Octane Boost and Capacity Increase for Hydrotreated Naphtha

ExoS™ - Extraction Desulfurization Technology

REFCOMM Galveston 2019

Brant Aggus
Refining Technologist
INVISTA Performance Technologies

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KOCH-GLITSCH®

ExoS™ - Sulfur Extraction Technology for Mid-Cut Naphtha

- A great investment for meeting 10 ppm sulfur limits in the blending pool
- Generates an olefin rich C6-C7 raffinate with less than 10 ppm Sulfur that bypasses the FCC naphtha hydrotreater for direct blending

- **Value Drivers:**
  - *Can reduce full range FCC Naphtha RON loss to <1*
  - *Reduces hydrotreater feed flow by up to 40% and H2 consumption by up to 50%*
  - *Reduces or eliminates light FCC naphtha treatment and heavy naphtha posttreatment*
    - *ExoS™ can treat C5 naphtha*
    - *Olefin bypass of the hydrotreater reduces mercaptan revision*
  - *For units already taking a mid-cut FCC napththa split pre-hydrotreater, ExoS™ eliminates the need to over-treat heavy cut to blend down total sulfur*
- **Commercially proven success – 8 units in operation and 7 in design**
  - *Can be installed with a new hydrotreater to reduce the size, CAPEX and OPEX of the hydrotreater*
  - *Can be installed as a revamp to save Octane and free up hydrotreater capacity*

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TOPICS

DEVELOPMENT AND BASIS

EXOS TECHNOLOGY OVERVIEW

BENEFITS OVERVIEW AND EXAMPLE

COMMERCIAL EXAMPLES AND SUMMARY

INVISTA / KOCH-GLITSCH PARTNERSHIP

ExoS™ DEVELOPMENT AND TECHNOLOGY BASIS

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How Best to Desulfurize FCC Gasoline?

Desulfurization vs. Olefin Recovery

1. Lose olefins to hydrogenation?

Or…….

2. Find a way to recover them.

- Oil product optimization
- Fuel upgrading to <10 ppm S

FCC

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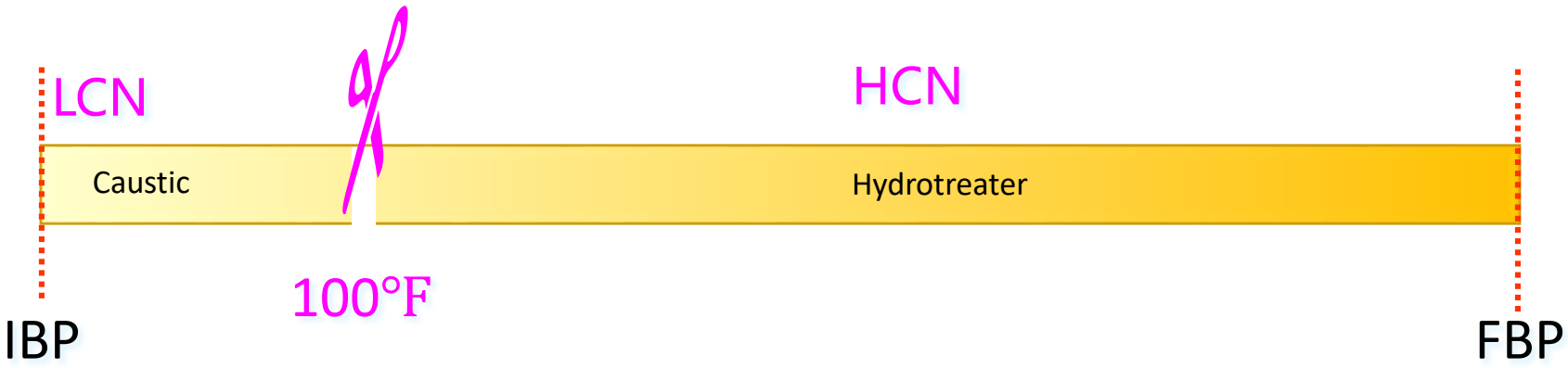
Traditional FCC Naphtha Sulfur Treating.....



BASIS

Typical FCC Gasoline Analysis

C	nP	iP	O	N	A	Total	wt%	Olefin wt%
4	0.1	/	0.6	/	/	0.7	87.5	1.6
5	1.2	7.8	18.0	/	/	26.9	66.8	44.2
6	1.1	5.9	11.9	2.0	0.8	21.6	55.0	29.3
7	0.9	2.2	4.3	3.2	3.7	14.3	30.3	10.7
8	0.4	2.7	3.6	1.8	6.4	14.9	24.2	8.9
9	0.3	1.6	1.4	1.3	7.8	12.3	11.2	3.4
10	0.2	0.7	0.7	0.2	4.0	5.7	11.7	1.5
11	0.3	1.5	0.1	/	1.0	3.0	5.4	0.4
Total	4.4	22.2	40.6	8.6	23.6	99.4	/	100.0

Mercaptans are Treated with Existing Technology -

- C5 Olefins : 40~50 wt%
- C6-C7 Olefins: ~40 wt%

But what about these?

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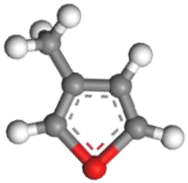
【Fundamental research findings】

BASIS

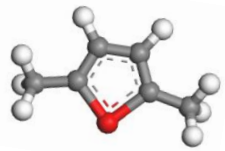
Typical Sulfides Distribution in FCC gasoline

Component	BP, °F	ppmw
COS	-58	0.9
C2SH	95	5
DMDS	99	2.5
CS_2	117	1.4
C3Thiol	133-154	9.2
C2H6S	149	0.3
C4SH	149-208	2.2
Thiophene	183	113
C2H6S2	230	0.8
iC5SH	243	0.4
Methylthiophene	237	241

Component	BP, °F	ppmw
Tetrahydrothiphn.	246	25.4
Ethylthiophene	271	40.5
Dimethylthiophene	273	205
Hexathiol	304	19.6
C Hexasulfide	295	19.8
Trithiophene	316	180
Octathiol	390	11.2
C Octasulfide	365	4.4
Tetrathiophene	358	108
Total		1000



- Thiophenic Sulfur： 91%
- Distributed in： 175~275 °F Range



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BASIS

IBP

~20wt%

LCN

- C5 Olefins and Alkanes
- Small Thiols/Mercaptans

100°F

~40wt%

MCN

- C6~7 Olefins and Alkanes, Small amount of Naphthenes/Aromatics
- Thiophene and Methylthiophene

?

~40wt%

HCN

- C_8^+, Low Olefins [~15wt%]
- Thiophenes, Benzothiophenes

FBP

? : 215°F

Solubility Advantage

With molecular properties of PONAS, mid cut naphtha feed is separated into PNO rich and AS rich oil, with S rich oil sent to Hydrotreating. Most of olefin is not sent to HDS unit, so that olefin is *not saturated*.

HC	Benzene	Toluene	Cyclohexane	Every other HC
Rel. Solubility	8.0	4.8	2.0	<1.0
Sulfide	Thiophene	Methyl-Thiophene	Thioether	Mercaptan
Rel. Solubility	10.5	5.2	5.0	4.7

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ExoS™ Technology Overview

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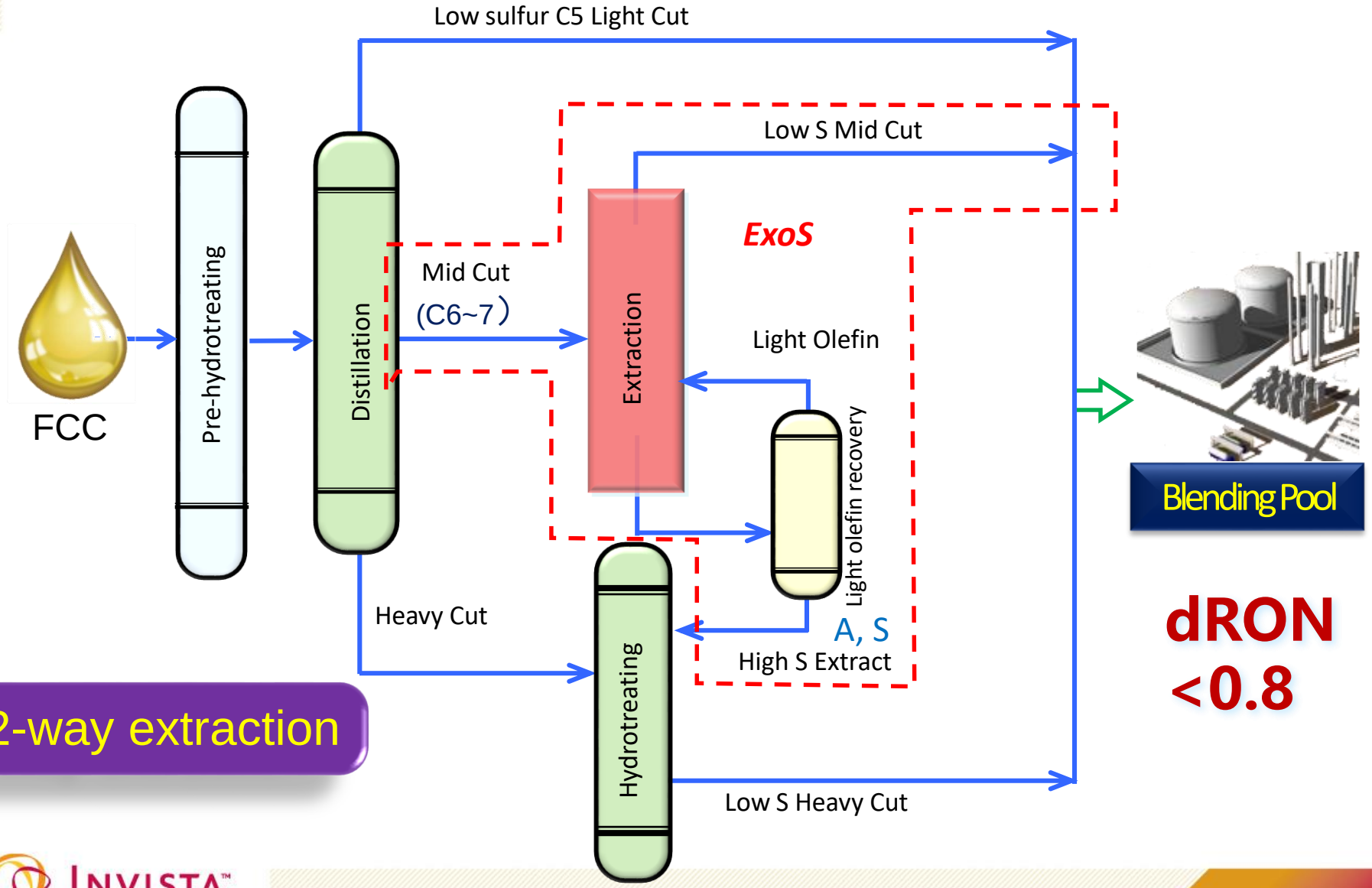
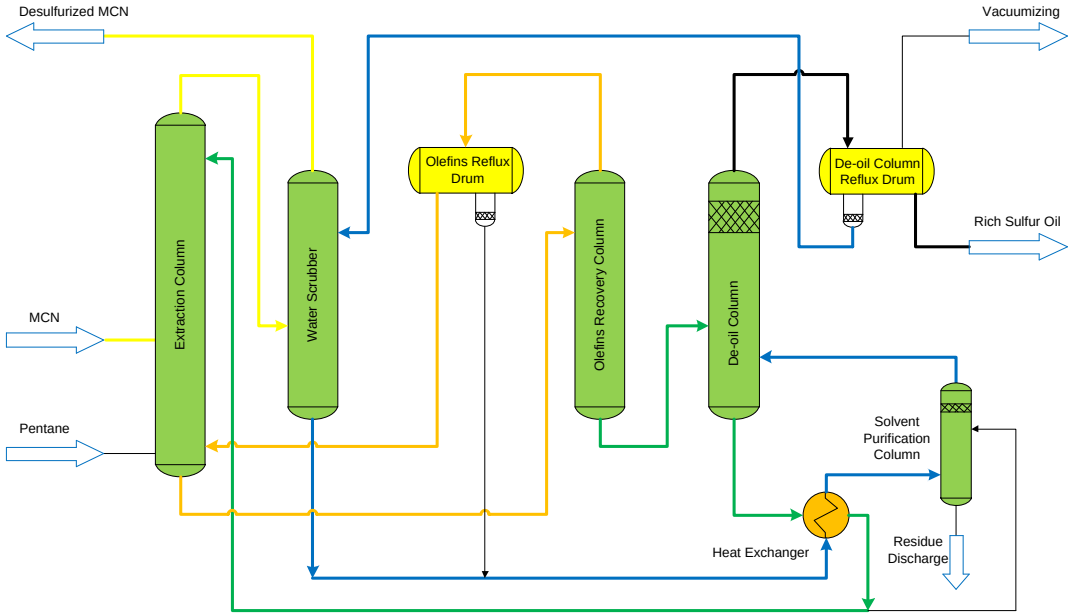
The Result: ExoS Technology – Targeted Separation and Desulfurization



4-3-2 of ExoS Technology



4 steps

1. Solvent extraction
2. Raffinate water washing
3. Olefin recovery
4. Solvent regen and purification

1. Light olefin
2. Process water
3. Solvent

3 Circulations

1. Olefin separation
2. Solvent circulation

2 Keys

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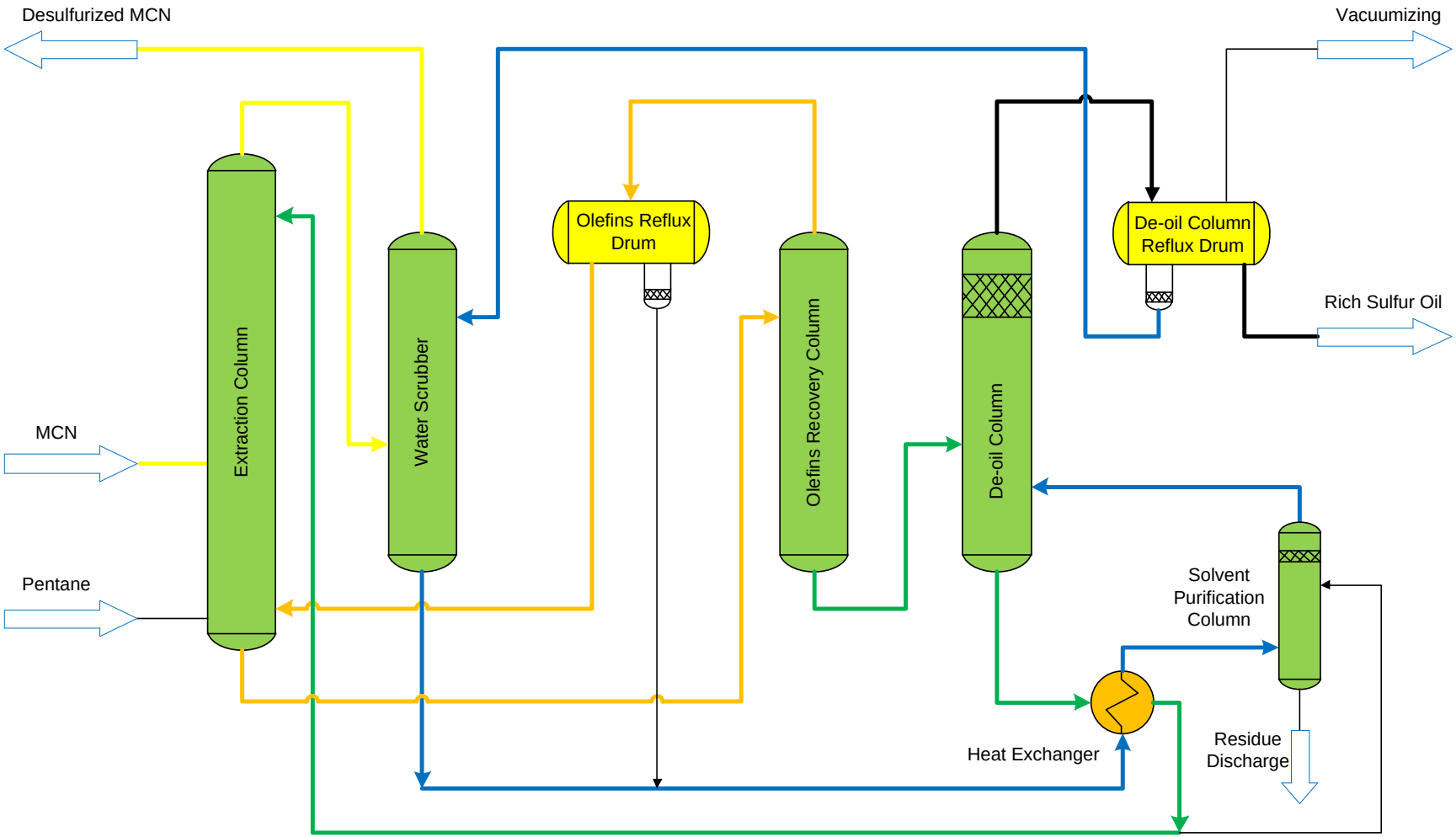
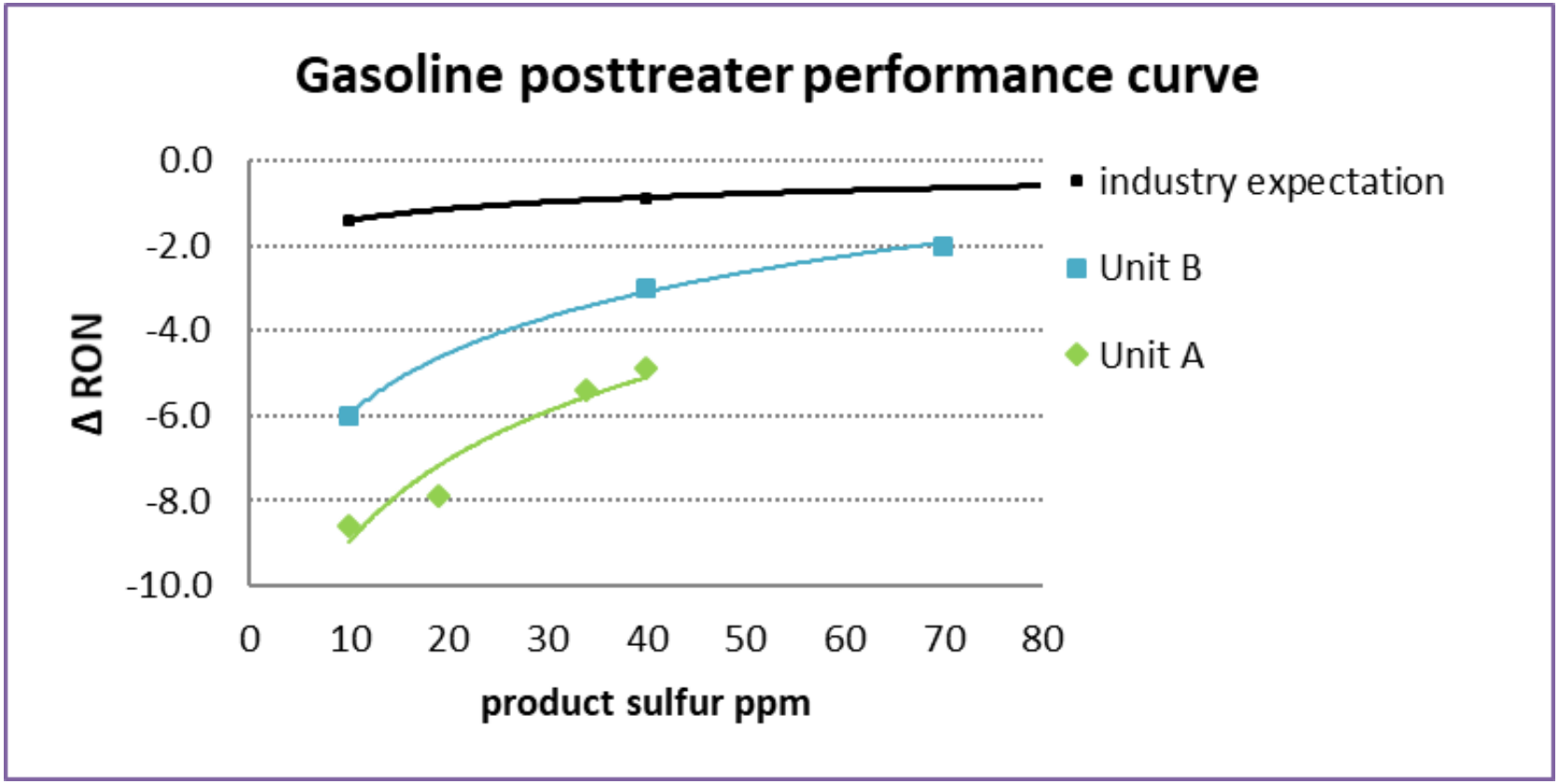
Simplified Flow Scheme for ExoS Process



Benefits Overview and Example

Hoekstra multi-client group has done field tests on 11 different posttreaters



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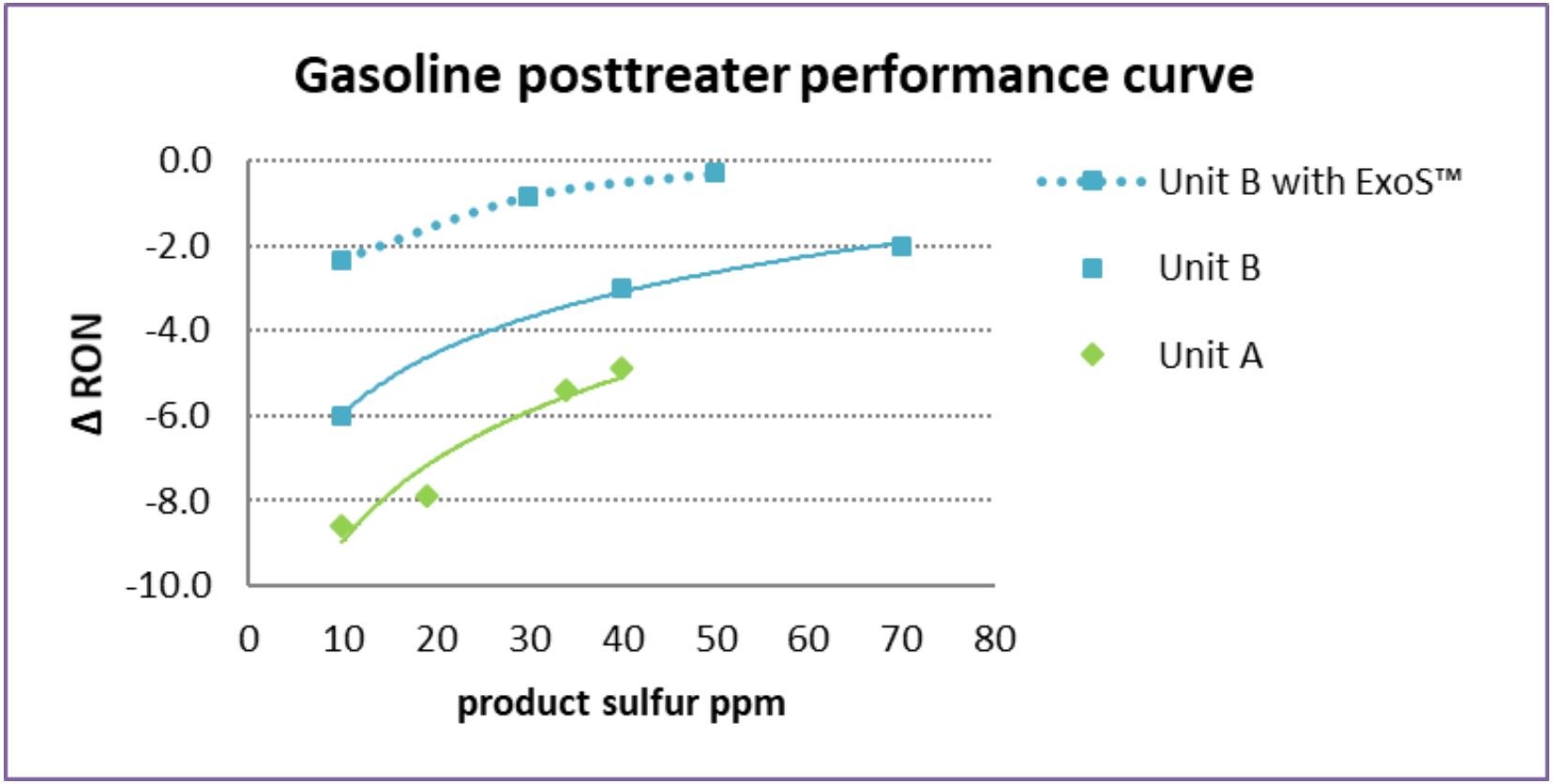
Hoekstra model estimates ExoS™ will save 3-4 RON on these units



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Commercial Example

MCN Feed
(30 wt% of Total FCC Naphtha)

	nP	iP	O	N	A	sum
5	1.2	1.3	6.1	0.4	0.0	9.0
6	4.9	11.7	29.5	6.5	6.7	59.2
7	3.1	8.4	7.3	6.3	2.5	27.6
8	0.1	0.5	0.5	0.5	0.5	2.0
9	0.1	0.2	0.3	0.1	0.6	1.3
10	0.1	0.1	0.2	0.1	0.4	0.8
	9.4	22.2	**43.9**	13.9	10.7	100.0
S	380.0 ppmw					

Raffinate

	nP	iP	O	N	A	sum
5	1.4	1.6	7.2	0.5	0	10.7
6	5.8	14.0	33.7	7.5	0	61.0
7	3.4	9.9	7.6	6.8	0	27.7
8	0	0.3	0.1	0.2	0	0.6
	10.6	25.8	**48.6**	15.0	0	100.0
S	8.0 ppmw					

Extract

	nP	iP	O	N	A	sum
5	0	0	0.8	0	0	0.8
6	0.2	0.1	8.8	1.6	39.7	50.4
7	1.4	1.2	6.1	3.6	14.7	27.0
8	0.7	1.3	2.3	1.8	3.0	9.1
9	0.6	1.0	1.8	0.8	3.7	7.9
10	0.5	0.8	0.9	0.4	2.2	4.8
	3.4	4.4	**20.7**	8.2	63.3	100.0
S	2212.4 ppmw					

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(All values are wt%)

Commercial Example, 6.8 MBPD Mid-Cut Naphtha

Olefin/Sulfur Balance and Concentration

	Feed	Raffinate	Extract
Flow rate，Mlb/hr	70.6	58.7	11.9
Percentage，wt%	100.0	83.1	16.9
Olefin content，wt%	43.9	48.6	20.7
Olefin flow rate，Mlb/hr	30.9	28.5	2.4
Olefin split，%	100.0	92.1	7.9
Sulfur content，ppmw	380.0	8.0	2212.4
Elemental S split, %	100.0	1.8	98.2

- Olefin Recovery：92.0%
- Sulfur Recovery：98.2%

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Commercial Example

Utility Consumption

		Consumption (/ton feed)	
		unit	Cons
1	Cooling water	ton	14.7
2	Power	Kw·h	10.5
3	300 psig steam	ton	0.3
4	Condensate	ton	-0.3
5	N2	scf	64.0
6	Instrument air	scf	64.0

Low energy consumption, low cost

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Key Advantages , ExoS™ vs Hydrotreating Alone

	ExoS	HDS Alone
Product S	<10 ppmw	<10 ppmw
Ron Loss (A)	0.5-1.5 (worth $31 USD/t)	2.0-4.0 ($0 benefit-base)
H2 Consumption	1/3-1/2	1 (base)
Selective Hydrogenation Ratio	45 wt%	80%
Product Loss	0.2-0.4 wt% (worth $6 USD/t)	0.8 wt% ($0 benefit-base)
Capex (B)	45MM USD	45 MM USD
Opex	$17 USD/t	$19 USD/t
$ Benefit	$39 USD/t	$0 - base

(A) Based on gasoline spec w/ <10 ppm S requirement.
(B) Based on 1000 kTPA plant capacity, built in China.

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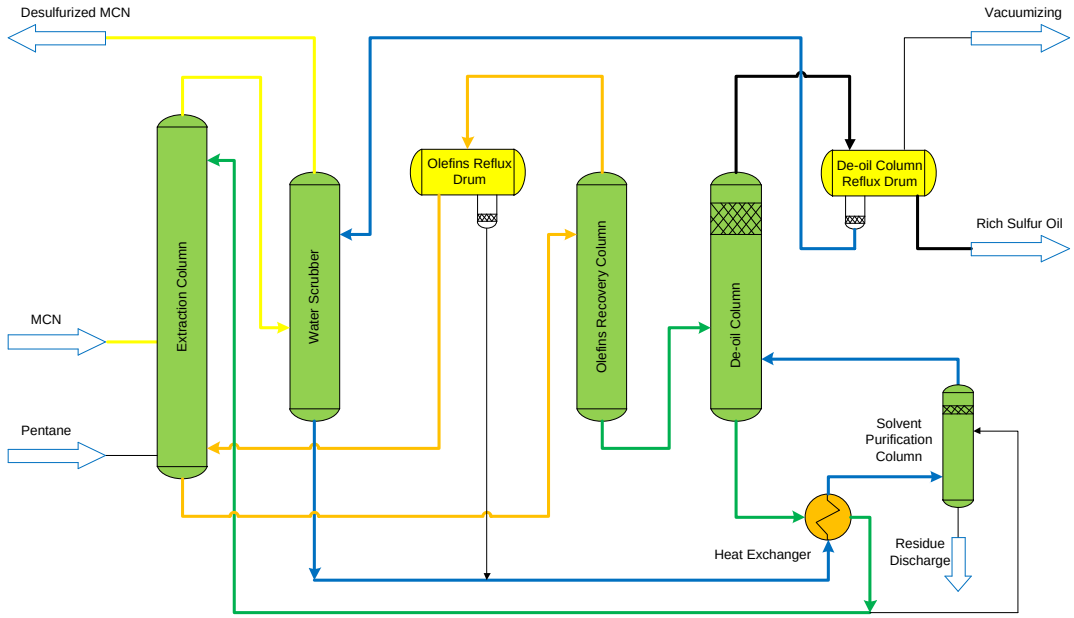
Environmental Benefits

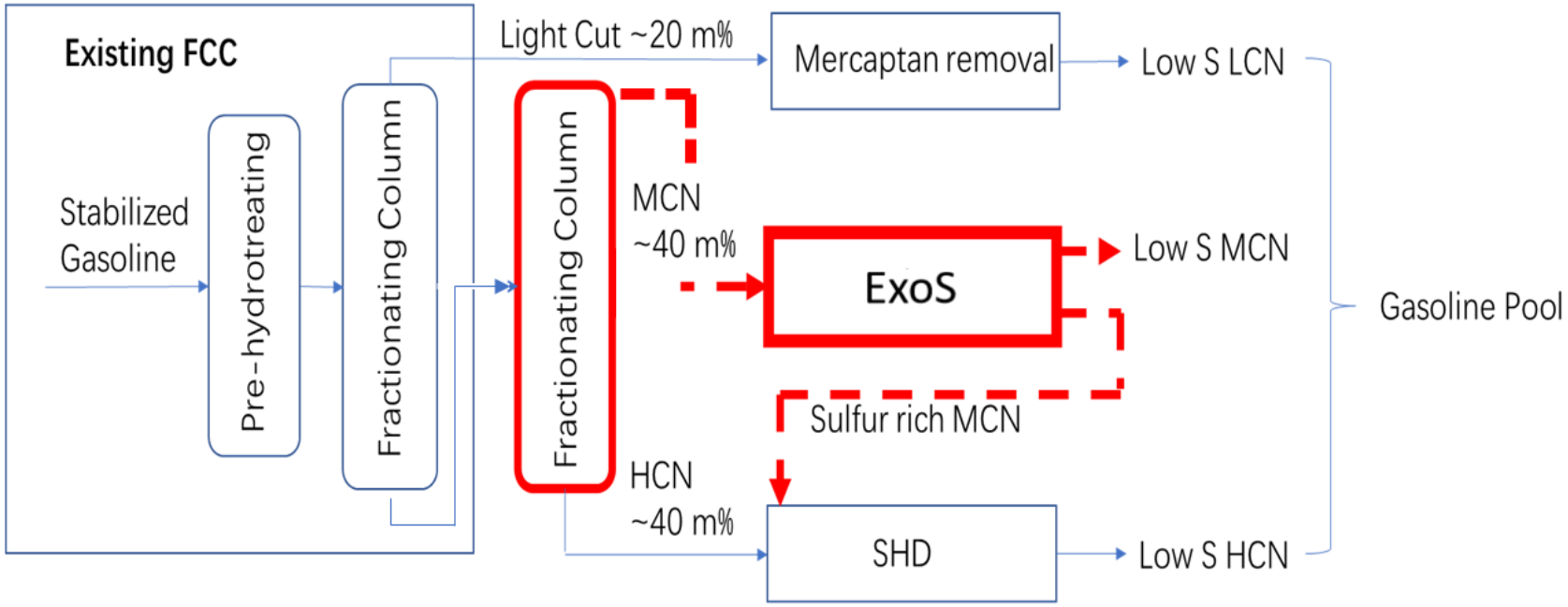
No wastes

Solvent consumption: 1lb/100Mlb gasoline

Less H2 needed!



Can be coupled with existing hydrotreating tech



~50% FCC gasoline to be hydrotreated with **ExoS** vs ~80% FCC gasoline to be hydrotreated without

Process can drop into an existing plant

Can revamp aromatics extraction units

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Commercial Examples and Summary

Commercial Example

Client: A Chinese refinery

Capacity: 600 kta
(FCC Gasoline Upgrading ExoS Project)

Start up: Jan. 2015

RON loss: < 1.0 (vs original 4.0)
Sulfur content: < 5 ppm

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Commercial Example

Client: A PetroChina Refinery

Capacity: 350 kta

Start up: Oct. 2016

RON loss saving: ~4

Sulfur content: < 10 ppm

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Commercial Example

Client: A ChemChina Refinery

Capacity: 1,100 kta

Start up: Nov. 2016

RON loss: < 1.5

Sulfur content: < 5 ppm

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INVISTA / Koch-Glitsch Partnership

WE ARE KOCH

Commodity Trading

Electronic Components

Energy

Fertilizers

Forest and Consumer Products

Process and Pollution Control Equipment and Technologies (KG-JZ)

Minerals

Polymers and Fibers (IPT)

Ranching

Refining, Chemicals and Biofuels (FHR)

Glass

KOCH-GLITSCH · FLINT HILLS resources · INVISTA · Georgia-Pacific · molex · GUARDIAN INDUSTRIES

***Koch revenues fluctuate with the price of commodities. They have been estimated by Forbes as high as $115 billion.*

IPT – KG Partnership

IPT is INVISTA's technology transfer business with more than 40 years in continuous licensing

Licensed more than 100 license projects for PTA, Polyester, BDO, PTMEG and Nylon 66 since joining KII in 2004

Supporting technology development, commercialization and licensing within KII since 2013

Entry into the refining space spawned by collaborations with KII Affiliates … Flint Hills Resources and Koch-Glitsch

IPT-KG Partnership to Offer Exos™, DTL™, IsoA™ and other Refining Technologies to the Market

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Summary

- Exos™ is an advantaged option for meeting 10 ppmw Tier 3 Sulfur Limits
  - Generates an olefin rich C6-C7 raffinate with less than 10 ppm Sulfur
  - Reduces Octane loss to <1
  - Reduces hydrotreater feed flow by up to 40%, and
  - Reduces hydrotreater H2 consumption by up to 50%

- We'd appreciate the opportunity to provide a detailed proposal to meet your specific needs

- Questions?

THANK YOU

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