NCUT

National Centre for Upgrading Technology

'a Canada–Alberta alliance for bitumen and heavy oil research'

Comparison of the Reactivity of Naphthenic Acids in Athabasca bitumen and San Joaquin Valley

Parviz Rahimi, Tomoki Kayukawa, Ryan Rodgers and Teclemariam Alem

For presentation at
Joint CCQTA/COQA Meeting
February 10-11, 2010
New Orleans, LA

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Outline

- Background
  - Comparison of reactivity of NA in gas oil fractions
  - Methods for measuring reactivity
  - Effect of sulfur types on NA corrosion
- Continuous Fe powder test
- Separation of Reactive and non-reactive NA
- Identification/Characterization

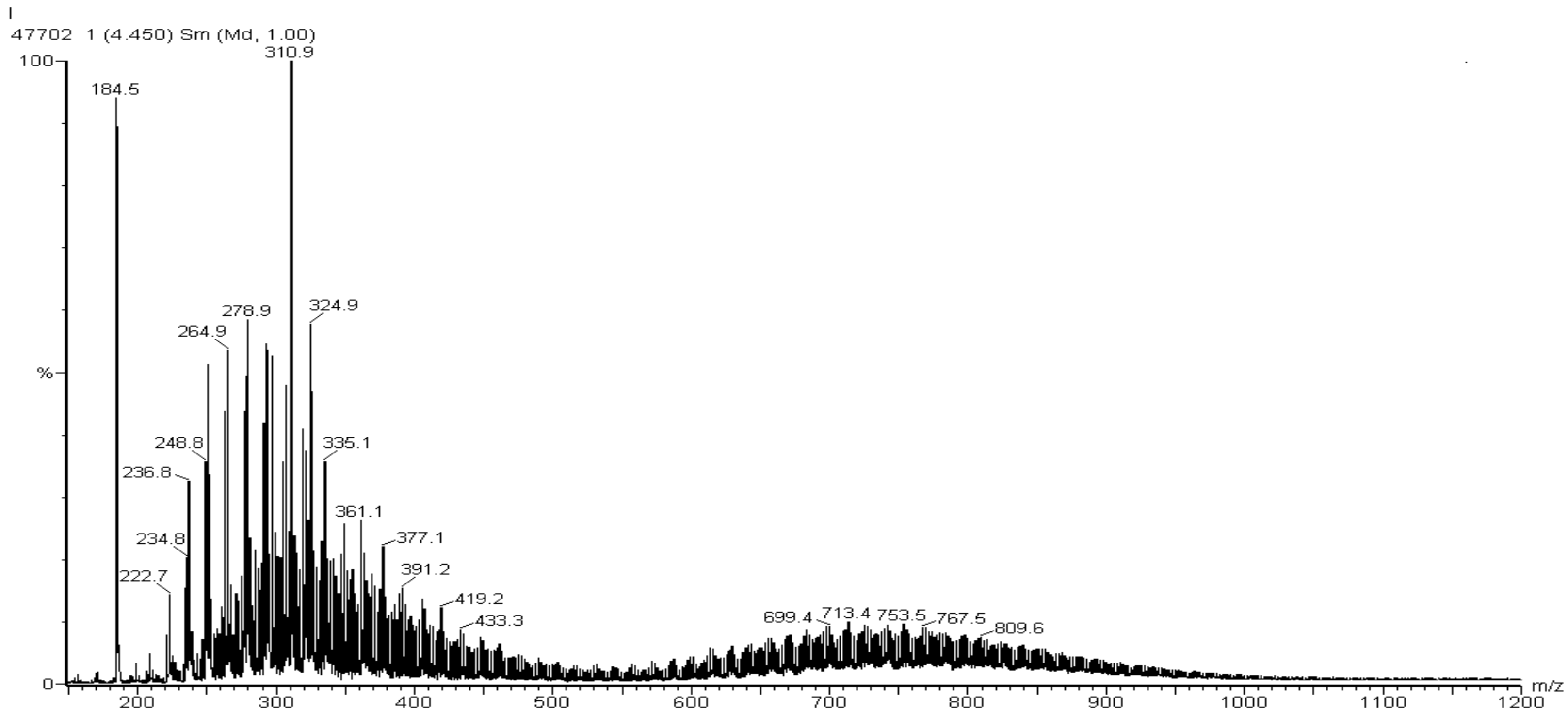
Background

- Athabasca bitumen contains approx. 1wt% organic acids, and that are mostly concentrated in the gas oil fraction
- These acids can cause corrosion in the refinery
- There is a wide range distribution of NA in AB
- Are all NA corrosive?

Background - Proposed naphthenic acid corrosion in Athabasca bitumen

- Two types of naphthenic acids - α and β
- α (low Mw - bad) and β (high Mw – good)
- β acids are prohibitive through steric effect

ESI (LRMS) – Naphthenic Acids



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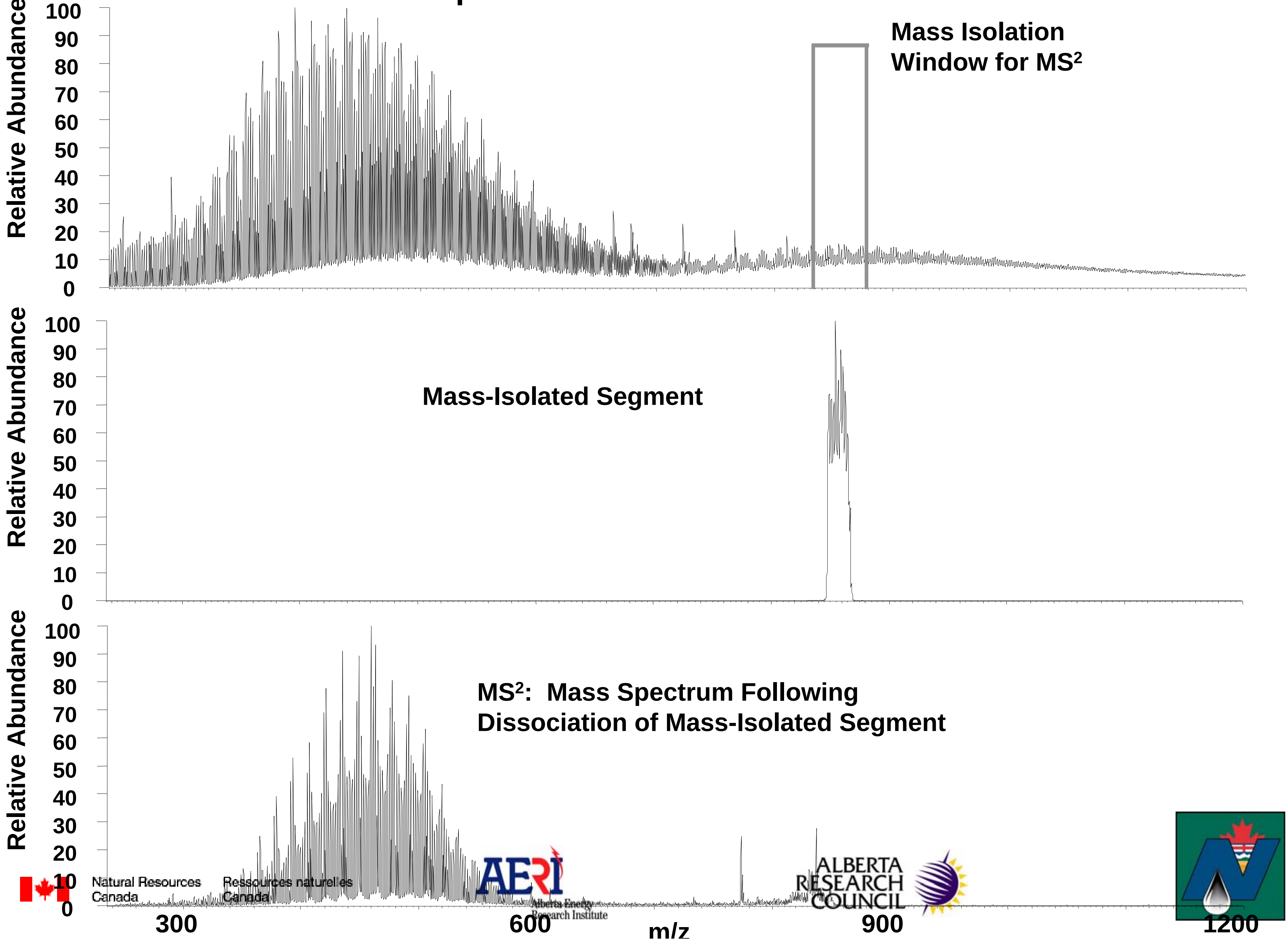
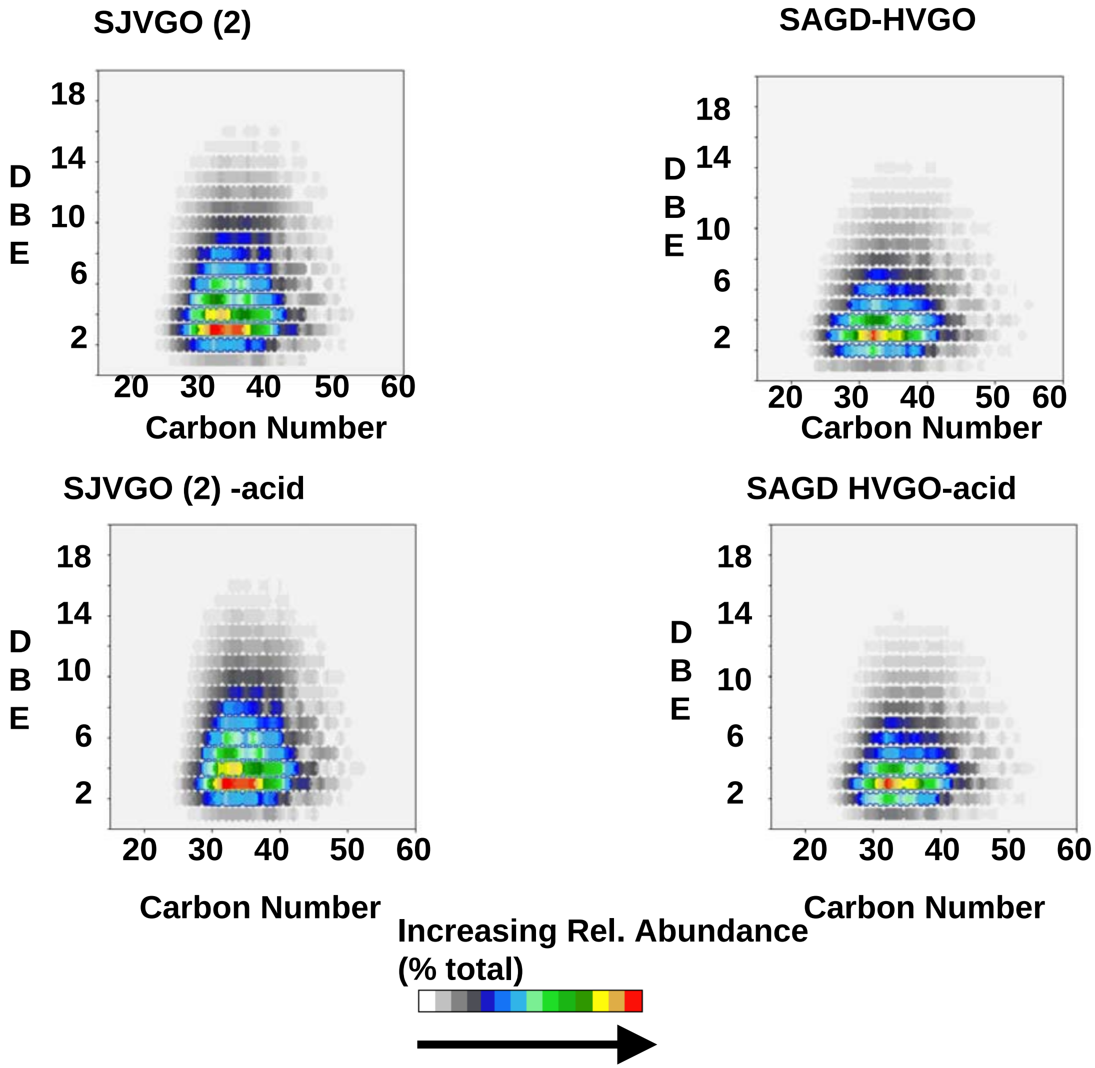
Broadband ESI Mass Spectrum of Athabasca Bitumen



References

1. Donald F. Smith, Tanner M. Schaub, Parviz Rahimi, Alem Teclemariam,Ryan P. Rodgers, and Alan G. Marshall, "Self-Association of Organic Acids in Petroleum and Canadian Bitumen Characterized by Low- and High-Resolution Mass Spectrometry", *Energy & Fuels* **2007**, *21,* 1309-1316
2. Donald F. Smith, Parviz Rahimi, Alem Teclemariam, Ryan P. Rodgers, and Alan G. Marshall, "Characterization of Athabasca Bitumen Heavy Vacuum Gas Oil Distillation Cuts by Negative/Positive Electrospray Ionization and Automated Liquid Injection Field Desorption Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry", *Energy & Fuels* **2008**, *22,* 3118–3125
3. Donald F. Smith, Tanner M. Schaub, Sunghwan Kim, Ryan P. Rodgers, arviz Rahimi, Alem Teclemariam, and Alan G. Marshall "Characterization of Acidic Species in Athabasca Bitumen and Bitumen Heavy Vacuum Gas Oil by Negative-Ion ESI FT-ICR MS with and without Acid-Ion Exchange Resin Prefractionation" *Energy & Fuels* **2008**, *22,* 2372–2378
4. 3- Donald F. Smith, Ryan P. Rodgers, Parviz Rahimi, Alem Teclemariam, and Alan G. Marshall, "Effect of Thermal Treatment on Acidic Organic Species from Athabasca Bitumen Heavy Vacuum Gas Oil, Analyzed by Negative-Ion Electrospray Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry", *Energy & Fuels* **2009**, *23,* 314– 319

FT-ICR mass Spectrometry
SJV and AB-SAGD



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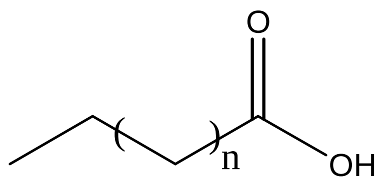
Typical naphthenic acid chemical structures



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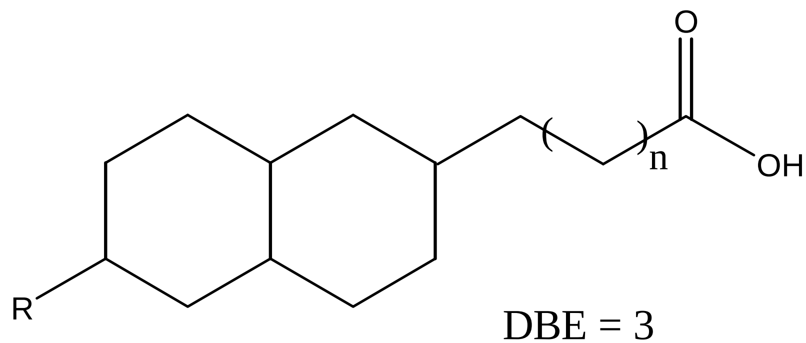

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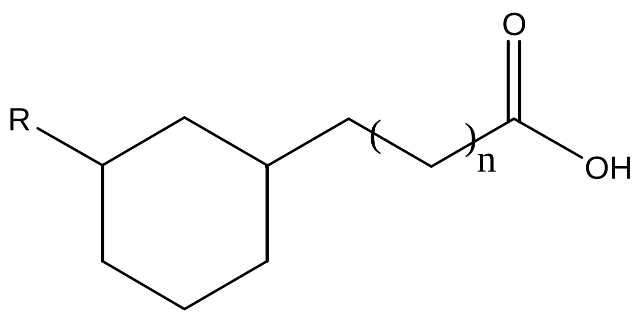

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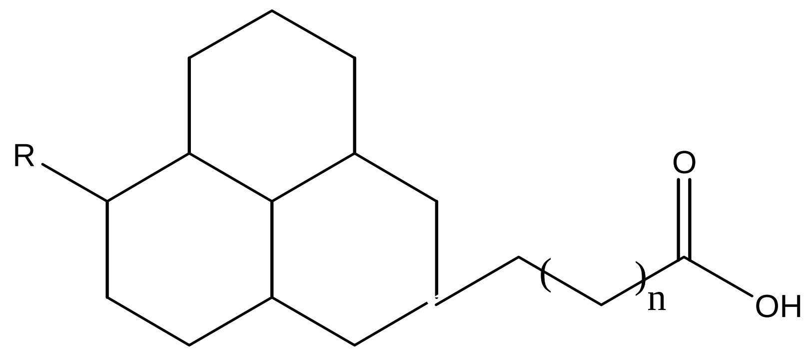

DBE= 4

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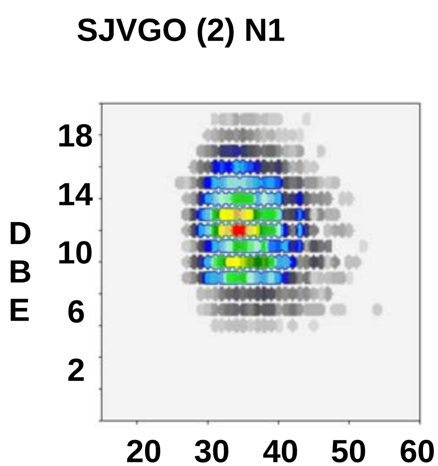
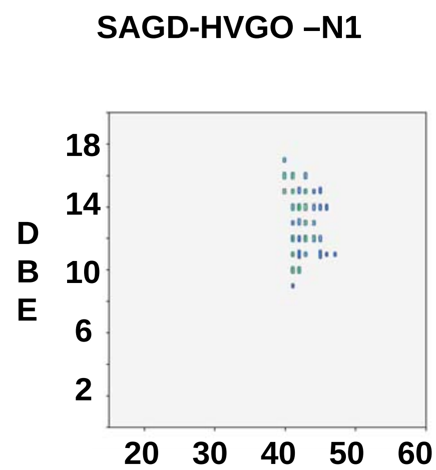
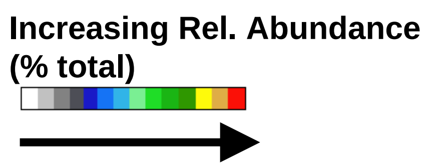
FT-ICR mass Spectrometry
SJV and AB-SAGD







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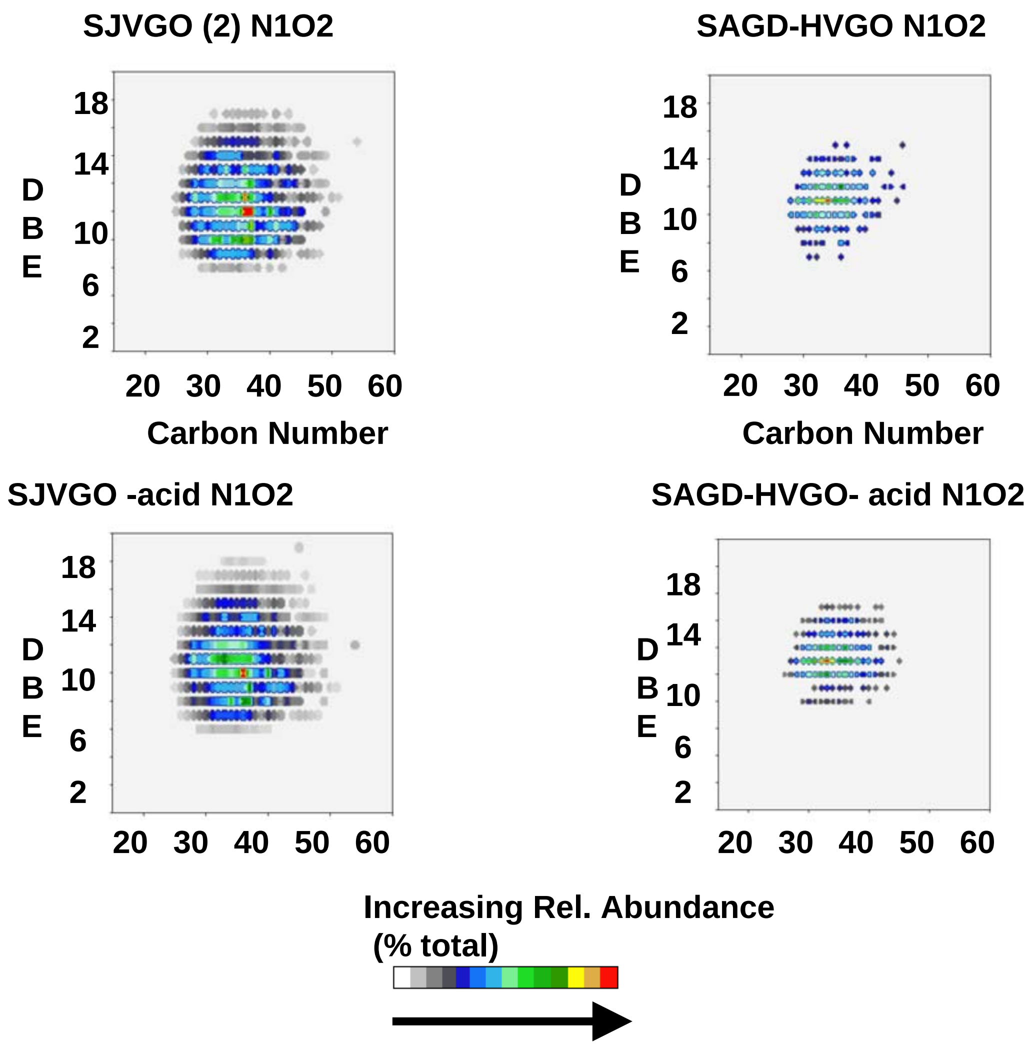
FT-ICR mass Spectrometry
SJV and AB-SAGD



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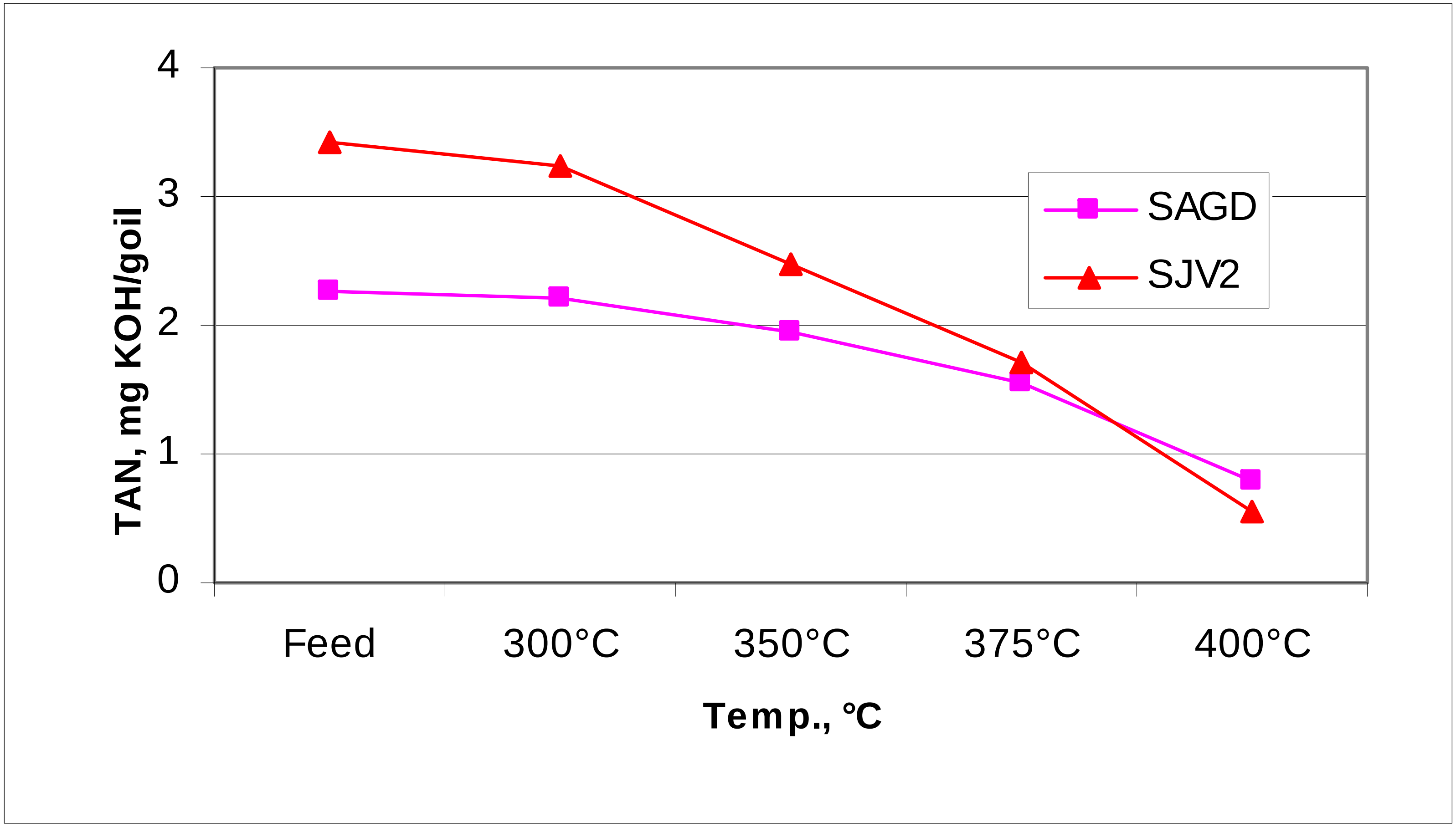
Effect of temperature on TAN reduction
AB-SAGD-HVGO
SJV-HVGO



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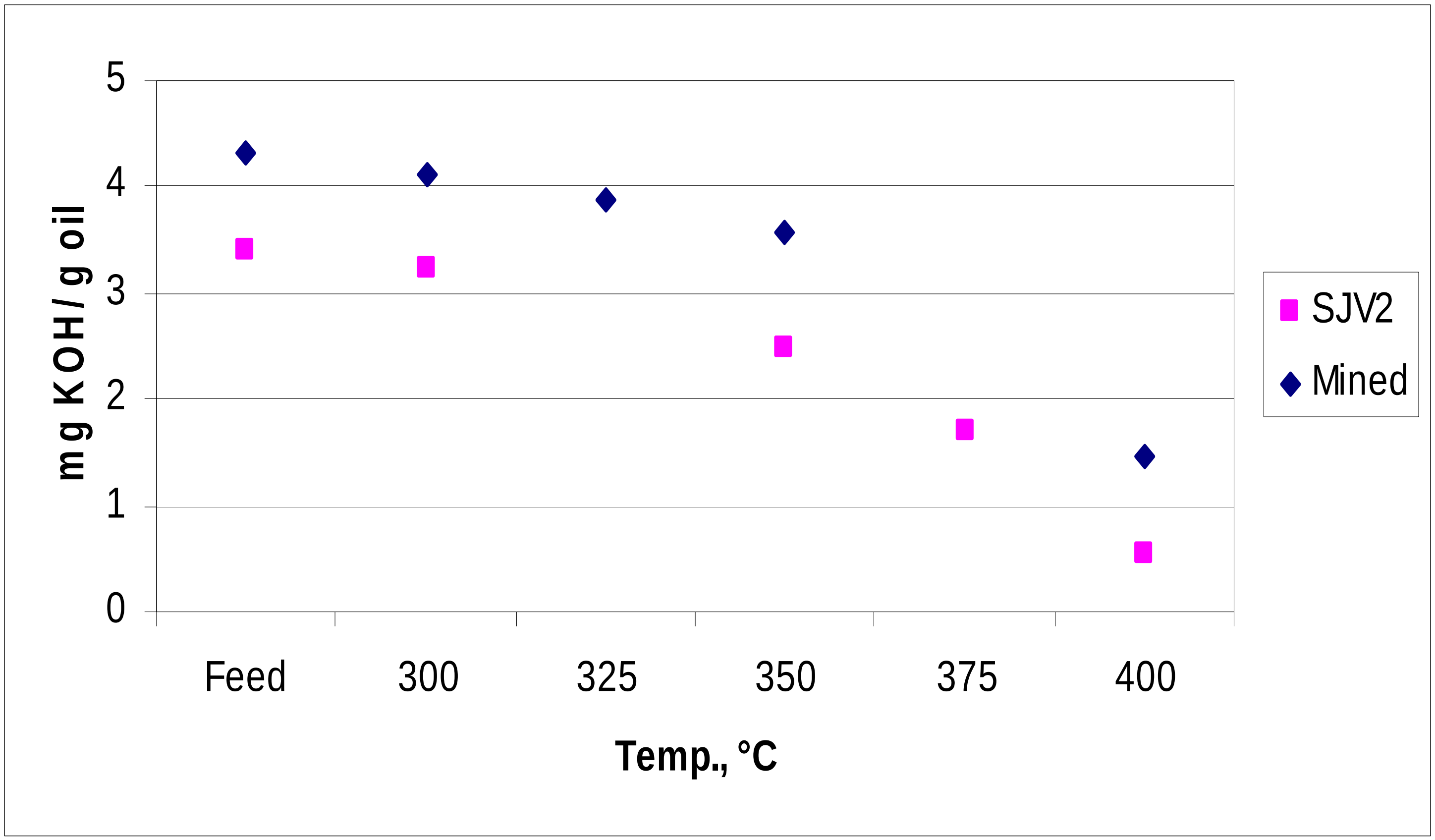
Effect of temperature on TAN reduction
AB-Mined-HVGO
SJV-HVGO



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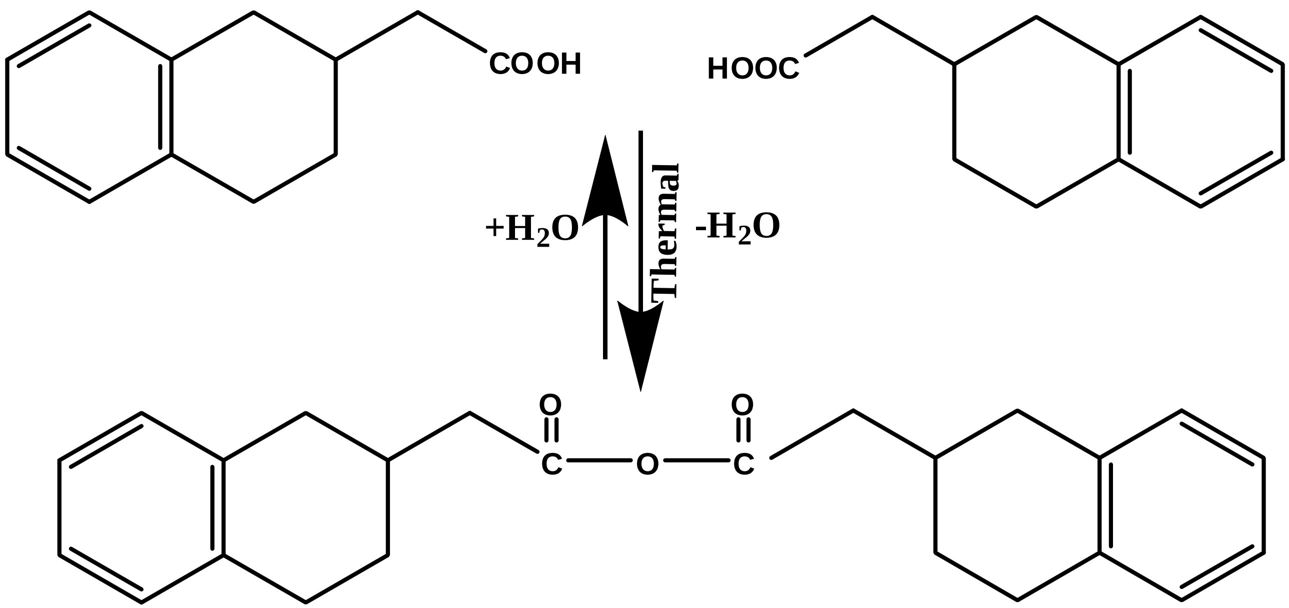
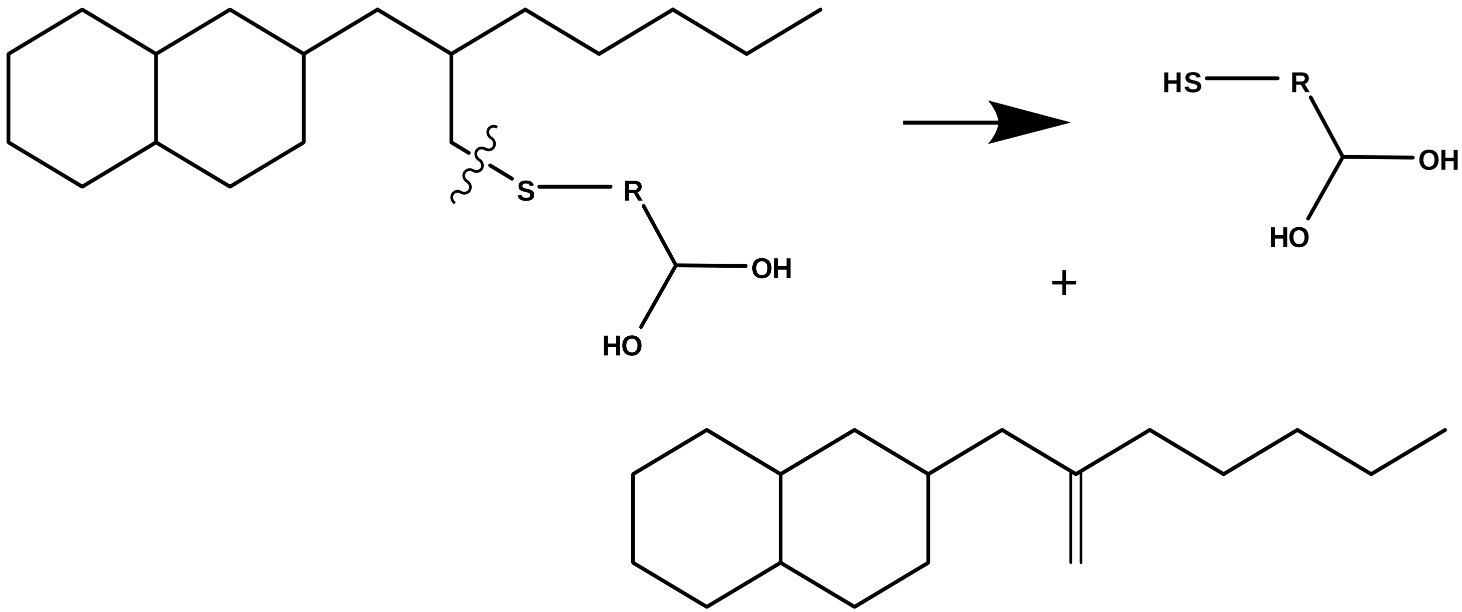
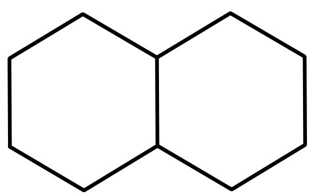
Dehydration mechanism of Naphthenic acids



Autoclave experiments should be carried out in an open system

Possible mechanism of NA size reduction



R = 

Petrobras – NCUT Collaboration 2010

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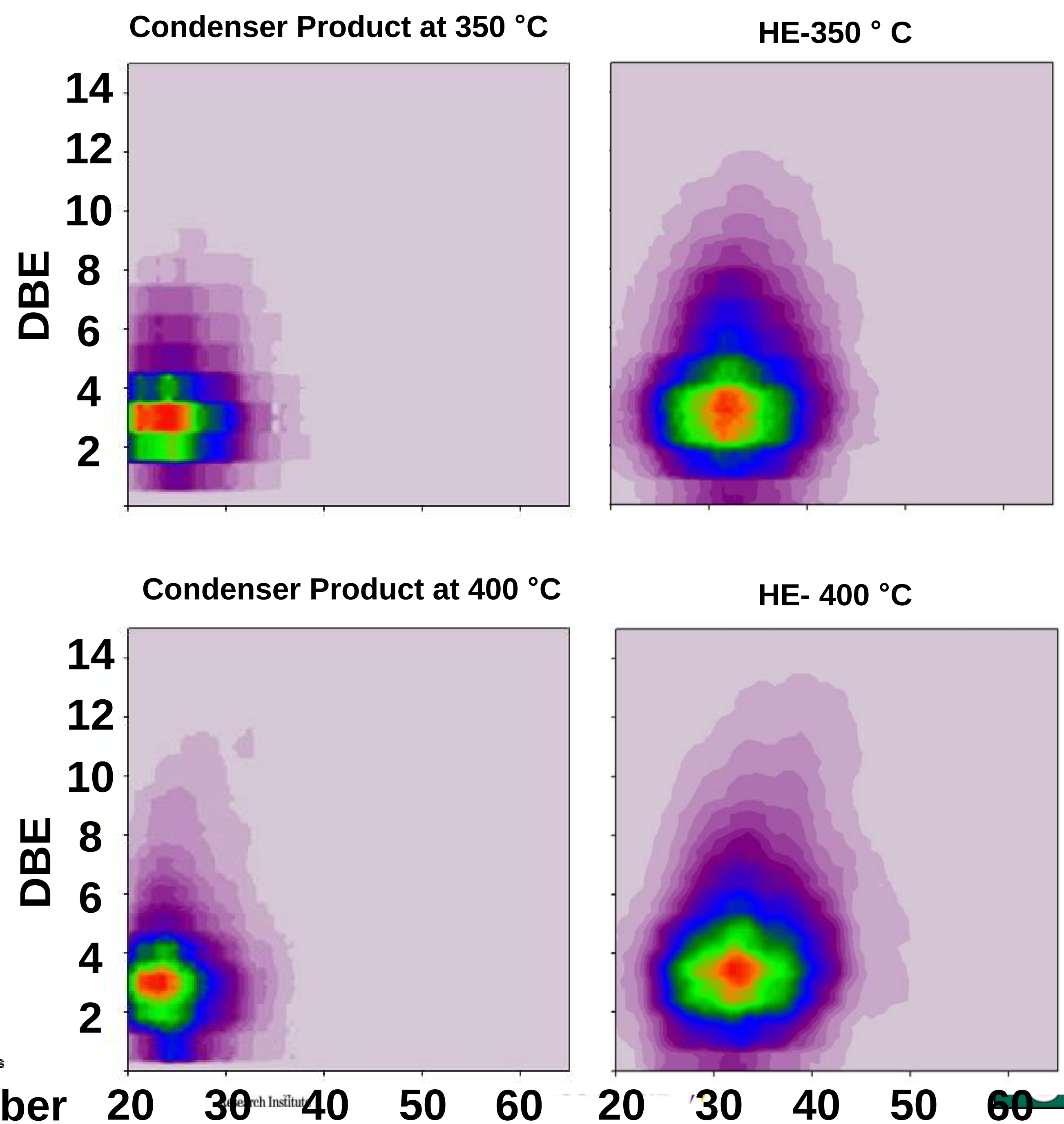
Condenser Products

O_2



Corrosion Mechanism

$$R\text{-}COOH + Fe \longrightarrow (R\text{-}COO)_2\,Fe + H_2$$

$$(R\text{-}COO)_2\,Fe + H_2S \longrightarrow 2\,R\text{-}COOH + FeS$$

$$H_2S + Fe \longrightarrow FeS + H_2$$

Ye'pez, O. On the chemical reaction between carboxylic acids and iron, including the special case of naphthenic acid. Fuel 2007, *86, 1162-1668*.

Effect of Sulfur type on corrosion

$$R_2S = O + 2RSH \longrightarrow R_2S + RSSR + H_2O$$

$$R_2S = O + H_2 \longrightarrow R_2S + H_2O$$

Ye'pez, O. Influence of different sulfur compounds on corrosion due to naphthenic acid. Fuel 2005*, 84, 97-104.*

Reactive and non- reactive acids separation

Objective

- **Separate Reactive acids and Non-Reactive acids from HVGO fraction**

Methods

Iron Powder Test (IPT)

- **Examine reactivity of acids using iron powder**
- **Reactive acids are converted to Iron naphthenates**

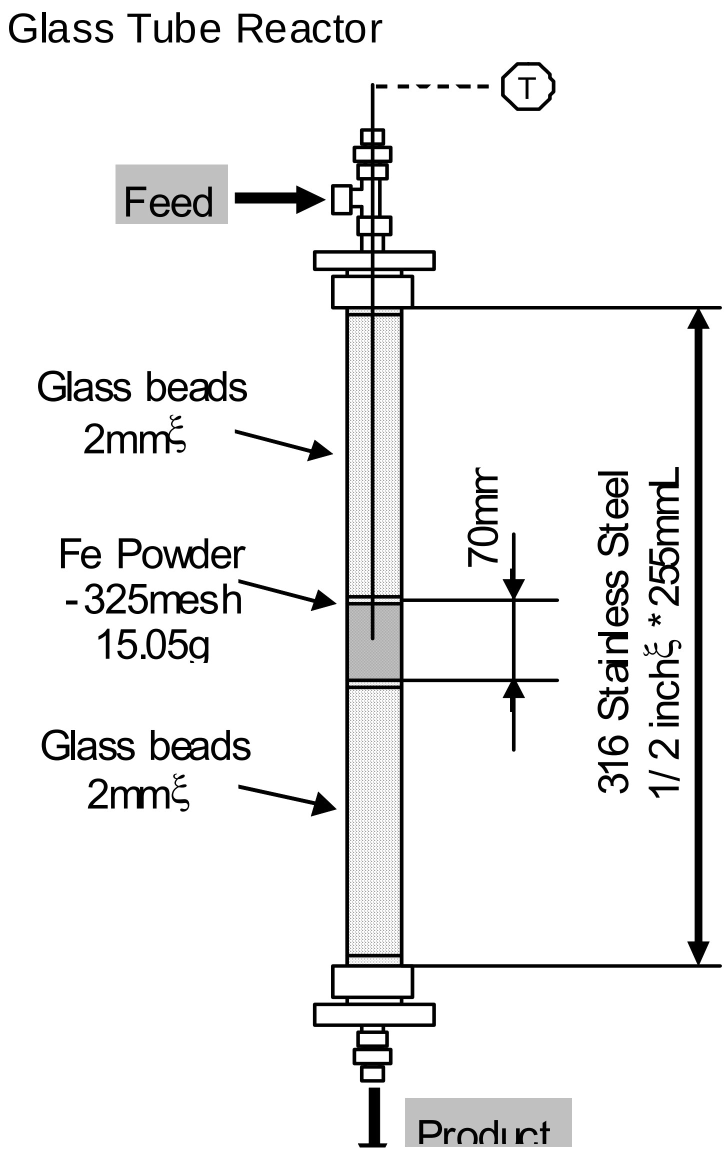
New Acid-IER

- **Separate Reactive acids and Non-Reactive acids from Product of IPT using 2 types of ion exchange resin**

Issues with Fe Powder test using Batch reactor

- Water formation
  - Complicates reaction chemistry
- Decomposition of Iron naphthenate above 300°C
  - Underestimates reactive acids

Experimental Unit – Continuous Flow



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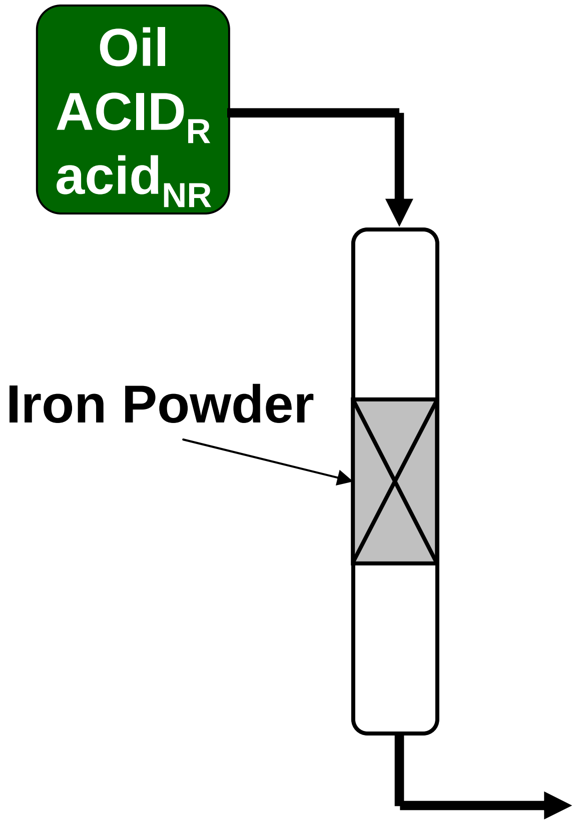
Reaction Conditions

- **Feed – HVGO from Mined, SJV**
- **Temperature : 250 ~ 350^{o}C**
- **Flow rate : 0.17 ~ 0.50 cc/min**
- **LHSV : 2 ~ 6 h^{-1}**
- **Residence Time : 10 ~ 30 min**
- **Fe powder : 5 cc (15 g)**
- **N_2 flow rate : 5~10 ml/min**

Residence Time [min] = Fe powder [cc] / Flow rate [cc/min]
LHSV [h^{-1}] = 60 / Residence time [min]

Iron Powder Test



- Gas oils are contacted with Fe powder in a packed bed reactor in a continuous unit
- Reactive acids are converted to iron salt

$$2\ R\text{-}COOH + Fe \rightarrow (R\text{-}COO)_2Fe + H_2$$

$$R\text{-}COOH \rightarrow R\text{-}H + CO_2$$

Test Conditions

Temperature:	250~350 C^o
Pressure:	Atmosphere
Residence time:	30 min.

Analyses

Product:	TAN
Gas:	H_2, CO_2

Reaction Mechanism

$$R\text{-}COOH + Fe \xrightarrow{\text{Reactive}} (R\text{-}COO)_2 Fe + H_2$$

$$R\text{-}COOH \xrightarrow{\text{Decarboxylation}} CO_2 + RH$$

$$H_2S + Fe \longrightarrow FeS + H_2$$

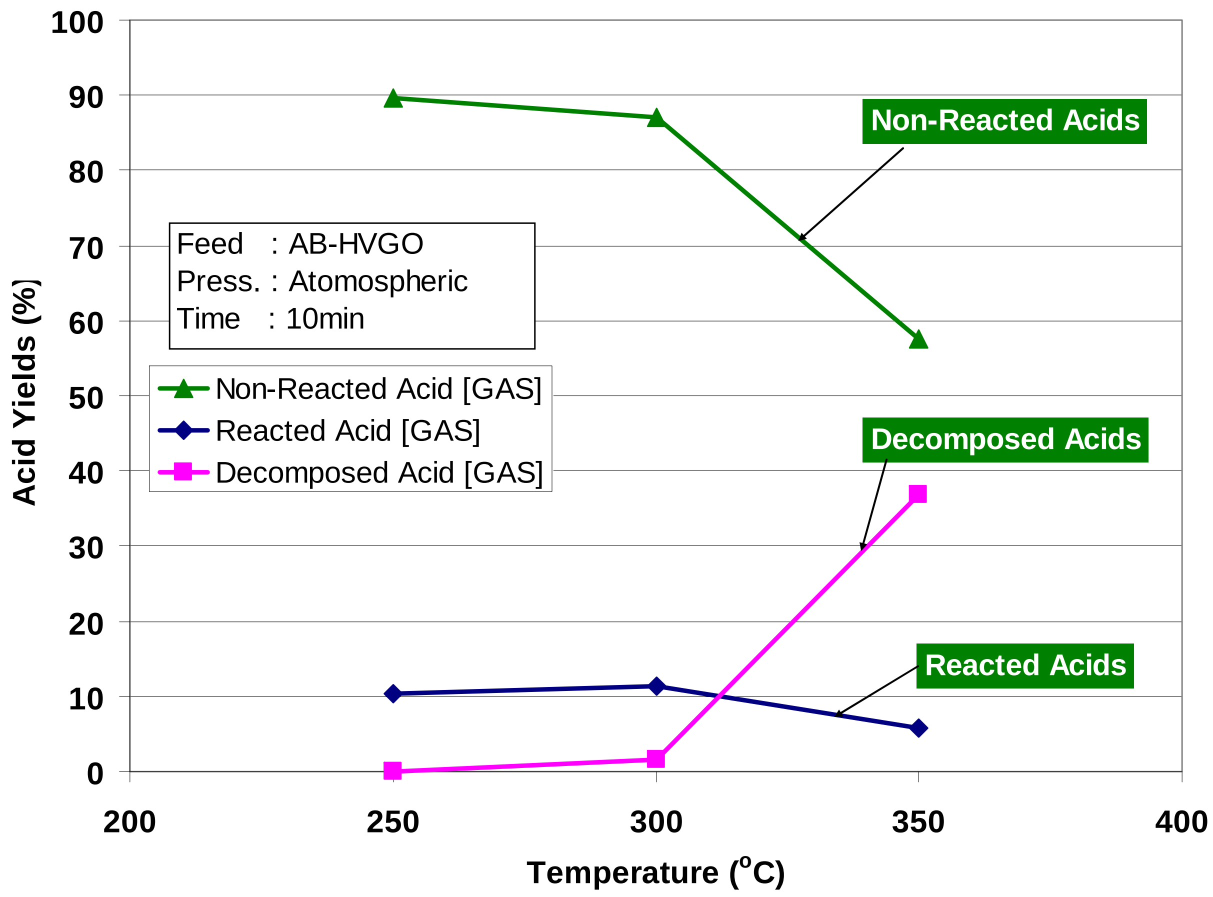
$$(R\text{-}COO)_2 Fe + H_2S \longrightarrow 2\ R\text{-}COOH + FeS$$

Ye'pez, O. On the chemical reaction between carboxylic acids and iron, including the special case of naphthenic acid. Fuel 2007, *86, 1162-1668*.

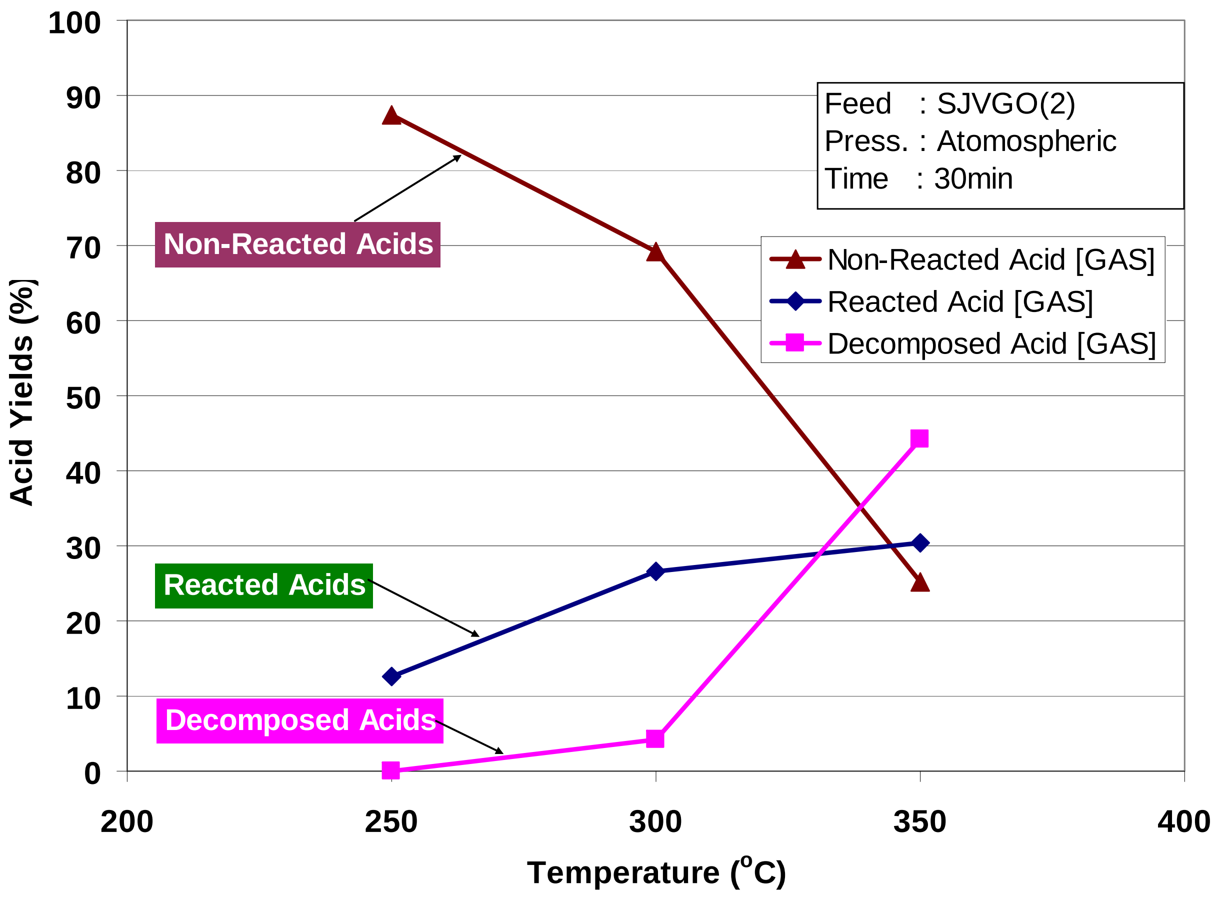
Effect of temperature on Sulfur and MW

	SJV2		HVGO	
Run Temp., °C	Sulfur % wt	MW g/mole	Sulfur % wt	MW g/mole
0	1.33	459	3.48	345
300	1.36	423	3.40	333
325			3.51	338
350	1.36	426	3.56	337
375	1.29	387		
400	1.14	389	3.32	343

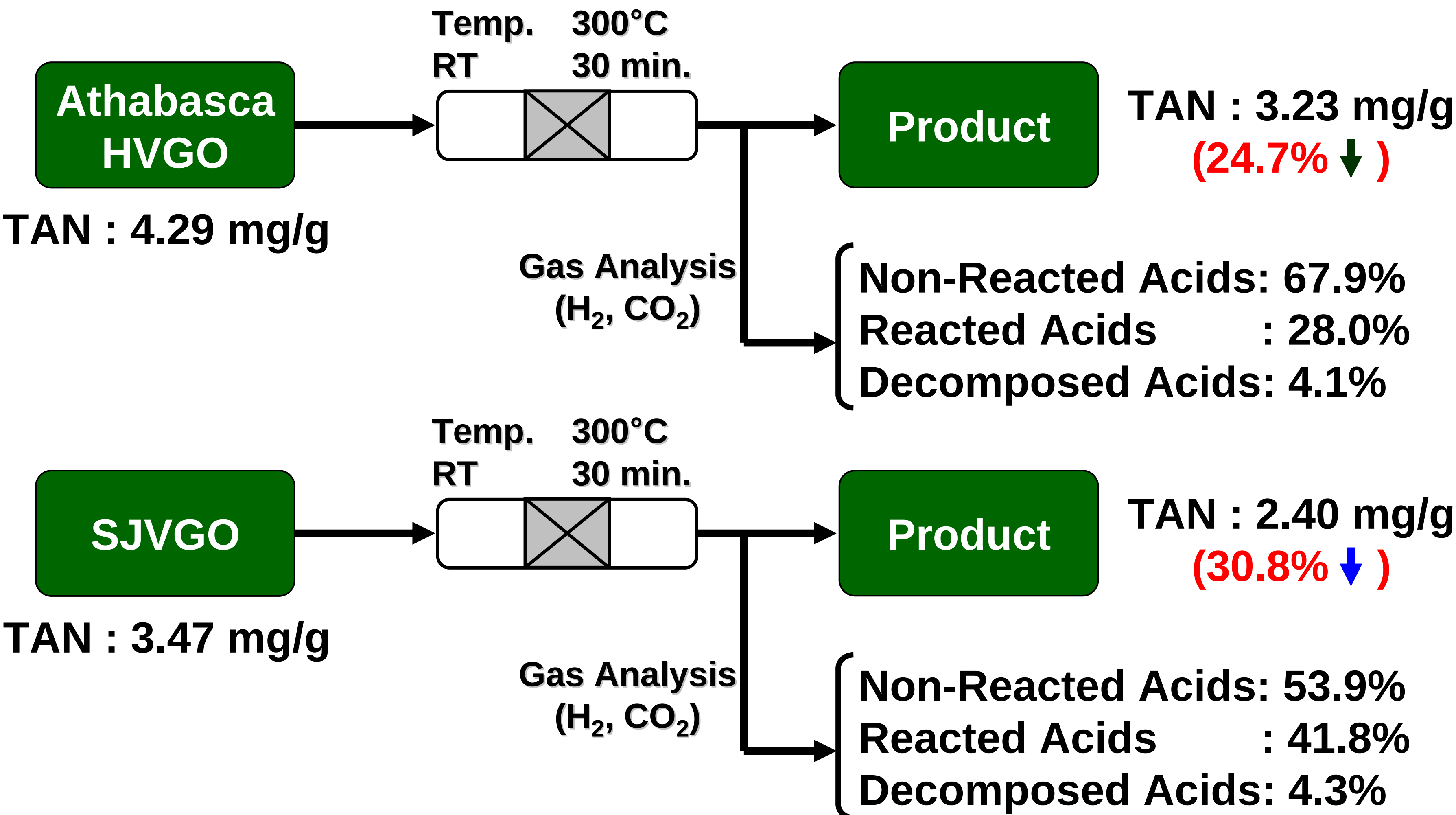
Reactivity of AB-HVGO



Reactivity of SJV-HVGO



Results of IPT



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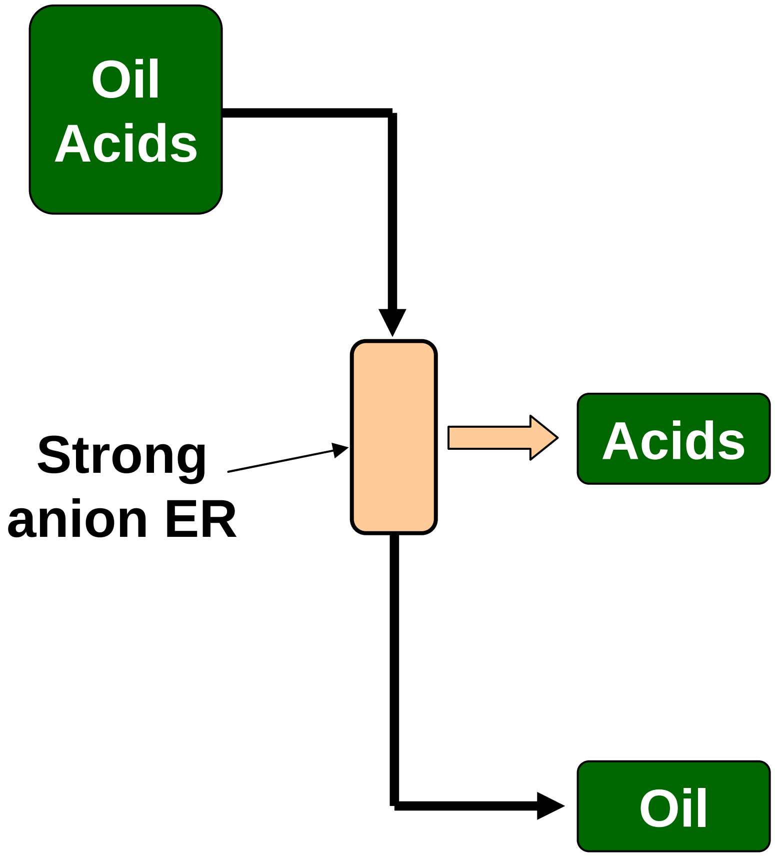
Comparison of the reactivity of gas oil fractions at 300°C

Feedstocks		AB-HVGO	SJV-VGO
TAN Feedstock	mg KOH/g oil	4.3	3.5
TAN Product	mg KOH/g oil	3.2	2.4
Reacted ACID (TAN)	%	24.7	30.8
Reacted Acid (gas)	wt%	28	41.8
Decarboxylation (gas)	wt%	4.1	4.3
Non-Reacted Acid (gas)	wt%	67.9	53.9

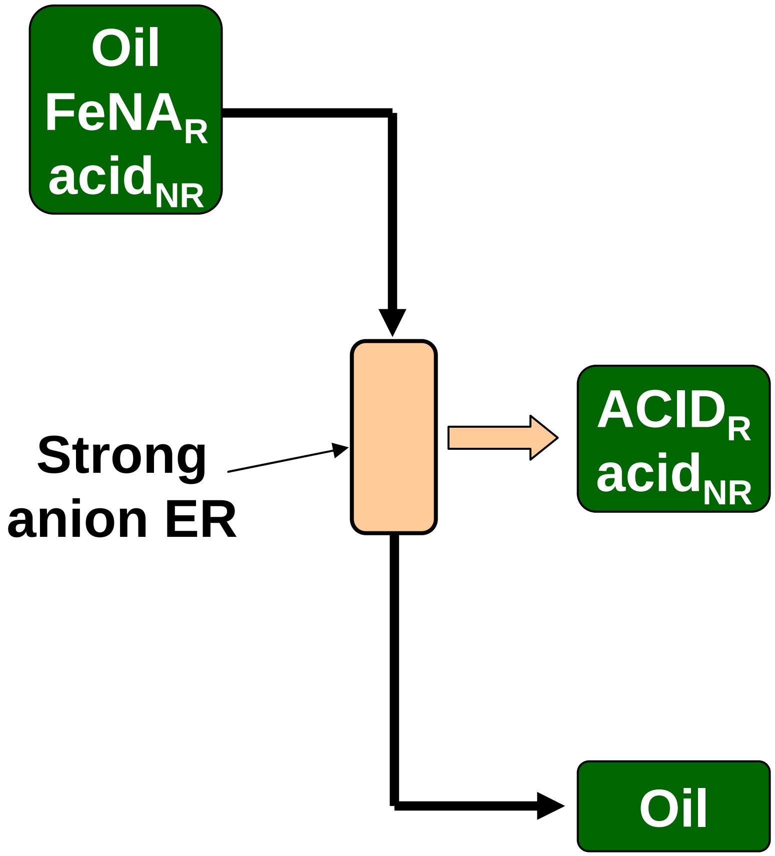
1. Acids Separation

Acid-IER Method (Statoil)



- **Selective isolation of carboxylic acids from crude oils using QAE Sephadex A-25 IER (Strong Anion ER)**

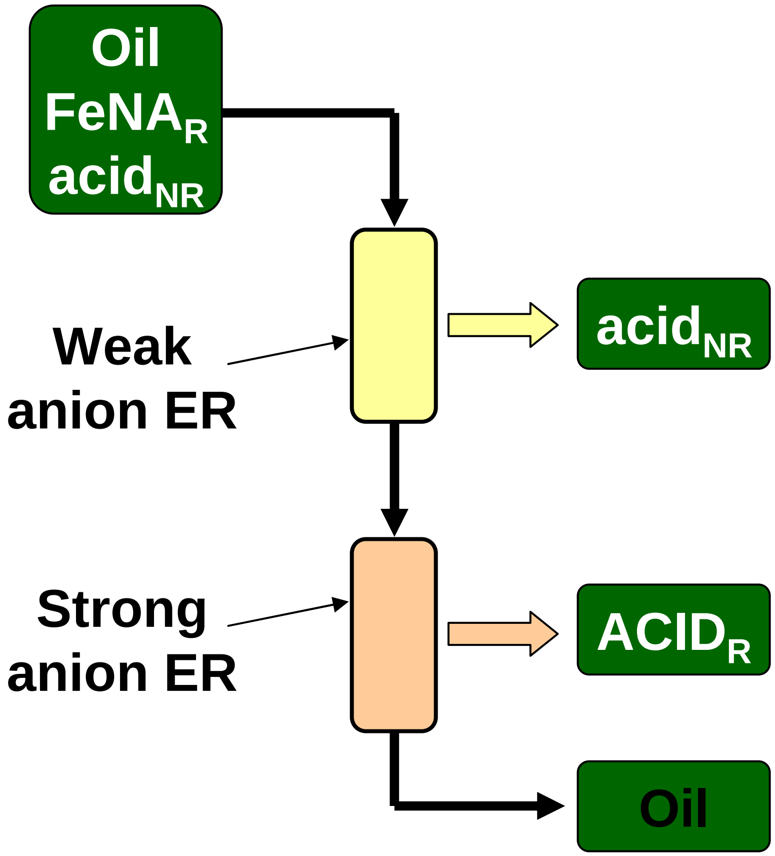
Acid-IER Method (Statoil)



- **Selective Isolation of Carboxylic Acids from Crude Oils using QAE Sephadex A-25 IER (Strong Anion ER)**
- **ER absorbs not only Acids but also FeNA**

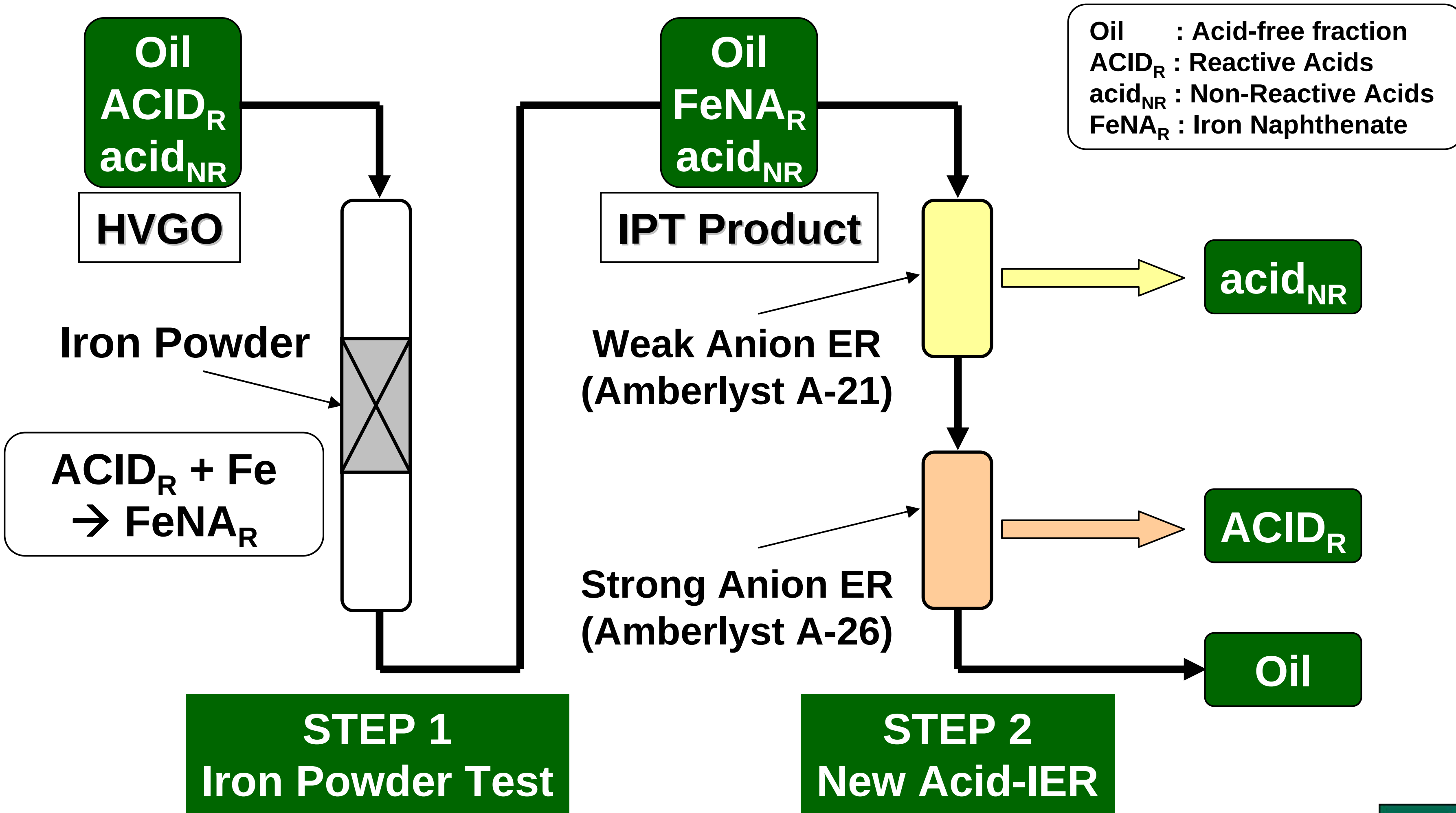
This method can NOT distinguish Reactive Acids and Non-Reactive Acids

New Acid-IER Method



- Selective Isolation of NA and FeNA from IPT product using 2 types of resins
- Weak anion ER isolates only Non-Reactive Acids
- Strong anion ER adsorb FeNAs, and Reactive Acids can be released by formic acids

Procedure of Separation



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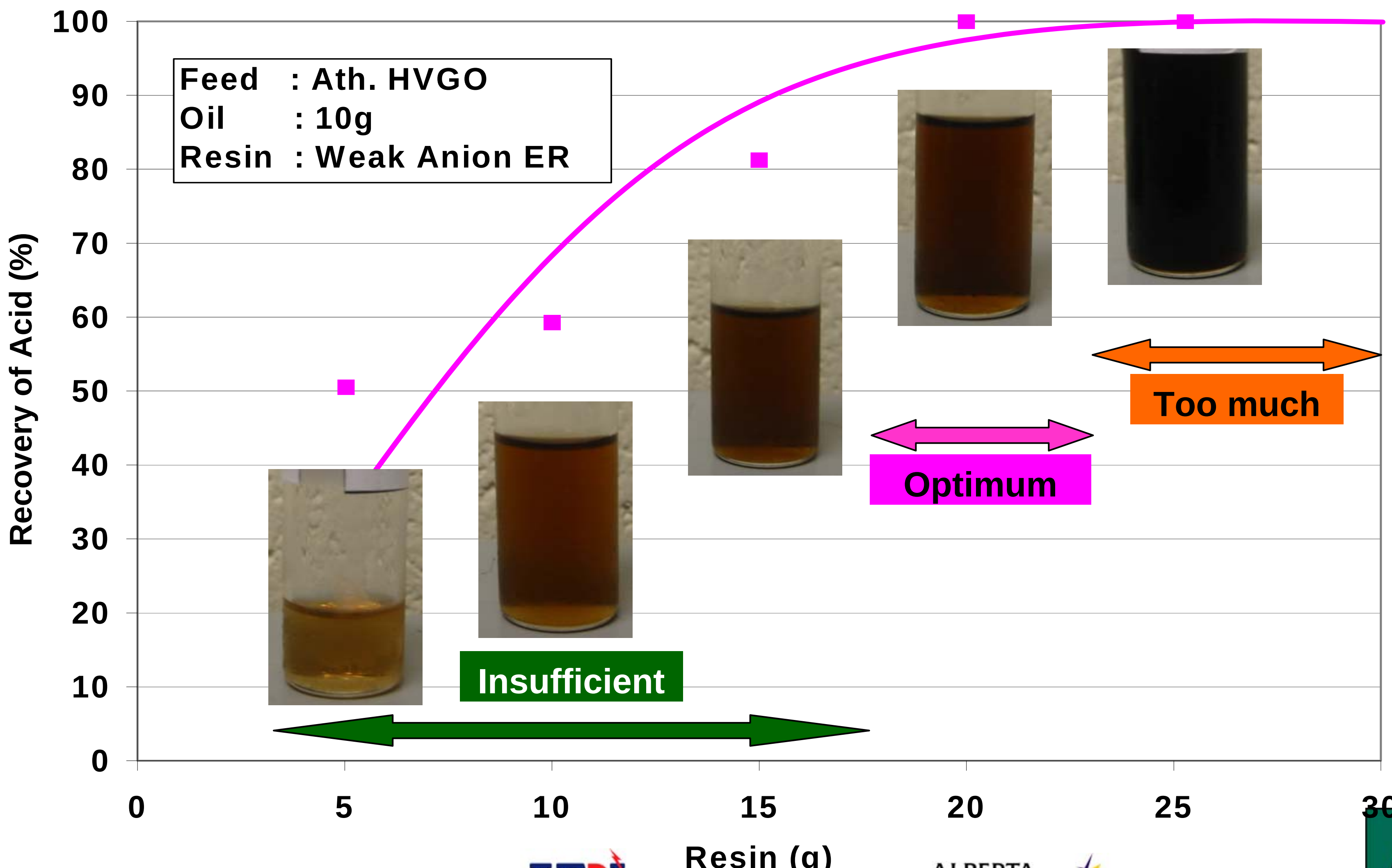
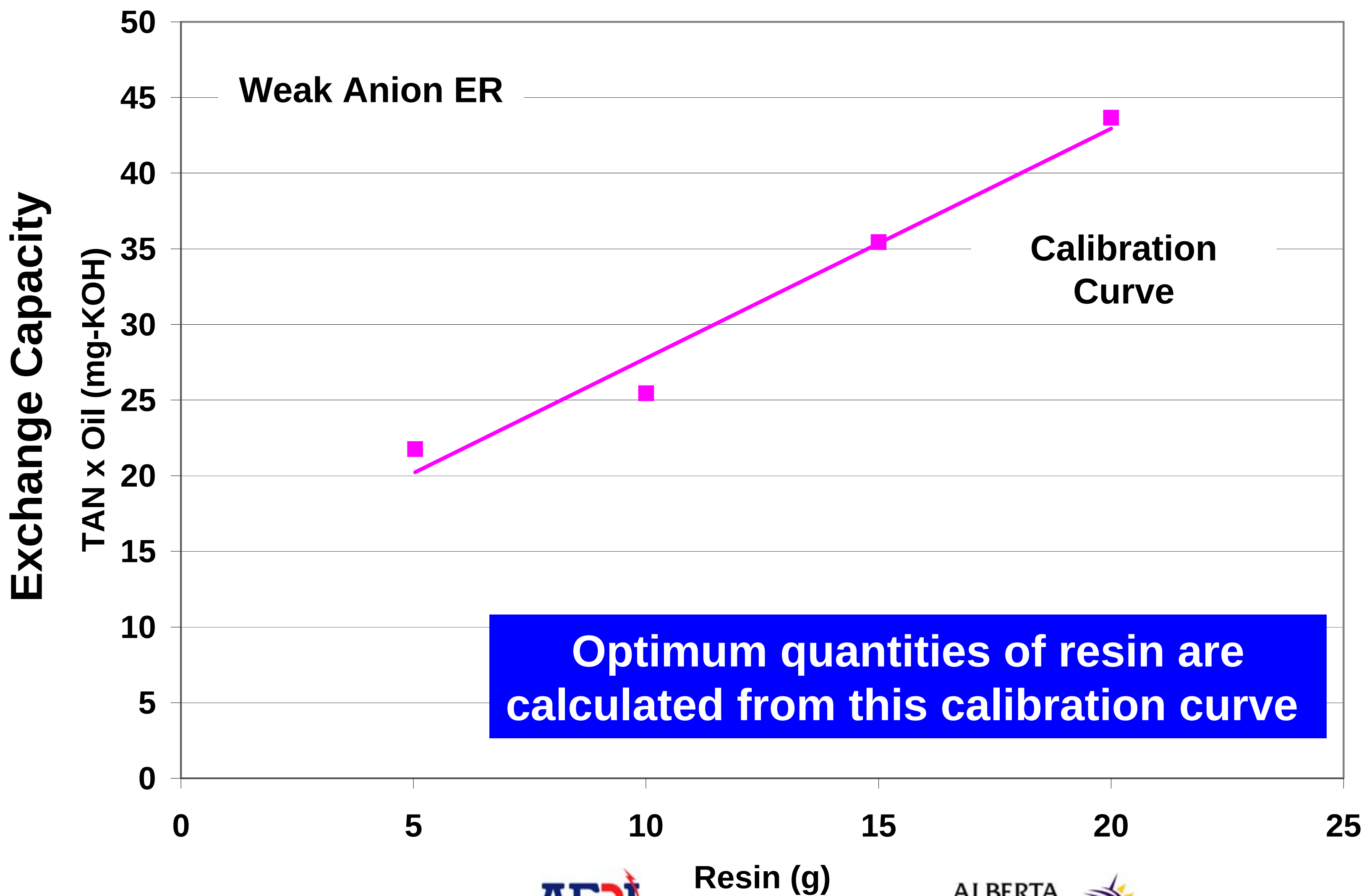
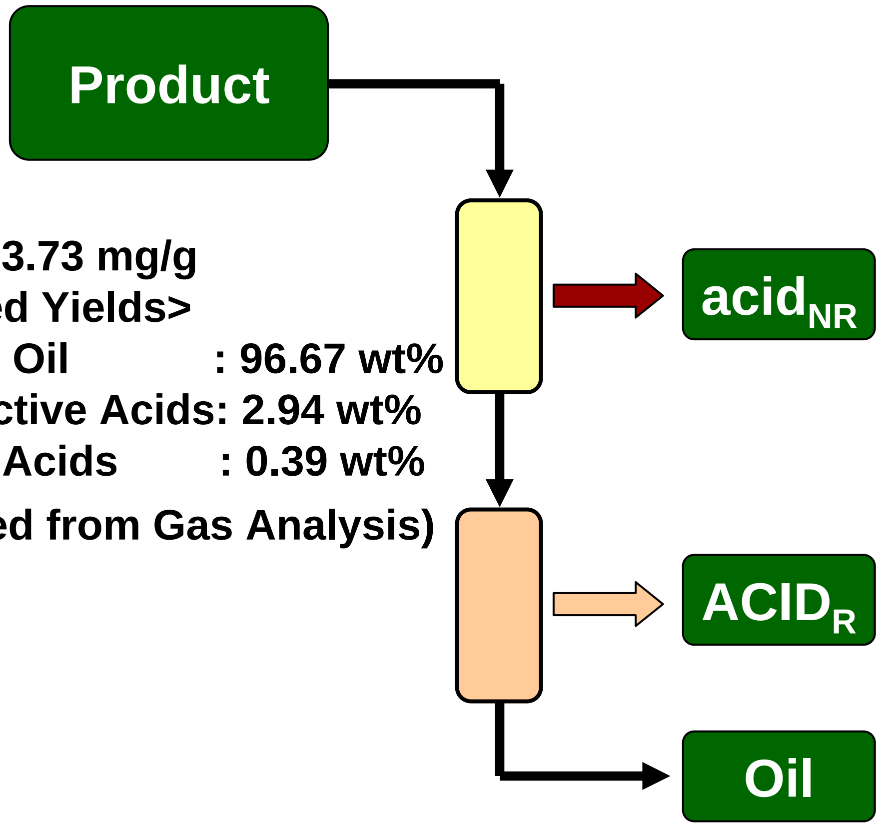
Optimum Quantity of Resin



Optimum Quantity of Resin



Results of Acids Separation



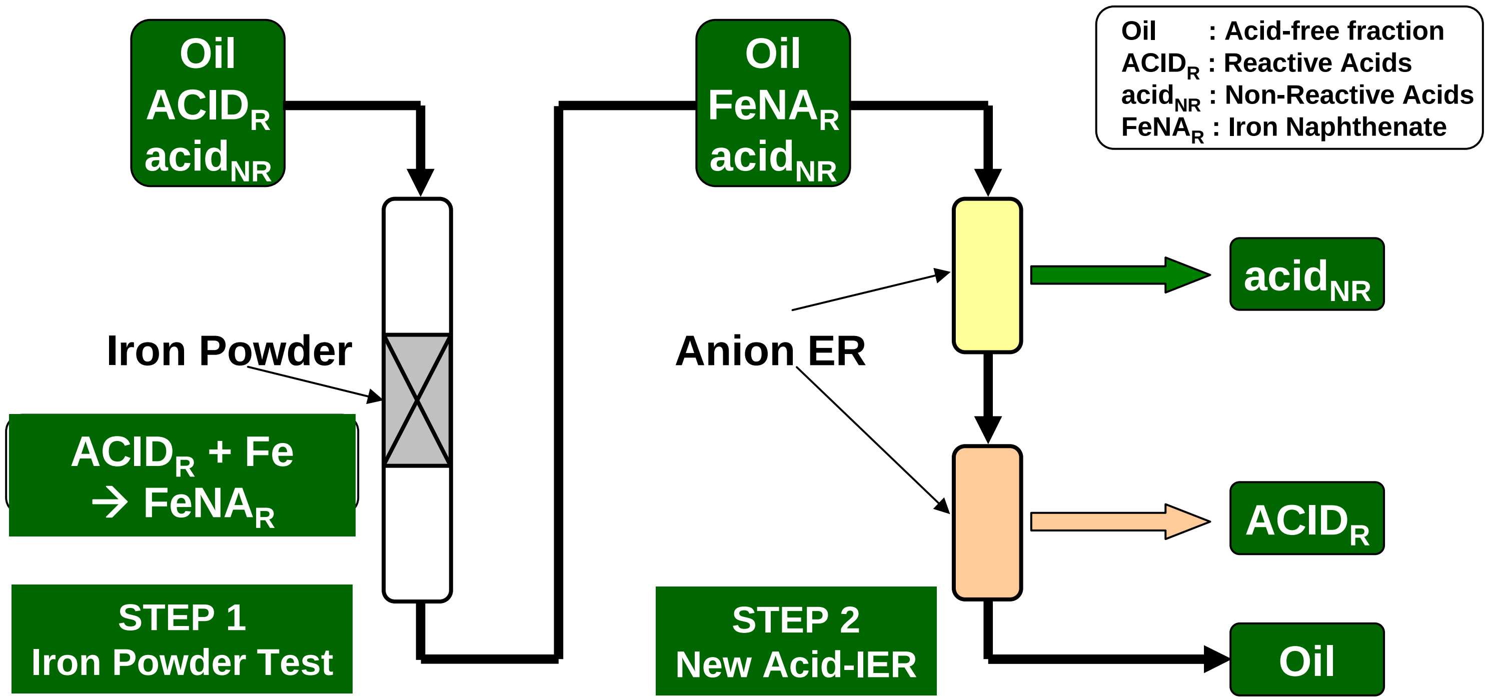
TAN : 3.73 mg/g
<Expected Yields>
Acid-free Oil : 96.67 wt%
Non-Reactive Acids: 2.94 wt%
Reactive Acids : 0.39 wt%
(Calculated from Gas Analysis)

2.71 wt%
(92% Recovery)

0.32 wt%
(82% Recovery)

TAN : 0.20 mg/g
96.97 wt%
(100.3% Recovery)

Summary of Acids Separation



- **Methods for isolation of Reactive Acids and Non-Reactive Acids were established**
- **This method achieves high recovery of Acids and Oil**

2. Analyses

Analytical Methods

Gas Chromatography

- **GC Analysis following methylation is often adopted**
- **Non-methylated NA doesn't elute from column**

Liquid Chromatography

- **HPLC enables rapid analysis at low temperature**

Conducted HPLC analysis according to method of Oil Plus Ltd. [J. Sep. Sci. 2007, 30, 375-380]

Methylation of NAs

Sample Preparation

- **Methylation of NAs is needed for GC Analyses and LC Analyses**
- **Methanol and BF_3 (Catalyst) are conventionally used for methylation [Morrison, W.R. (1964)]**

$$\text{R-COOH} + \text{MeOH} \xrightarrow{BF_3} \text{R-COO-Me} + H_2O$$

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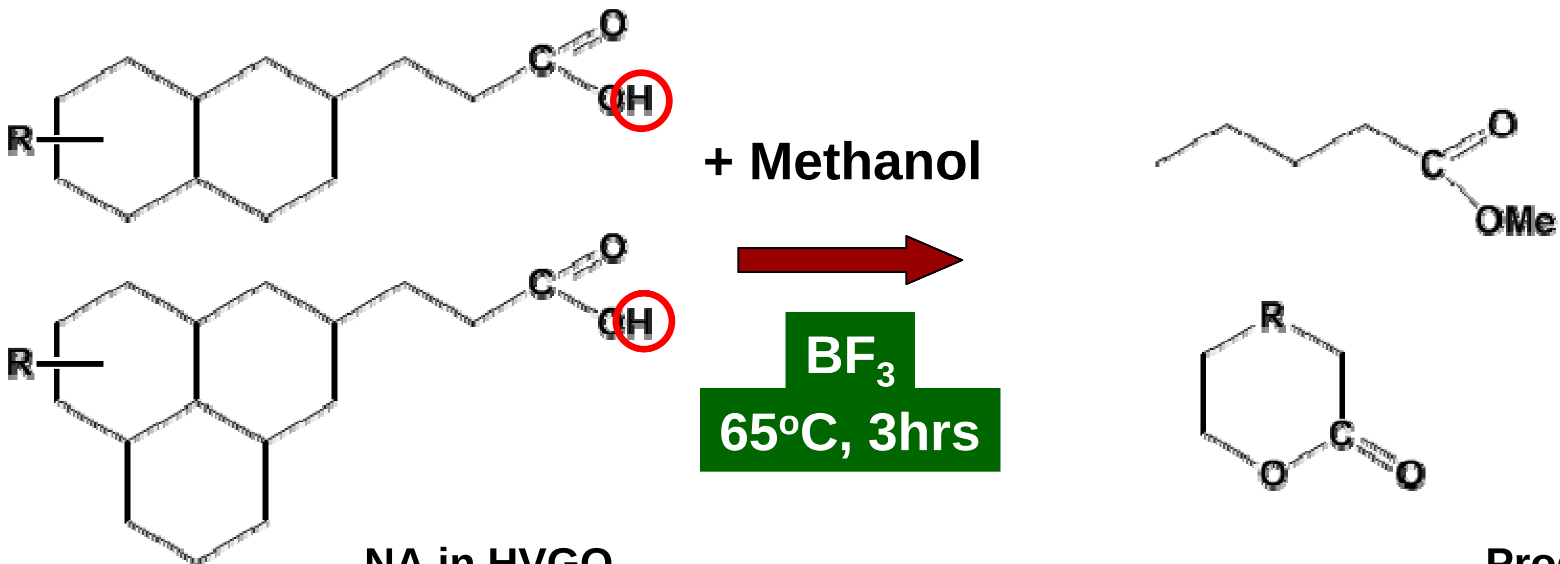
Methylation of NAs



NA in HVGO
(Ave. MW = 350)

Product
(Ave. MW < 100)

Chemical bonds were broken
Side reactions occurred

BF_3 is too strong acid

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Methylation of NAs

Sample Preparation

- **Esterification of NAs is needed for GC Analyses and HPLC Analyses**
- **Methanol and BF_3 (Catalyst) are conventionally used for methylation [Morrrison, W.R. (1964)]**

HCl (50^{o}C, Overnight)

~~BF_3~~

R-COOH + MeOH ⟶ R-COO-Me + H_2O

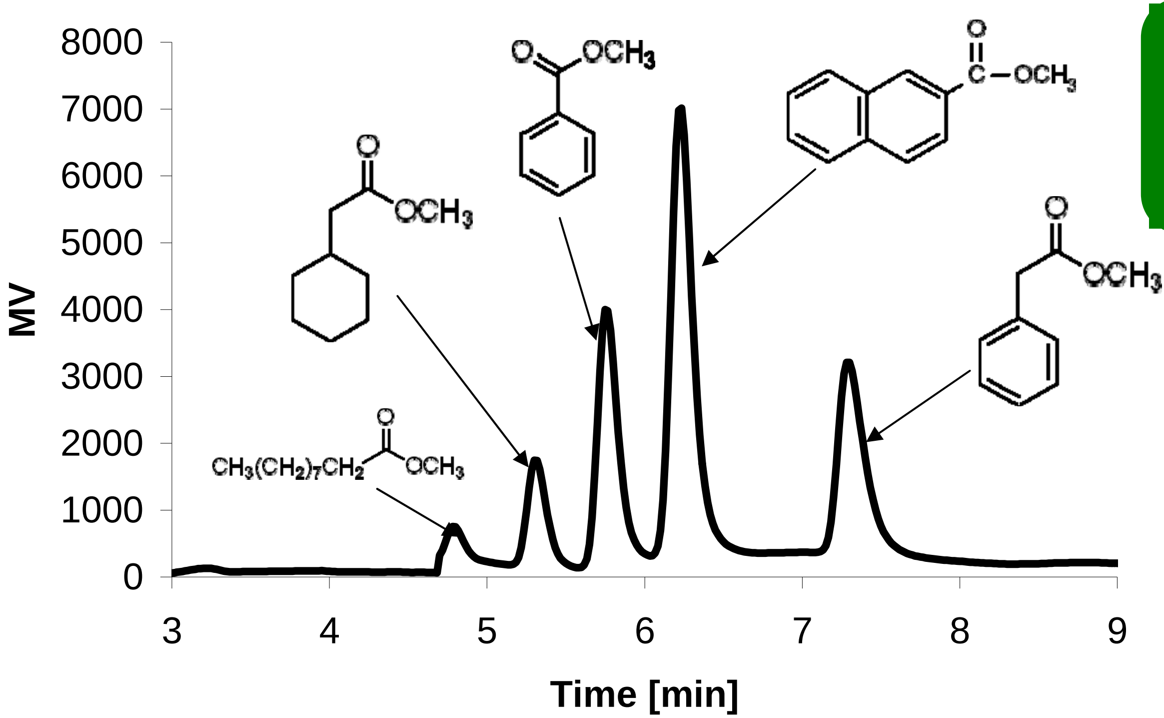
- **But BF_3 is so strong Lewis acid catalyst, it broke the structure of NA, or caused side reaction**

- **Apply an improved methylation method which use HCl as acid catalyst [Christie, W.W. (1993)]**

This method may not cause above problems!

Analytical Results (HPLC)

Pure Compounds of Methyl ester (1wt% for each)

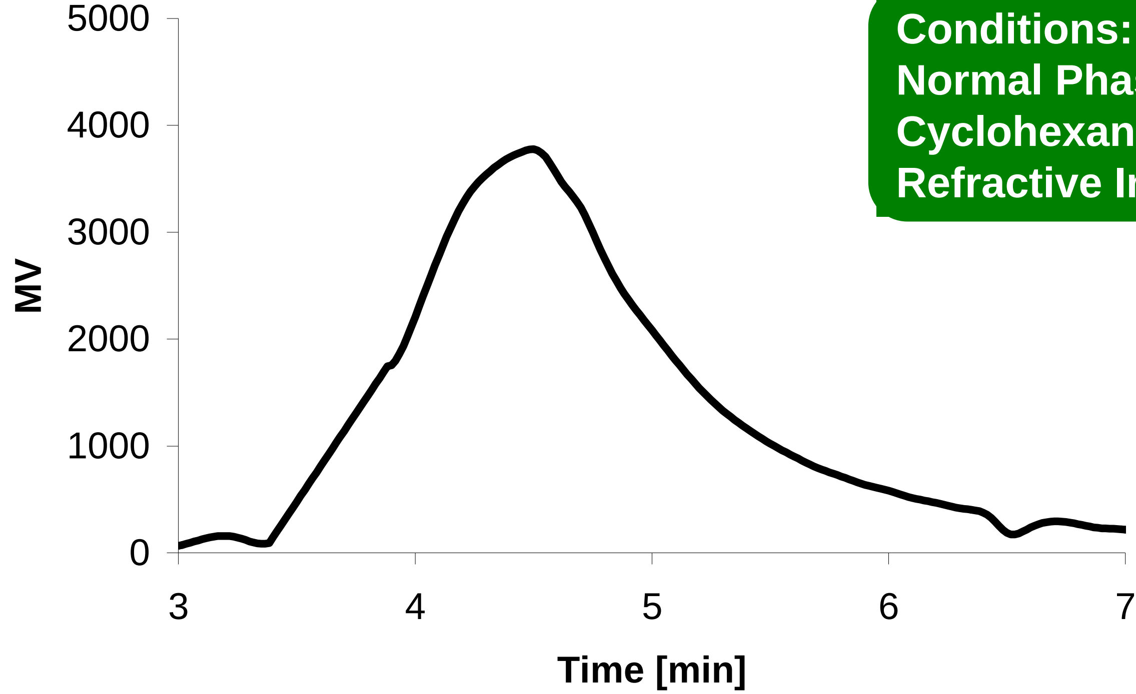


Conditions:
Normal Phase
Cyclohexane/DCM = 60 / 40
Refractive Index Detector

The performance of separation was good

Analytical Results (HPLC)

Methylated NAs in Athabasca HVGO



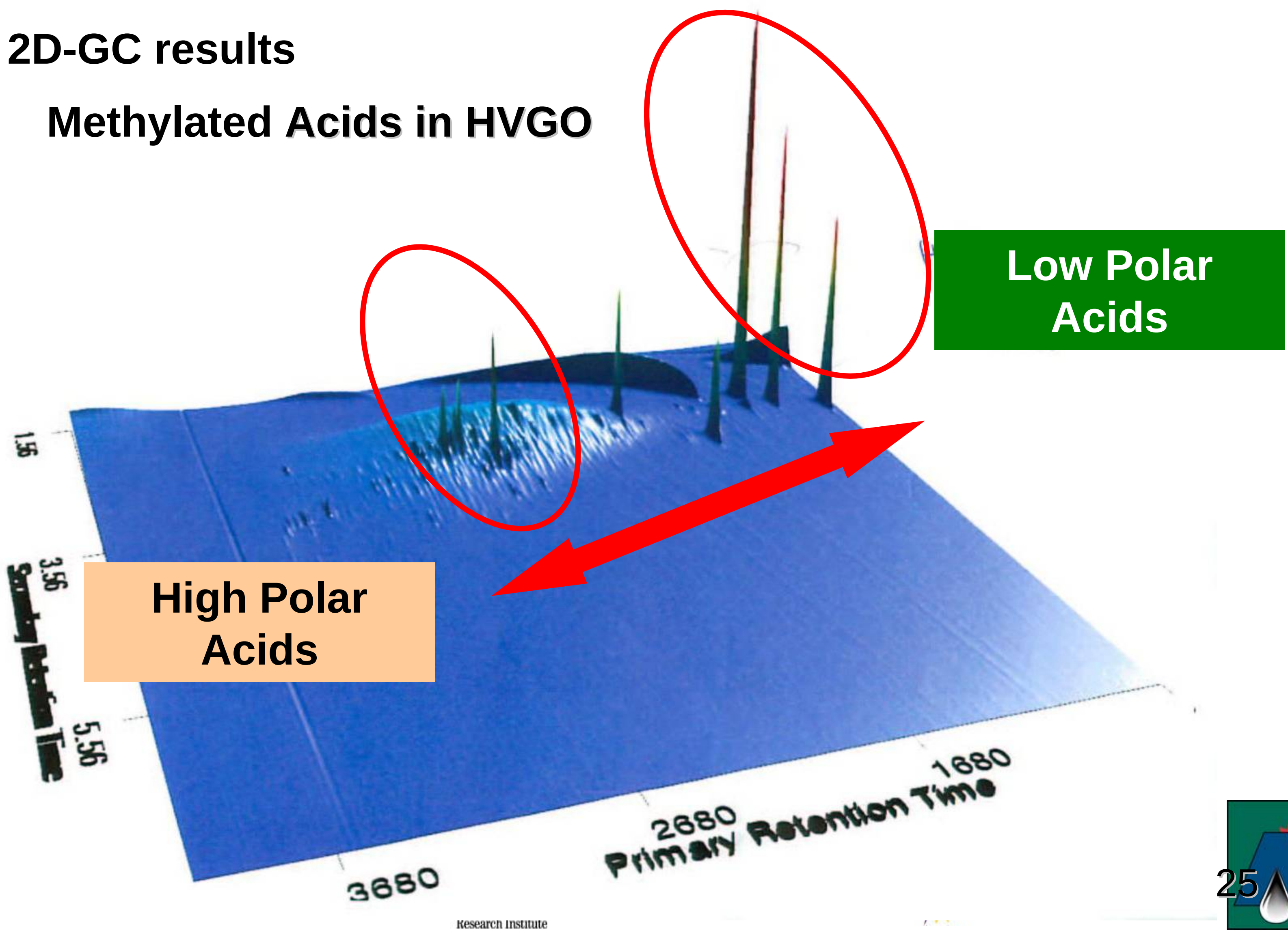
Conditions:
Normal Phase
Cyclohexane/DCM = 60 / 40
Refractive Index Detector

An unresolved broad peak was apparent
Difficult to identify NAs with HPLC…

Analytical Results (2D-GC)

2D-GC results

Methylated Acids in HVGO



Summary of Analyses

- Conventional methylation method using BF_3 did not work for NAs in HVGO
- HPLC is useful for analyzing of model compounds, but it did not work for NAs in HVGO
- 2D-GC following methylation using HCl may prove to be a good solution for analyzing of NAs in HVGO

Future Plans

Acid Separation

- **Repeat experiments at various conditions and feedstocks**

Analyses

- **Analyze methylated NAs with 2D-GC TOF MS**
- **Identify the type of Reactive acids with FT-ICR MS**

This Project is continuing in Collaboration between NCUT and JGC