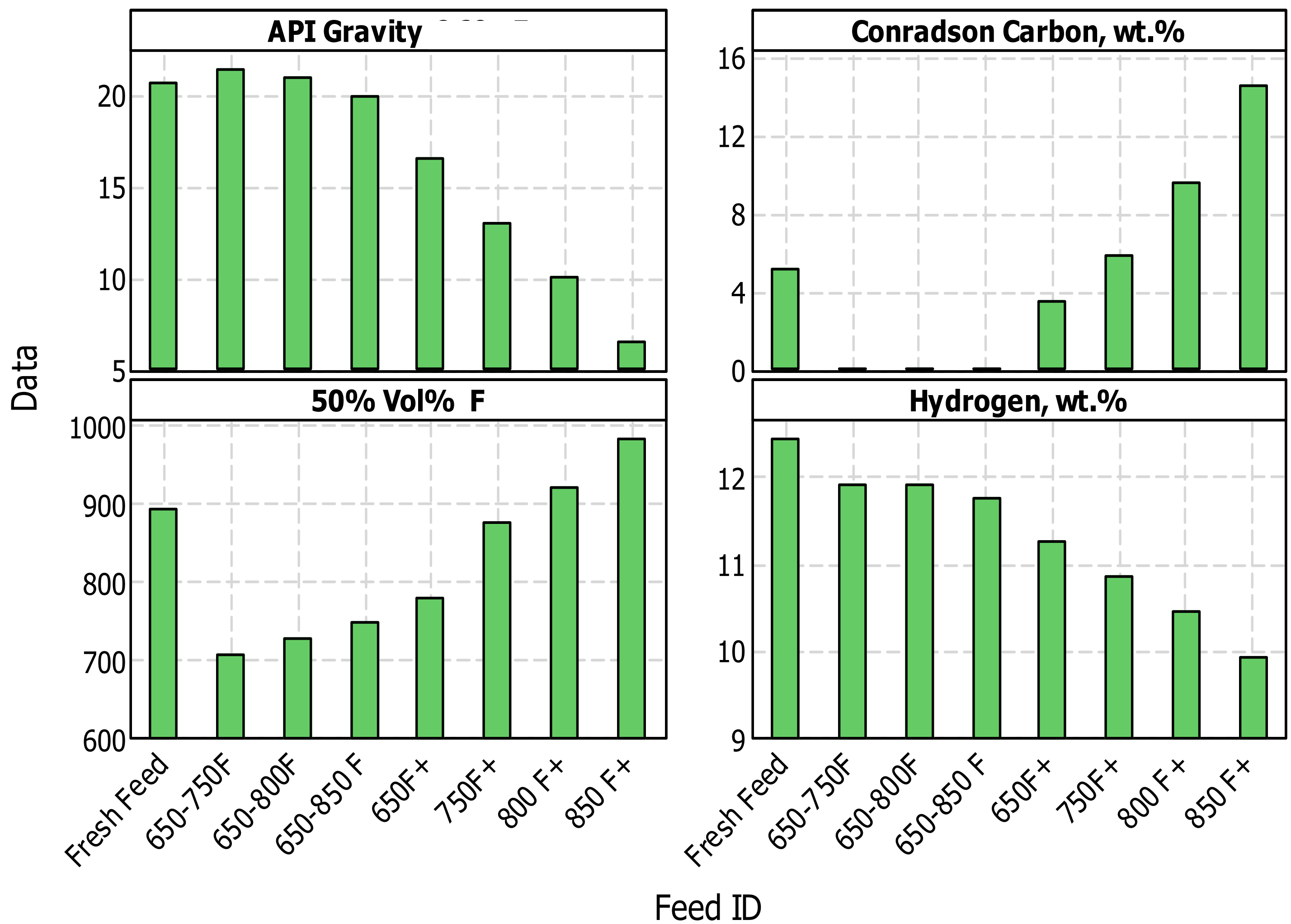
Properties of Recycle Streams at 54% Conversion from Resid



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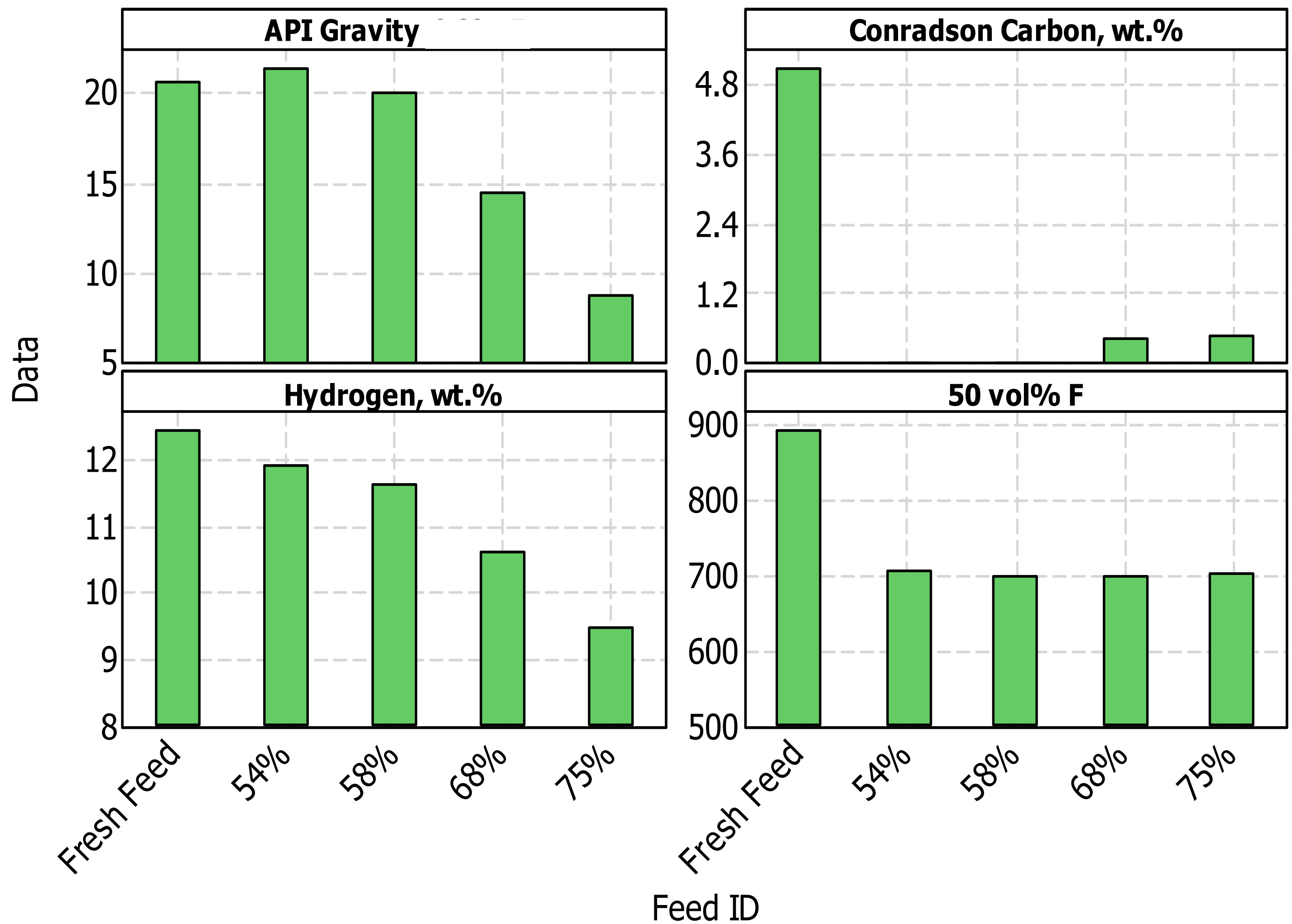
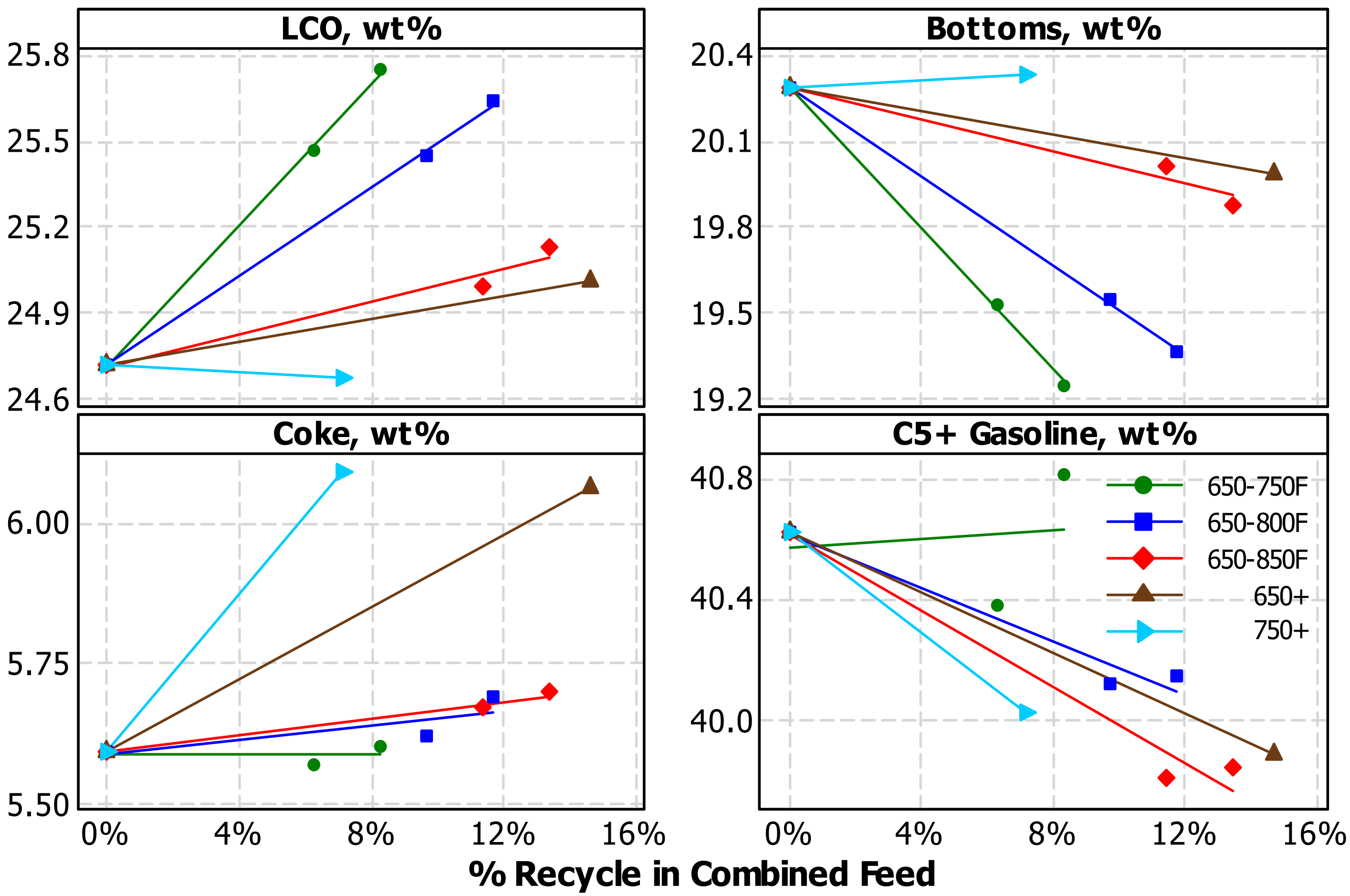
Properties of 650-750ºF Recycle Stream vs. Conversion for Resid



Properties of 650-750°F Recycle Stream vs. Recycle % - Resid

- **Key yields at 55 wt.% conversion vs. % recycle in combined feed**



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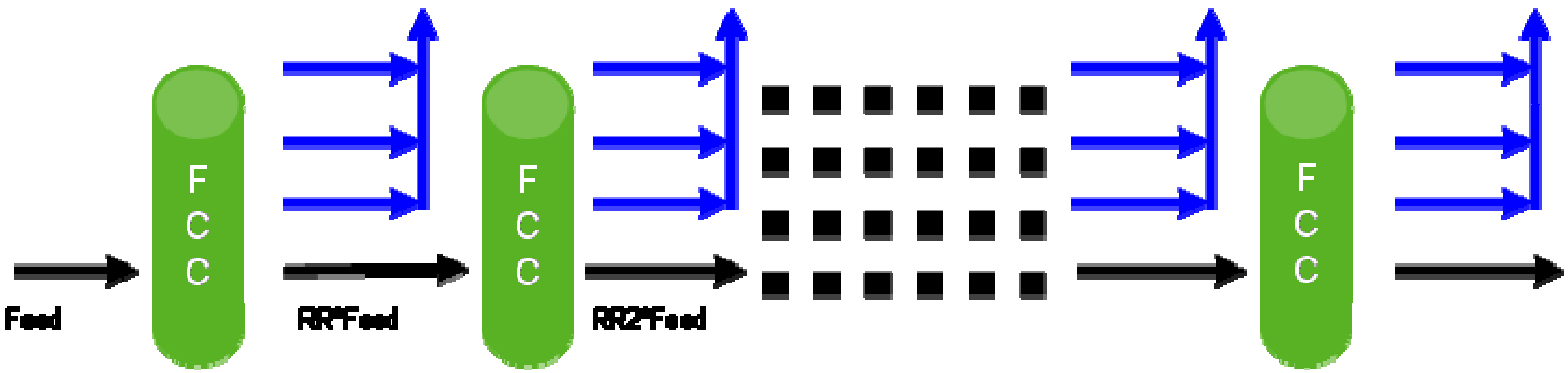
Element Tracking Approach

- **Element Tracking Approach can be used to simulate continuous recycle operation.**
- **Two-pass cracking can closely simulate steady-state.**



~0 for Recycle Ratios ~ <= 15%

$$LCO_{tot} = LCO_1 + RR * LCO_2 +$$

$$COK_{tot} = COK_1 + RR * COK_2$$

$$GAS_{tot} = GAS_1 + RR * GAS_2 +$$

$$BOT_{tot} = (BOT_1 - RR) + RR * (BOT_2 - RR) + RR^2 * ($$

Maximum LCO Yields – Fresh Feed Basis – Resid

	Max. Gasoline Base	Base No Recycle
Conversion, Wt.%	70.0	55.0
Recycle Ratio	0	0
Maximum recycle available		
Hydrogen, Wt.%	0.11	0.09
Total C1's & C2's, Wt.%	1.4	1.0
C3=, Wt.%	3.3	2.1
Total C3's, Wt.%	3.9	2.4
Total C4='s, Wt.%	5.1	3.9
Total C4's, Wt.%	8.5	5.6
C5+ Gasoline, Wt.%	49.4	40.5
RON	89.6	89.2
MON	78.6	77.3
LCO, Wt.%	**20.5**	**24.7**
Bottoms, Wt.%	9.5	20.2
Coke, Wt.%	6.7	5.6
	Max. Coke Allowed	

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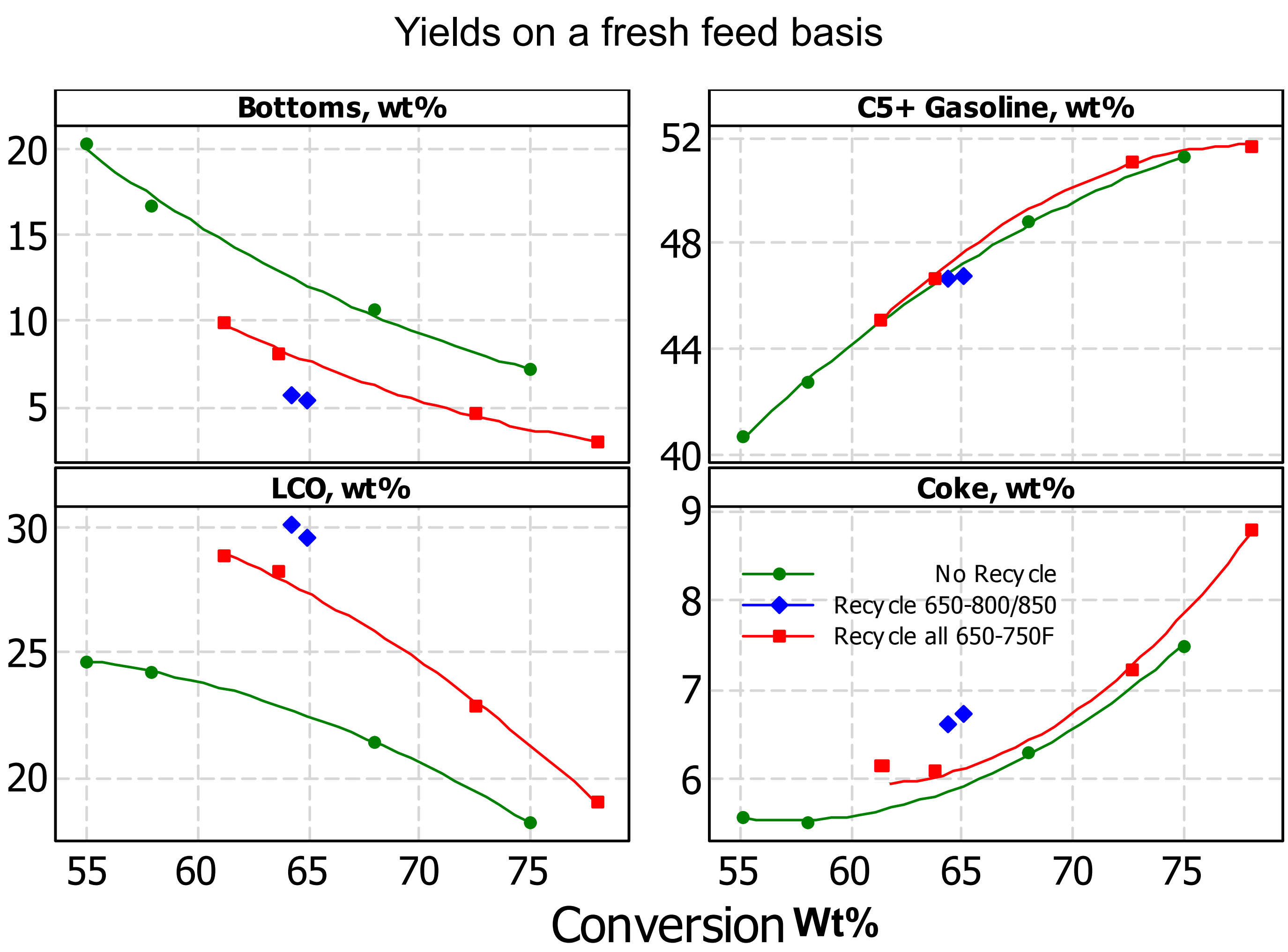
Product Selectivities with and without Recycle - Resid



650-800°F and 650-850°F produces the highest LCO selectivity with slight coke penalty

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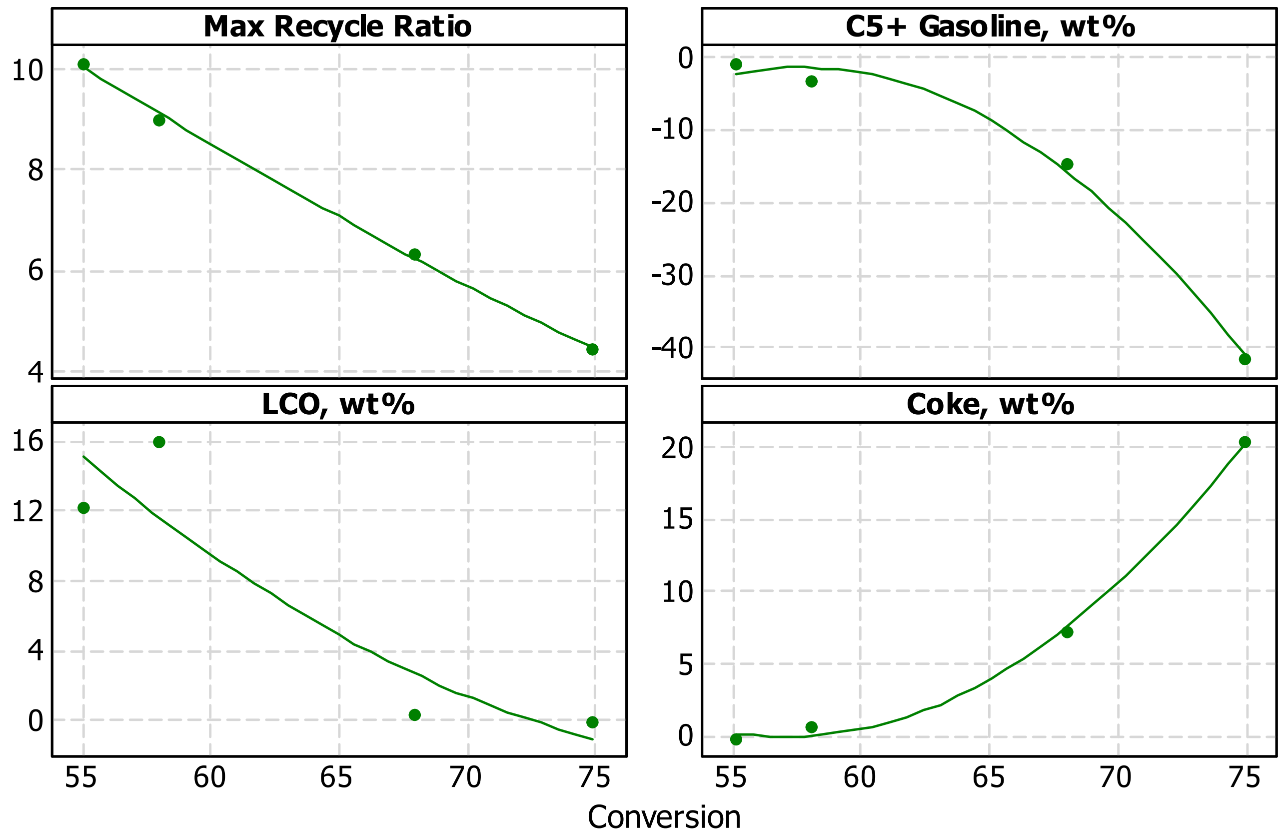
Fresh Feed & Recycle Cracking Selectivity Differences - Resid

- Yields of 2nd pass cracking (Recycle Cracking) minus Yields of Fresh Feed Cracking



2nd pass cracking of 650-750°F fraction obtained at reduced conversion made more LCO than cracking fresh feed with almost no penalty on coke and gasoline. Large coke debit at increased conversion.

Catalyst Strategies for Maximum LCO

- **Maximize Bottoms Cracking to LCO**
  - MIDAS® Technology Platform
    - Optimal matrix surface area, pore size, and pore distribution
- **Optimal Ecat MAT**
  - Lower within slurry yield and liquid yield target
  - Optimal rare earth for activity and hydrogen transfer
- **Reduced zeolite surface area**
  - Minimize LCO conversion via zeolite
- **ZSM-5**
  - OlefinsMax® additives
  - OlefinsUltra® additives
    - Maintain or increase liquid yield
    - Recover any loss of gasoline octane and LPG olefins

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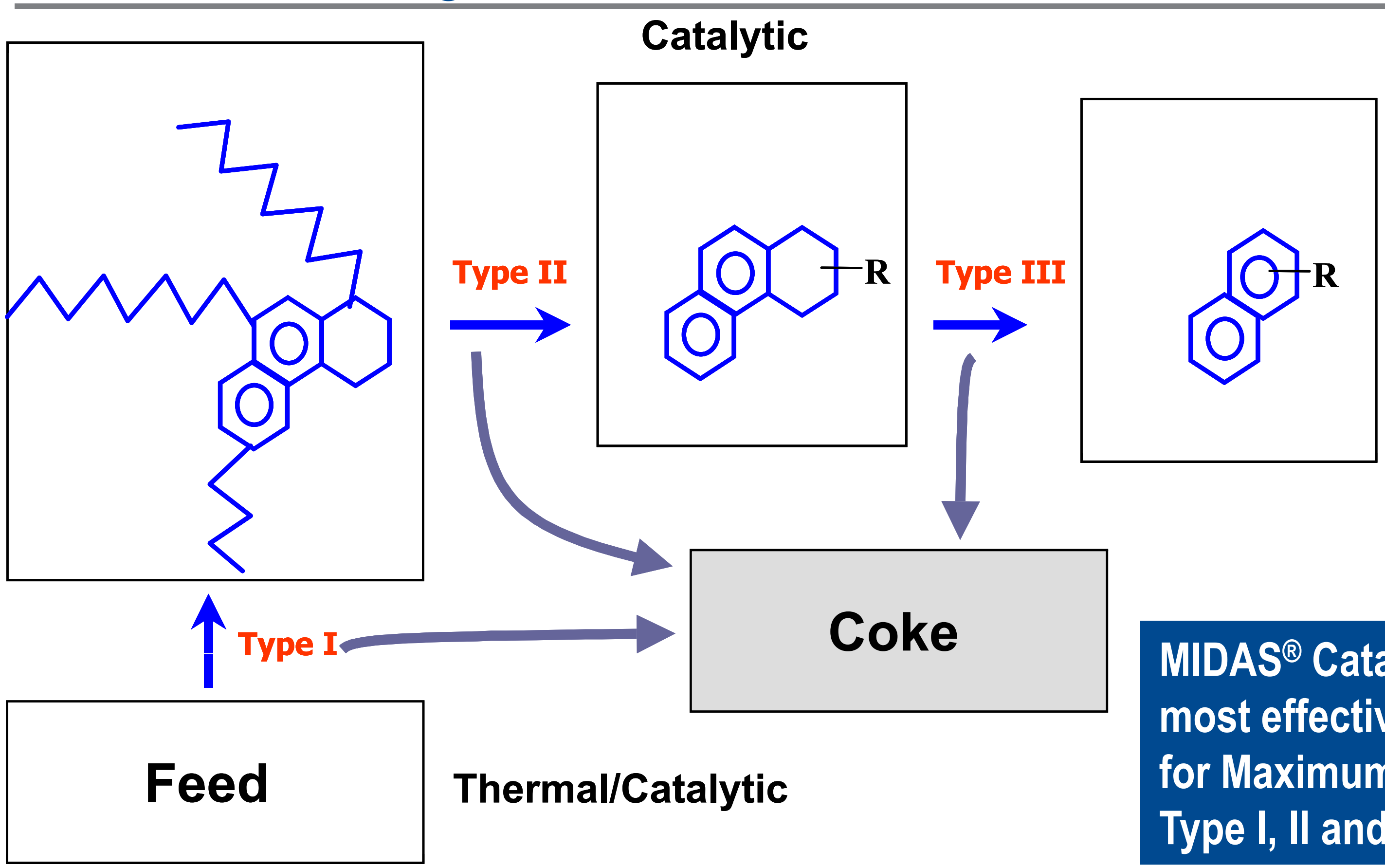
Bottoms Cracking Fundamentals

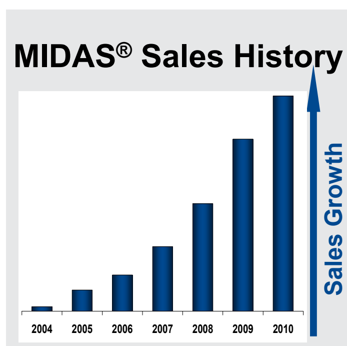


MIDAS® Catalyst is the most effective catalyst for Maximum LCO via Type I, II and III cracking

Type I	Precracking and Feed Vaporization
Type II	Dealkylation of alkyl aromatics
Type III	Conversion of naphthenoaromatics

MIDAS® Catalyst Family

- **MIDAS®-100**
  - Original invention - metals tolerant bottoms cracking
- **MIDAS®-200**
  - Higher activity
- **MIDAS®-2000**
  - Same performance as MIDAS®-100 in low metals applications
- **MIDAS®-300**
  - Introduced in 2008
  - Deep bottoms cracking
  - LCO maximization



Break the Bottom of the Barrel with MIDAS® Catalyst Technology

- **MIDAS®-300 is the latest result of Grace Davison's 60+ year commitment to understanding bottoms cracking mechanisms and catalysts**
  - Our best technology for a diesel driven market

- **BX™-450 Additive: LCO Maximization Additive**
  - Based on MIDAS®-300 technology and used at 10 to 20% of total catalyst additions

- **Full Burn FCC - Residual Feedstock**
  - Model yields and operating conditions
    - Base Resid Operation – Maximum Gasoline
    - Case 1 – Maximum LCO with 650-800°F recycle stream
    - Case 2 – Optimized maximum LCO operation

Base Maximum Gasoline Operation

Resid Feedstock Operation	Base
Catalyst	**MIDAS® -100**
Mode	Max Gaso.
Recycle %FF (650 to 800°F)	0.0
Reactor Temperature, °F	975
Air Blower, mscfm	Constraint
Wet Gas Compressor, scf/b	Constraint
LPG/Gaso., Vol%	23.9/56.7
RON/MON	92.6/80.6
LCO , Vol% FF	22.9
Slurry , Vol% FF	6.8
C_3^+, Vol% FF	110.3
Incremental $/b	Base

Product	Relative Price
C3=, $/b	-13.9
C4=, $/b	-2.5
Gaso., $/b	0.0
LCO, $/b	8.0
Slurry, $/b	-18.9

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Maximum LCO with Recycle

Resid Feedstock Operation	Base	1
Catalyst	MIDAS® -100	MIDAS® -100
Mode	Max Gaso.	Max LCO
Recycle %FF (650 to 800°F)	0.0	11
Reactor Temperature, °F	975	950
Air Blower, mscfm	Constraint	Constraint
Wet Gas Compressor, scf/b	Constraint	75% of Constraint
LPG/Gaso., Vol%	23.9/56.7	19.3/51.9
RON/MON	92.6/80.6	90.0/79.5
LCO , Vol% FF	22.9	32.0
Slurry , Vol% FF	6.8	6.0
C_3^+, Vol% FF	110.3	109.2
Incremental $/b	Base	+0.10

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Optimized Maximum LCO Operation with MIDAS-300 and OlefinsUltra

Resid Feedstock Operation	Base	1	2 (Optimized)
Catalyst	**MIDAS® -100**	**MIDAS® -100**	**MIDAS® -300 & OlefinsUltra ®**
Mode	**Max Gaso.**	**Max LCO**	**Max LCO**
Recycle %FF (650 to 800°F)	0.0	11	11
Reactor Temperature, °F	975	950	950
Air Blower, mscfm	Constraint	Constraint	Constraint
Wet Gas Compressor, scf/b	Constraint	75%Constraint	Constraint
LPG/Gaso., Vol%	23.9/56.7	19.3/51.9	30.0/44.0
RON/MON	92.6/80.6	90.0/79.5	92.9/80.7
LCO , Vol% FF	22.9	32.0	33.4
Slurry , Vol% FF	6.8	6.0	5.0
C_3^+, Vol% FF	110.3	109.2	112.4
Incremental $/b	Base	+0.10	**+1.40**

•ZSM-5 (OlefinsUltra® is critical to maintain profitability)

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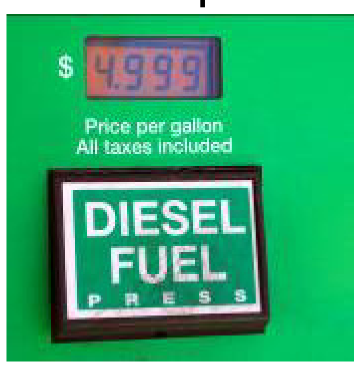
Summary

- **Maximum FCC LCO operation is challenged by bottoms yield and the need to preserve C3+ liquid yield and octane as conversion is reduced**
  - MIDAS®-300 catalysts and BX™-450 additives
    - Technology for increased LCO selectivity via improved bottoms cracking
  - OlefinsMax® and OlefinsUltra® additives - ZSM-5
    - Maintain liquid yield and gasoline octane during maximum LCO operations



Summary

- **Recycle is required to fully maximize LCO**
  - Due to the higher di-aromatic and lower tri-aromatic level, recycle stream of 650-750°F from Resid gives more LCO and less bottoms than that from VGO.
  - Recycle produced from 1st pass conversion of 55% is the optimal among 55%, 58%, 68% and 75%: more LCO with almost no penalty on coke and gasoline selectivity.
  - 650 to 800°F recycle stream produces the highest LCO when processed against a coke constraint.
  - Coke demand will be higher to maximize LCO using a 650+°F recycle stream.

The proper catalyst system, operating conditions and recycle ensure a profitable maximum FCC LCO operation.

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Questions?

FCC
Catalysts

- Propylene Maximization
- Resid Conversion
- Gasoline Maximization
- LCO Maximization
- Coke Selectivity

FCC
Additives

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Davison

- Controlling SOx, NOx & CO
- Reducing Gasoline Sulfur
- Boosting Octane
- Improving Fuel Quality
- Producing Petrochemical Feedstocks
- Reducing Environmental Emissions

We don’t just make FCC catalysts,
we make FCC catalysts for you.

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