

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



Natural Resources
Canada

Ressources naturelles
Canada



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



Natural Resources Canada
Ressources naturelles Canada



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?



Natural Resources
Canada

Ressources naturelles
Canada



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

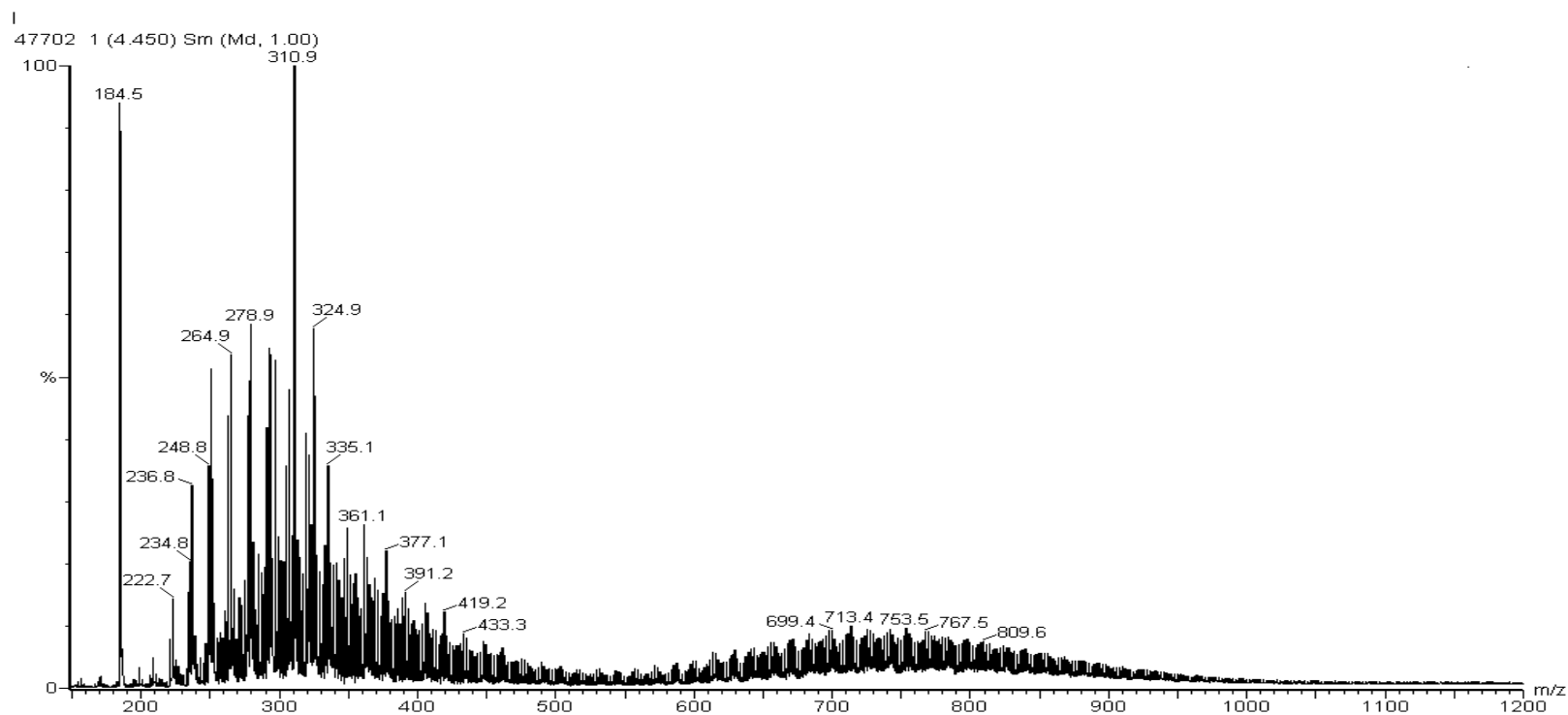


Natural Resources
Canada

Ressources naturelles
Canada



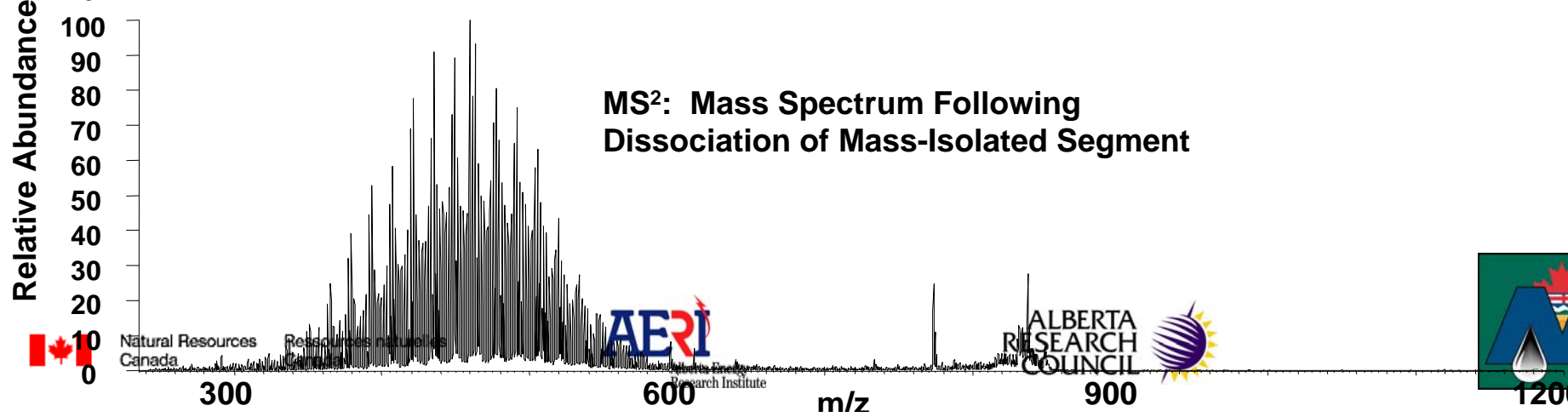
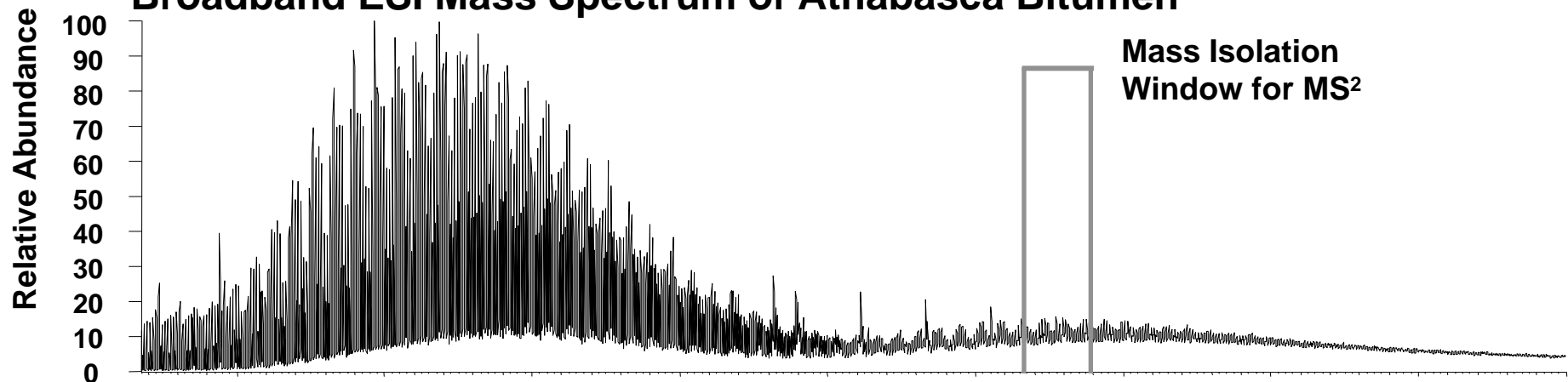
ESI (LRMS) – Naphthenic Acids



Natural Resources Canada
Ressources naturelles Canada



Broadband ESI Mass Spectrum of Athabasca Bitumen

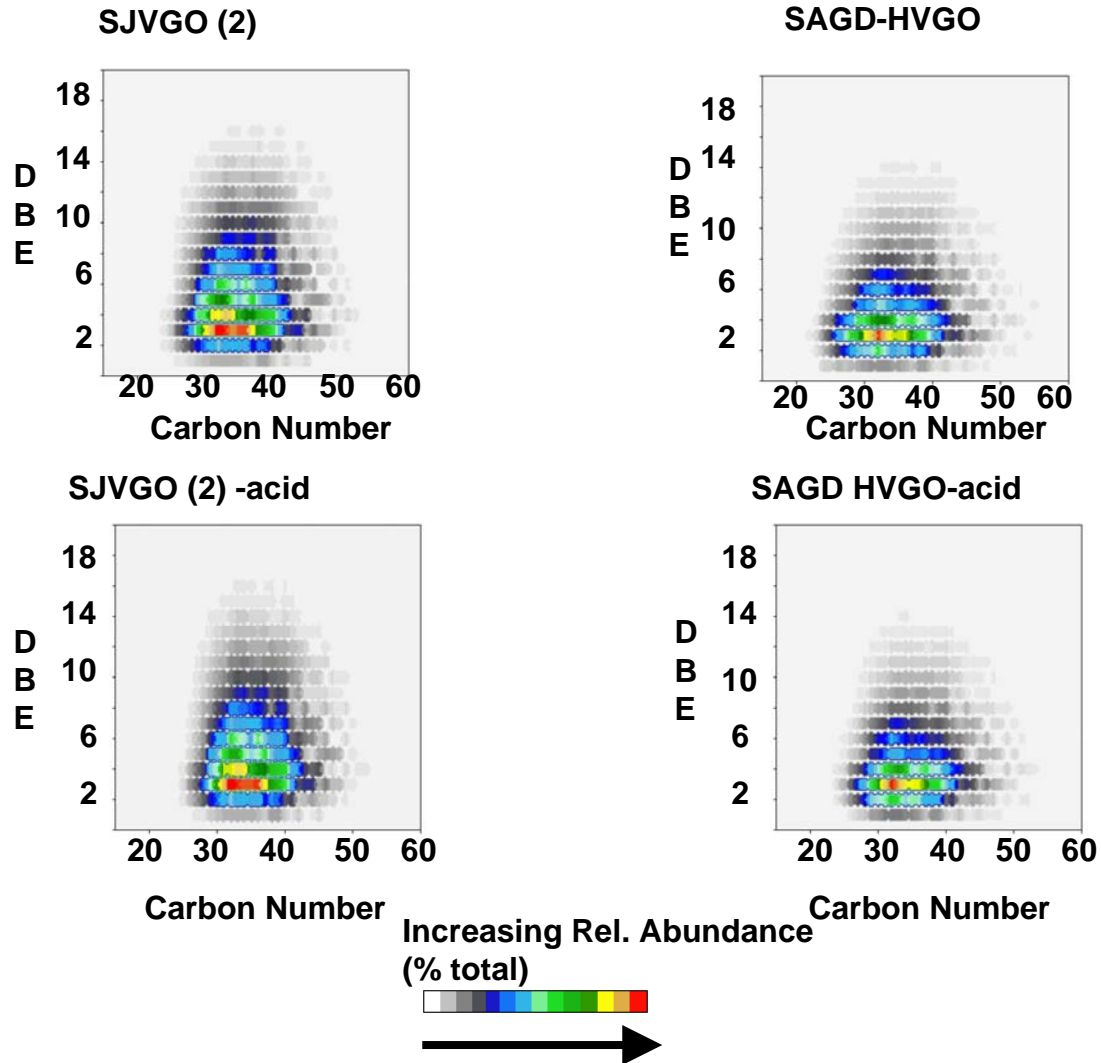


References

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, Parviz 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



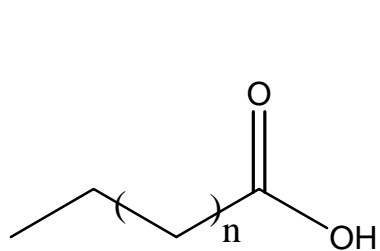
FT-ICR mass Spectrometry SJV and AB-SAGD



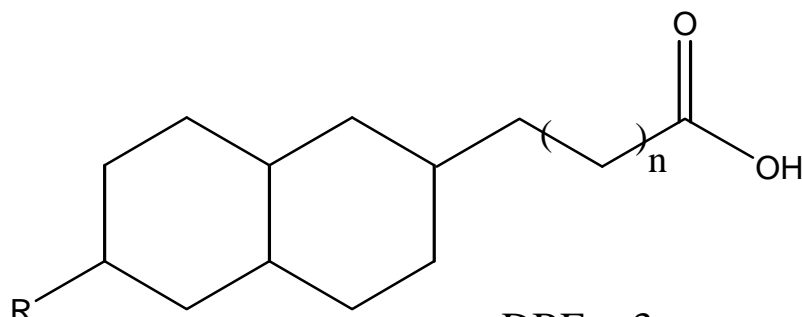
Natural Resources Canada
Ressources naturelles Canada



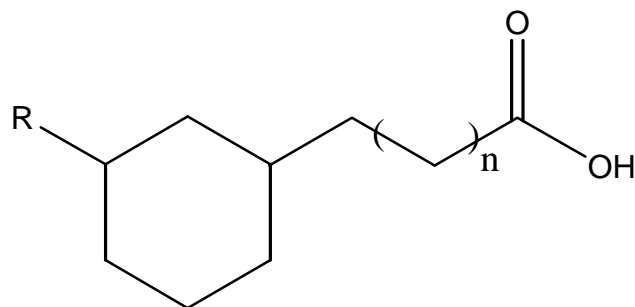
Typical naphthenic acid chemical structures



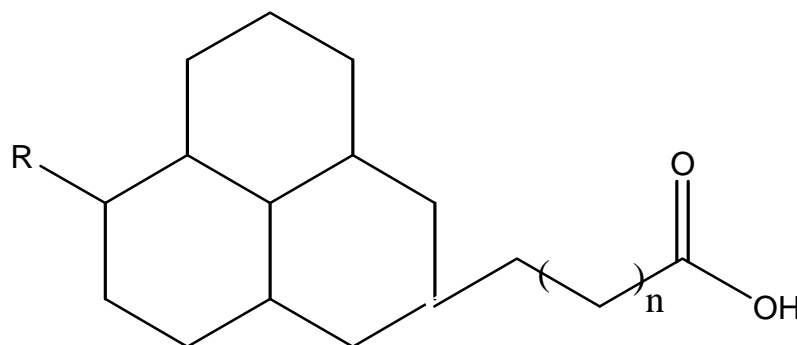
DBE = 1



DBE = 3



DBE = 2

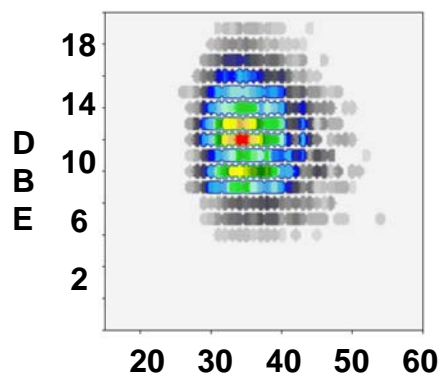


DBE = 4

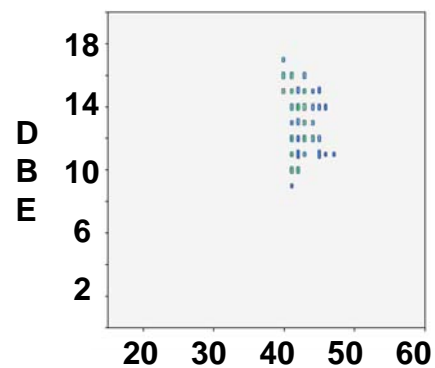


FT-ICR mass Spectrometry SJV and AB-SAGD

SJVGO (2) N1



SAGD-HVGO -N1



Increasing Rel. Abundance
(% total)



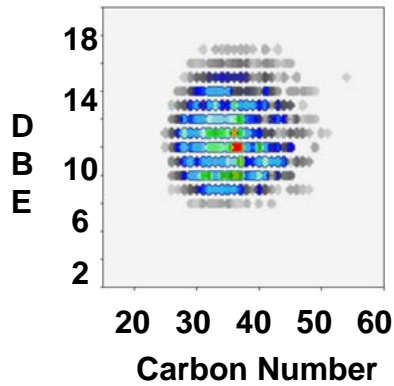
Natural Resources
Canada

Ressources naturelles
Canada

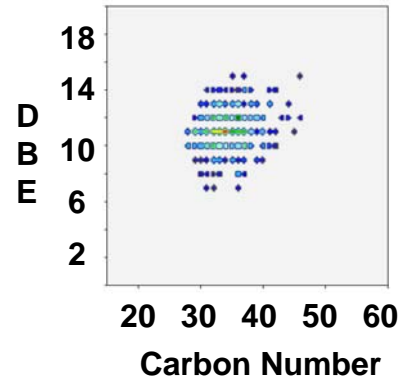


FT-ICR mass Spectrometry SJV and AB-SAGD

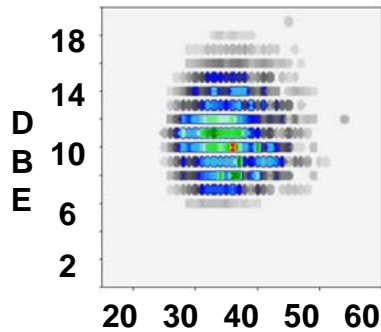
SJVGO (2) N1O2



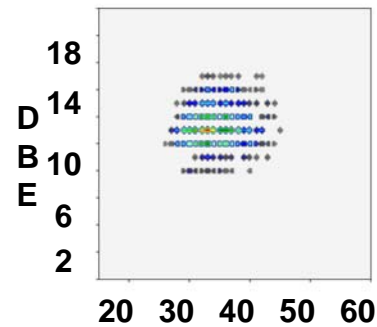
SAGD-HVGO N1O2



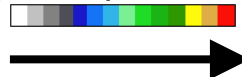
SJVGO -acid N1O2



SAGD-HVGO- acid N1O2



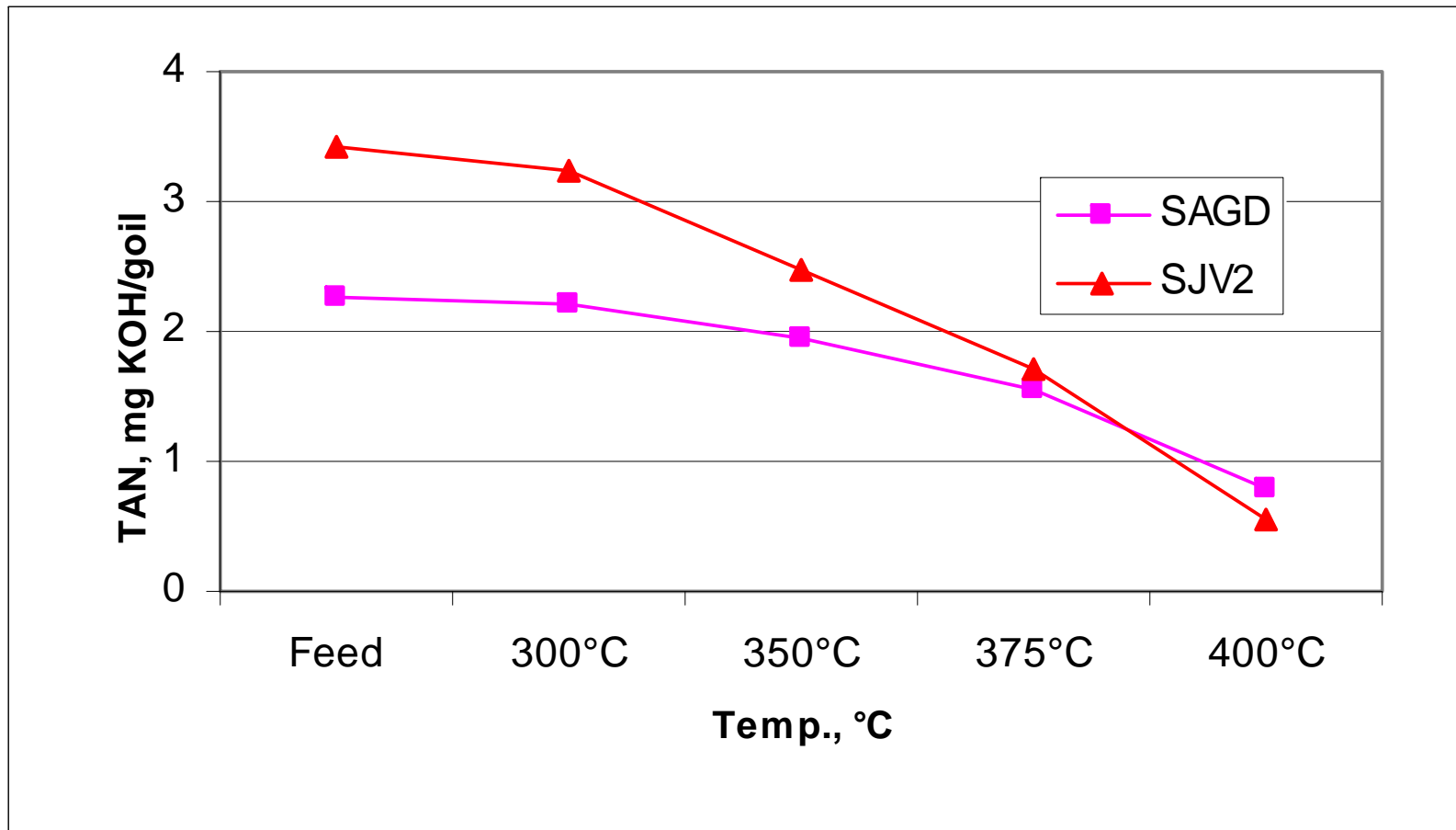
Increasing Rel. Abundance
(% total)



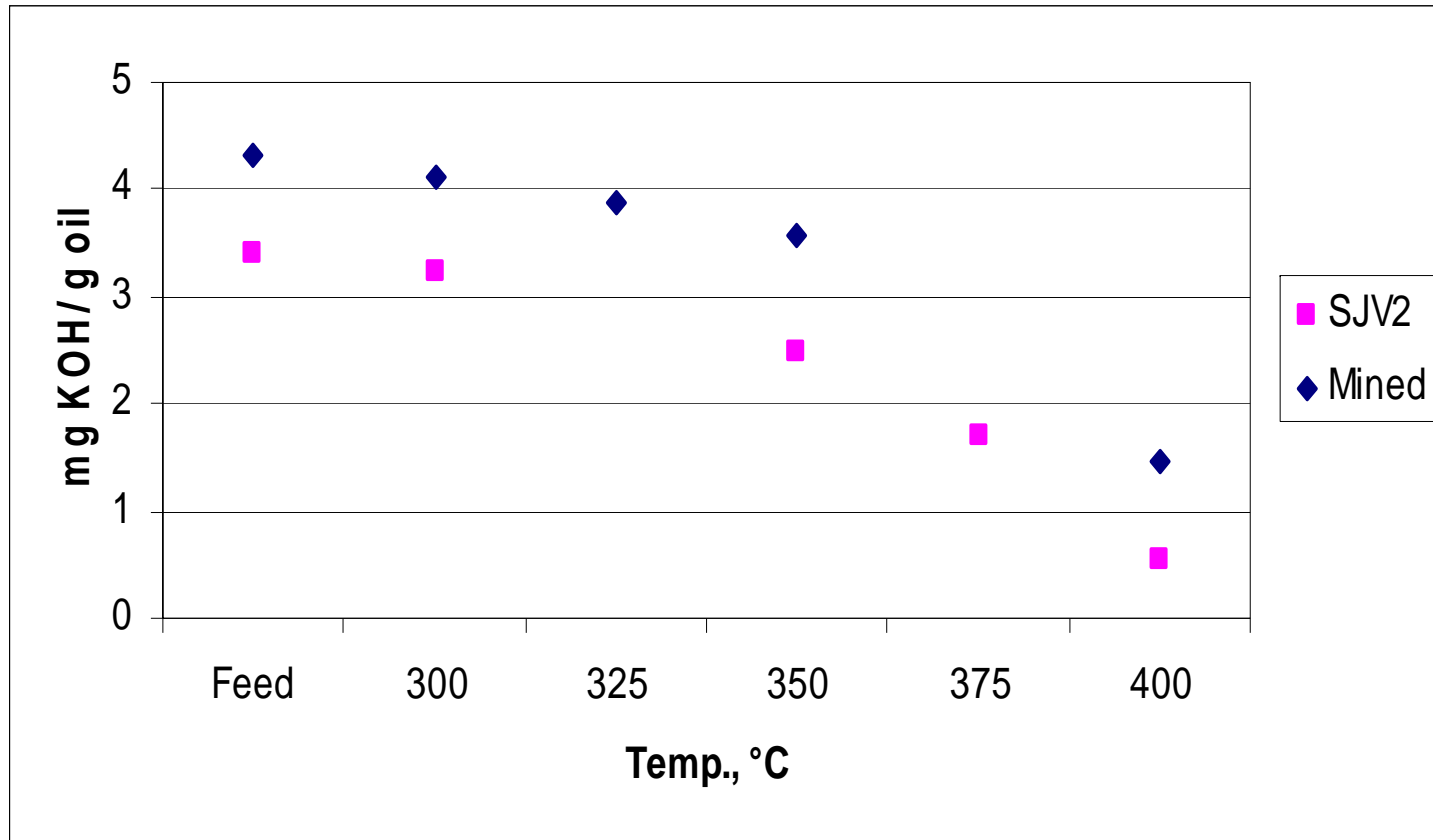
Natural Resources Canada
Ressources naturelles Canada



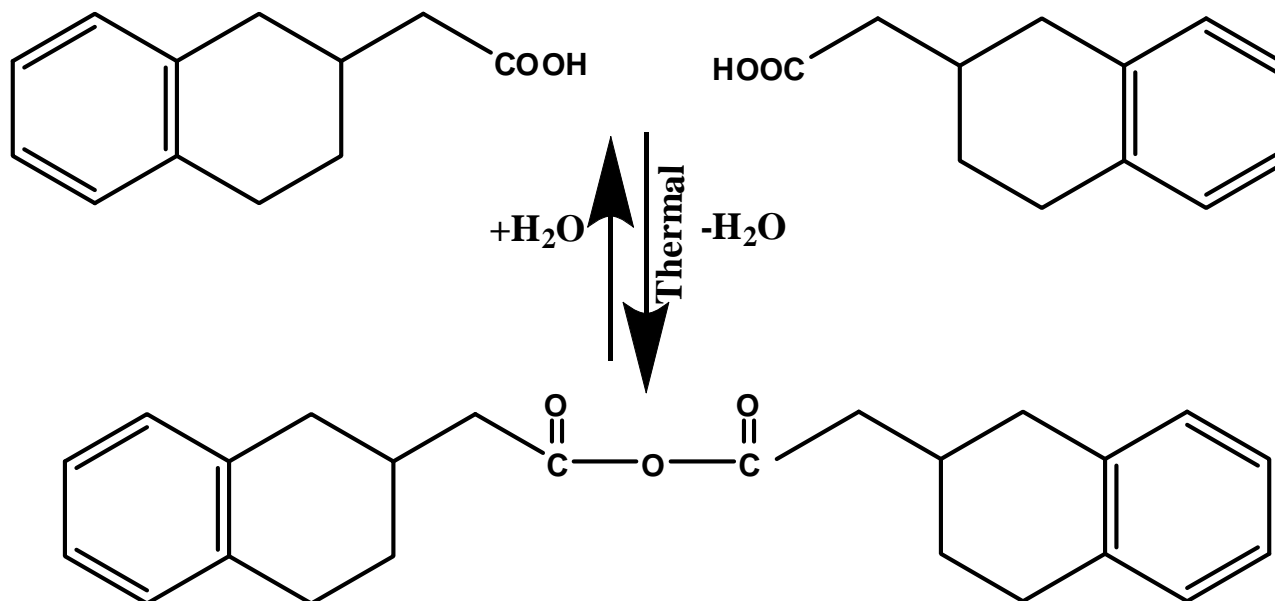
Effect of temperature on TAN reduction AB-SAGD-HVGO SJV-HVGO



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



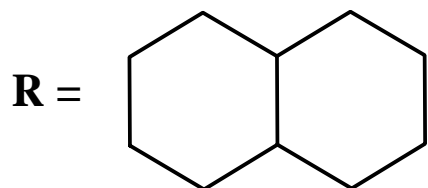
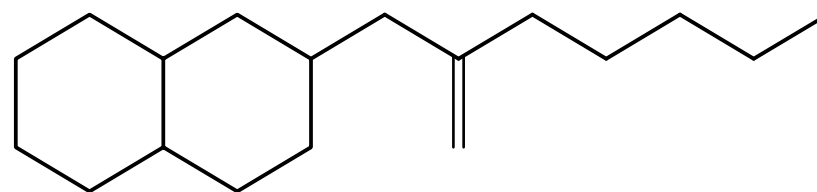
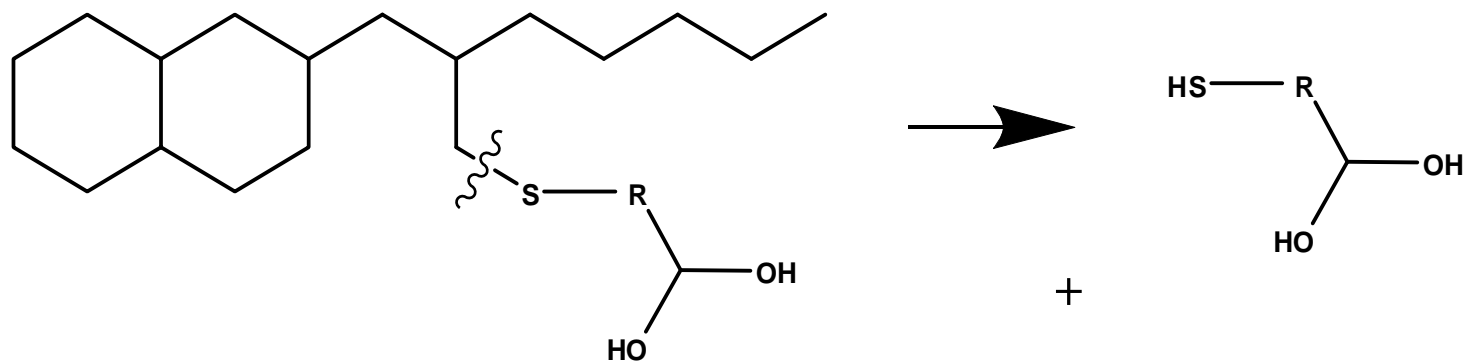
Dehydration mechanism of Naphthenic acids



**Autoclave experiments
should be carried out in an
open system**



Possible mechanism of NA size reduction



Petrobras – NCUT Collaboration 2010

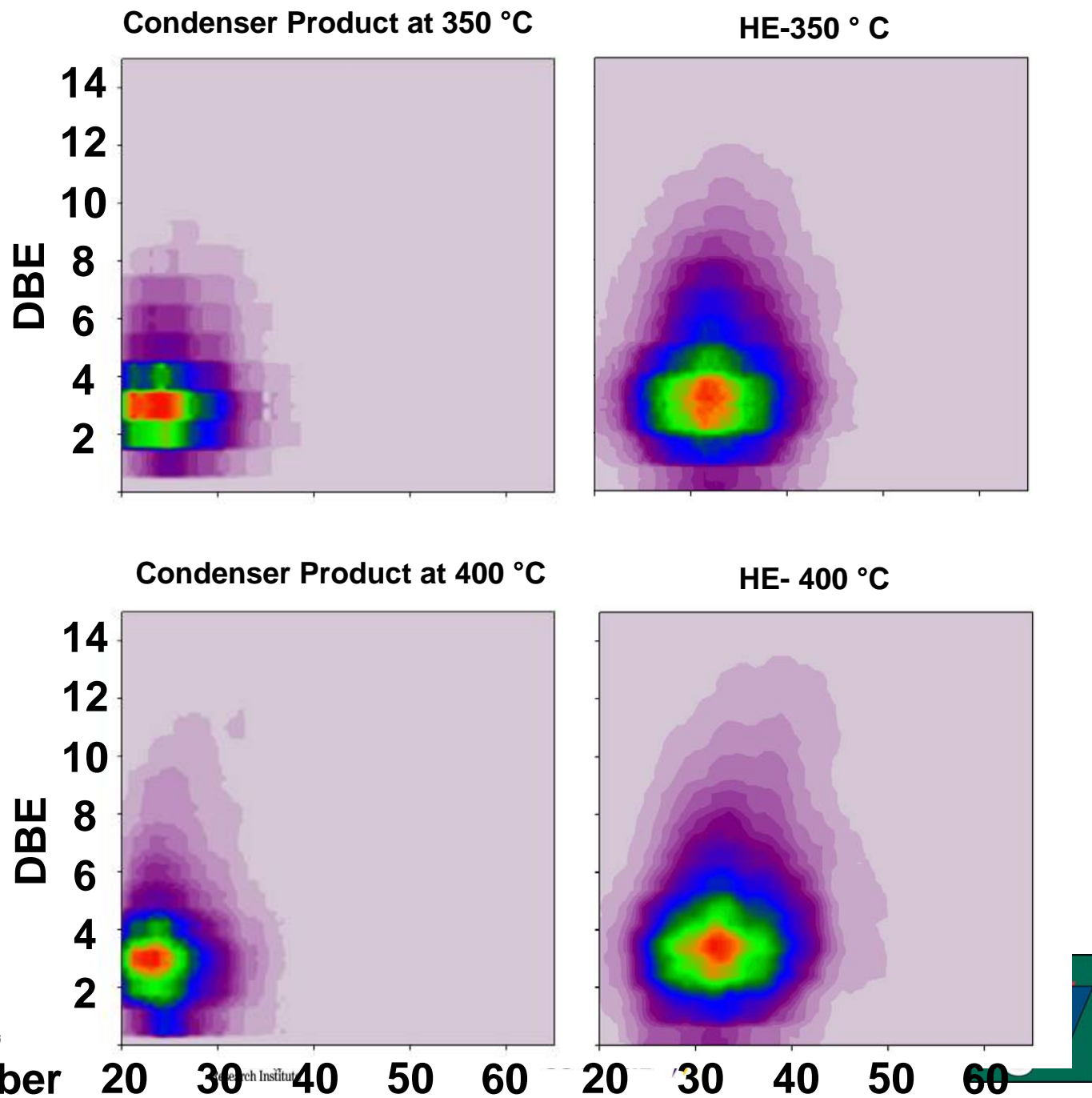


Natural Resources Canada
Ressources naturelles Canada



Condenser Products

O₂



Corrosion Mechanism



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



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



Natural Resources
Canada

Ressources naturelles
Canada



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



Natural Resources
Canada

Ressources naturelles
Canada



Issues with Fe Powder test using Batch reactor

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



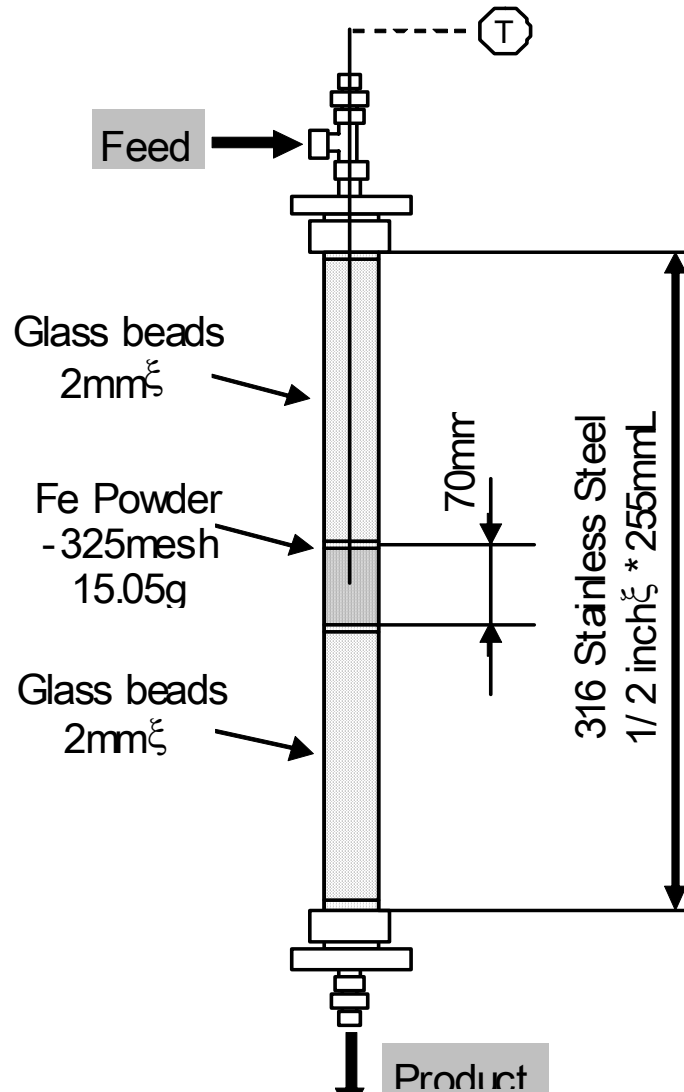
Natural Resources
Canada

Ressources naturelles
Canada



Experimental Unit – Continuous Flow

Glass Tube Reactor



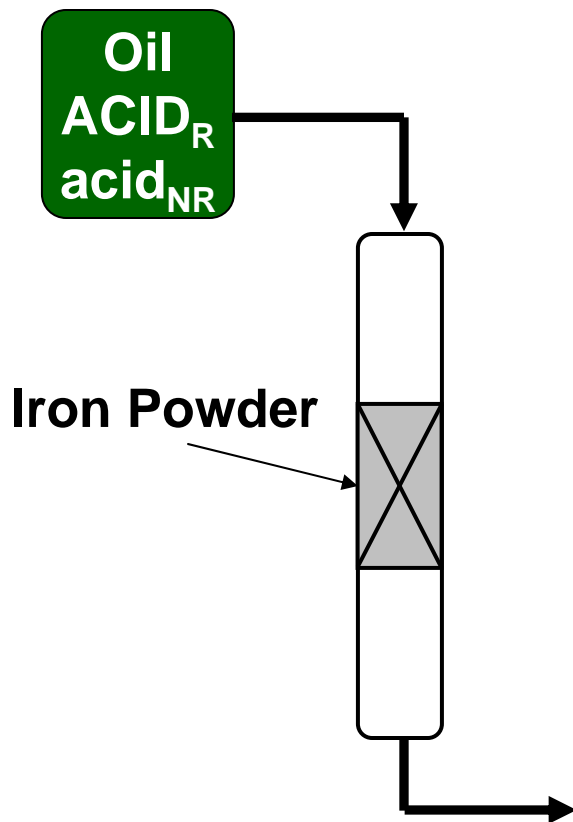
Reaction Conditions

- Feed – HVGO from Mined, SJV
- Temperature : 250 ~ 350°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)
- N₂ flow rate : 5~10 ml/min

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



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



Test Conditions

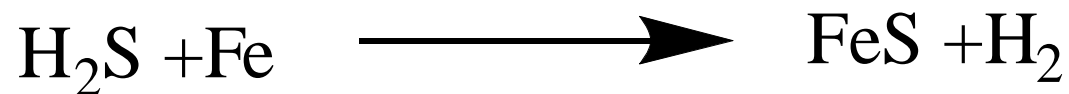
Temperature: 250~350 C°
Pressure: Atmosphere
Residence time: 30 min.

Analyses

Product: TAN
Gas: H₂, CO₂



Reaction Mechanism



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

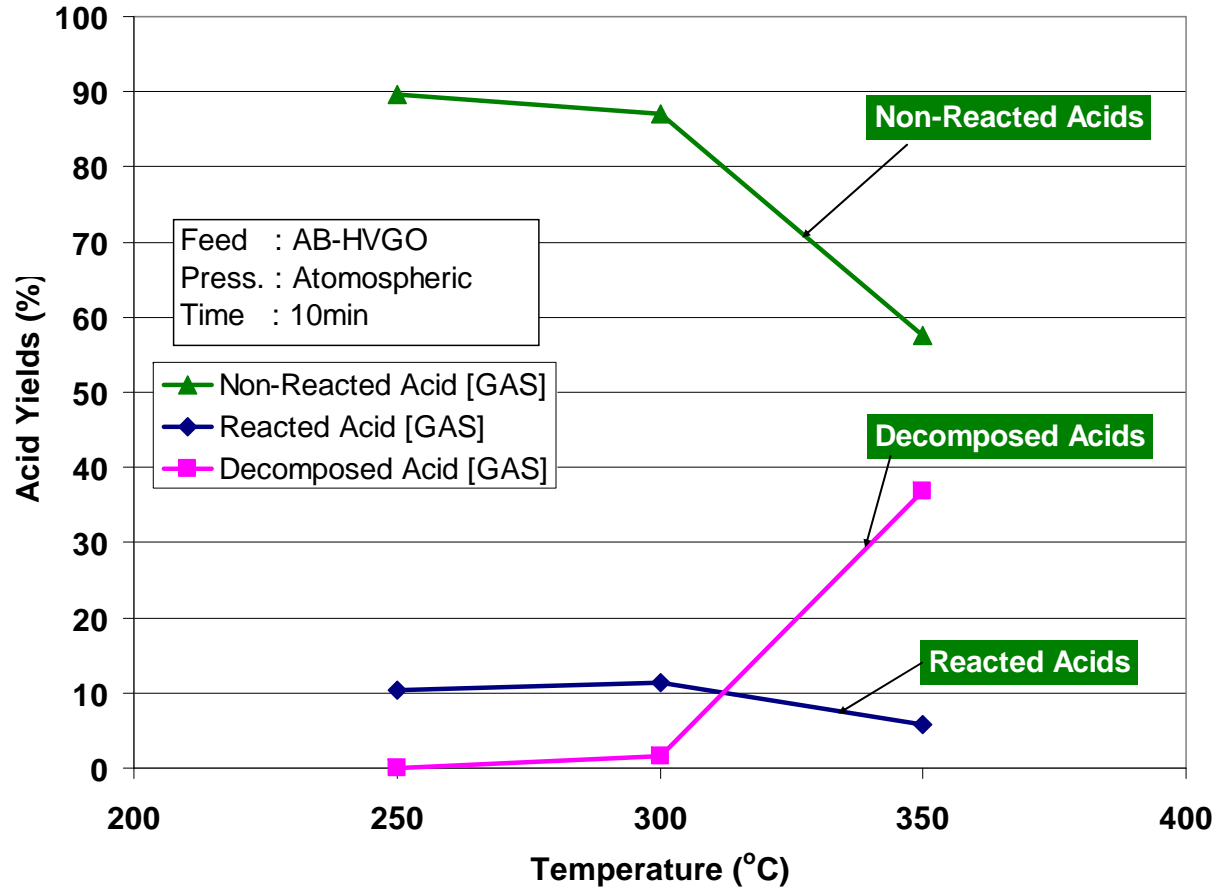


Effect of temperature on Sulfur and MW

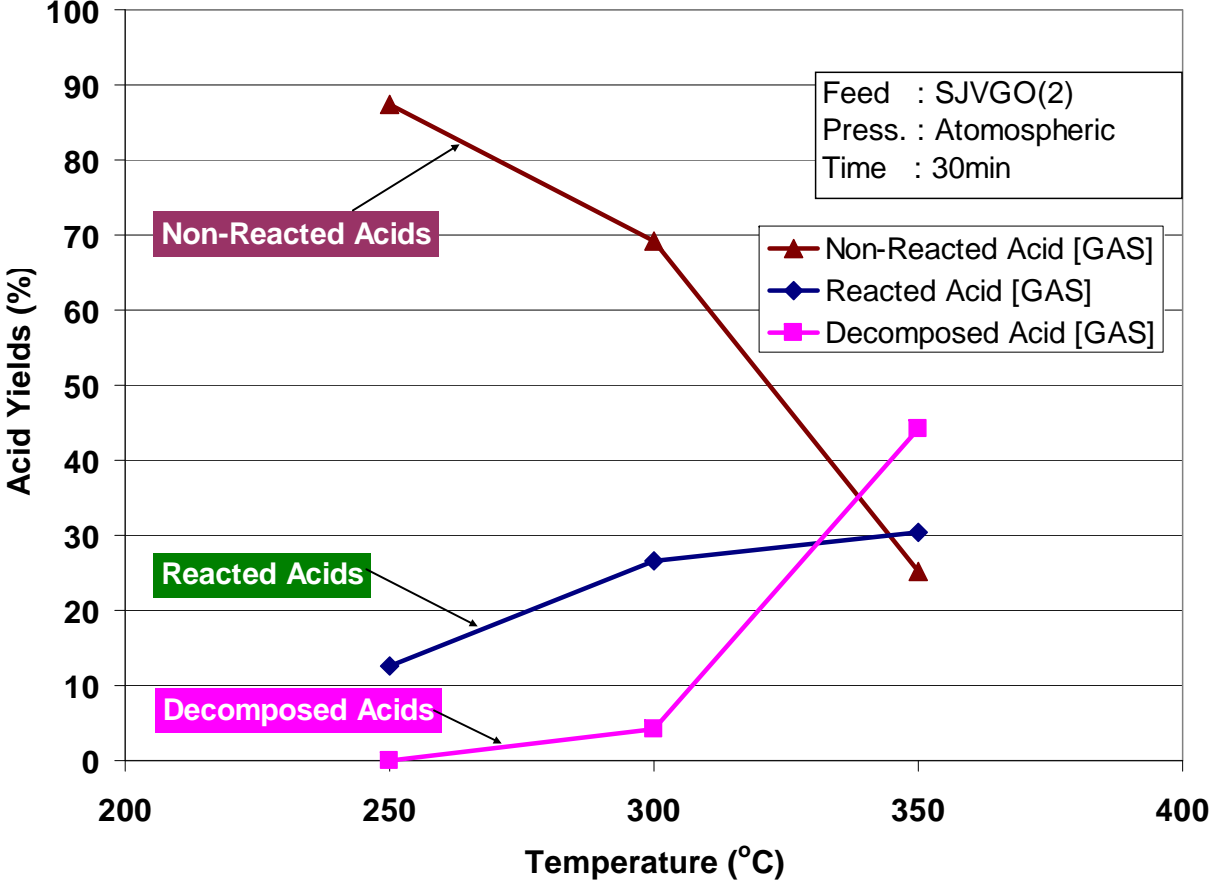
Run Temp., °C	SJV2		HVGO	
	Sulfur % wt	MW g/mole	Sulfur % wt	MW g/mole
0	1.33	459	3.48	345
300	1.36	423	3.40	333
325			3.51	338
350	1.36	426	3.56	337
375	1.29	387		
400	1.14	389	3.32	343



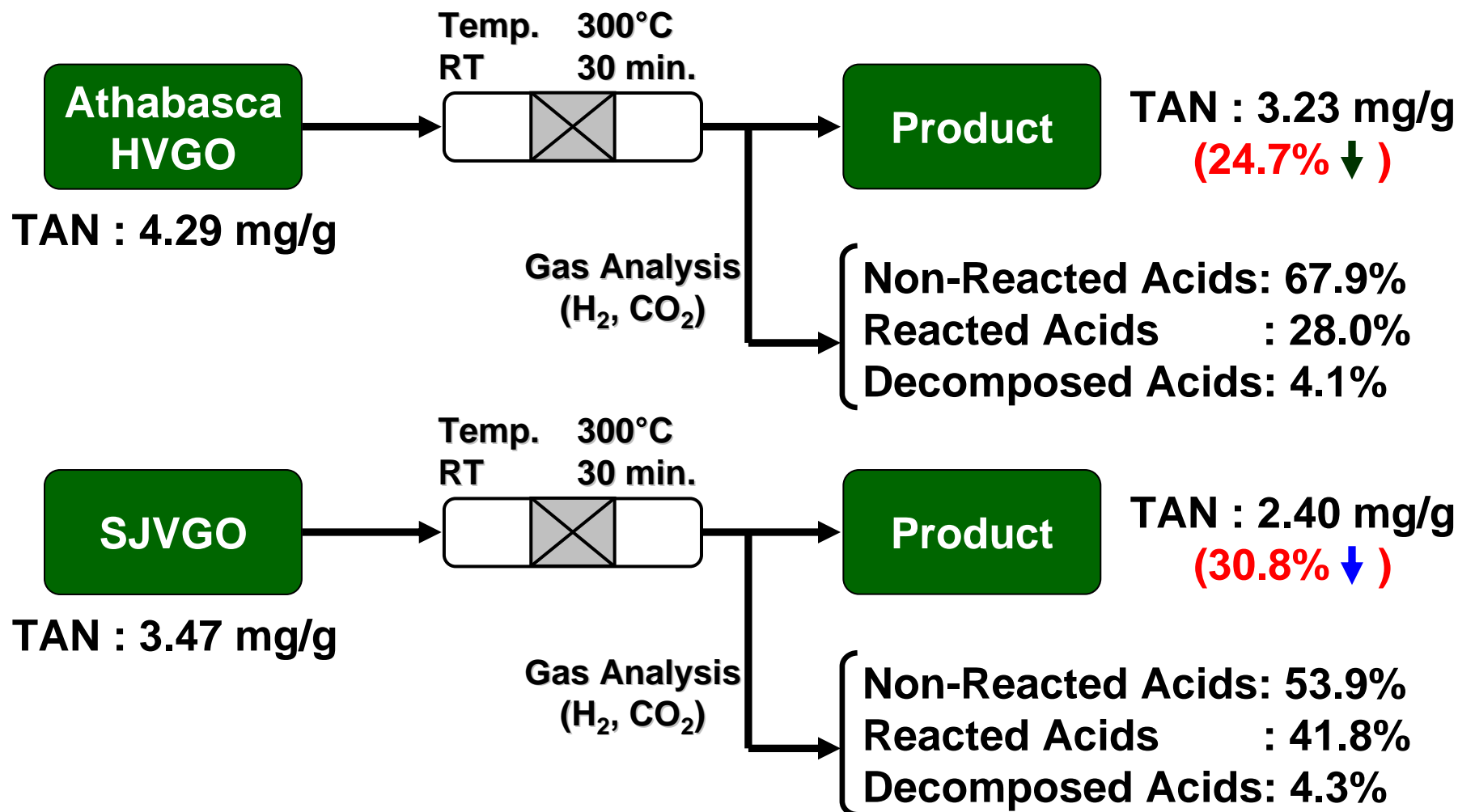
Reactivity of AB-HVGO



Reactivity of SJV-HVGO



Results of IPT



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

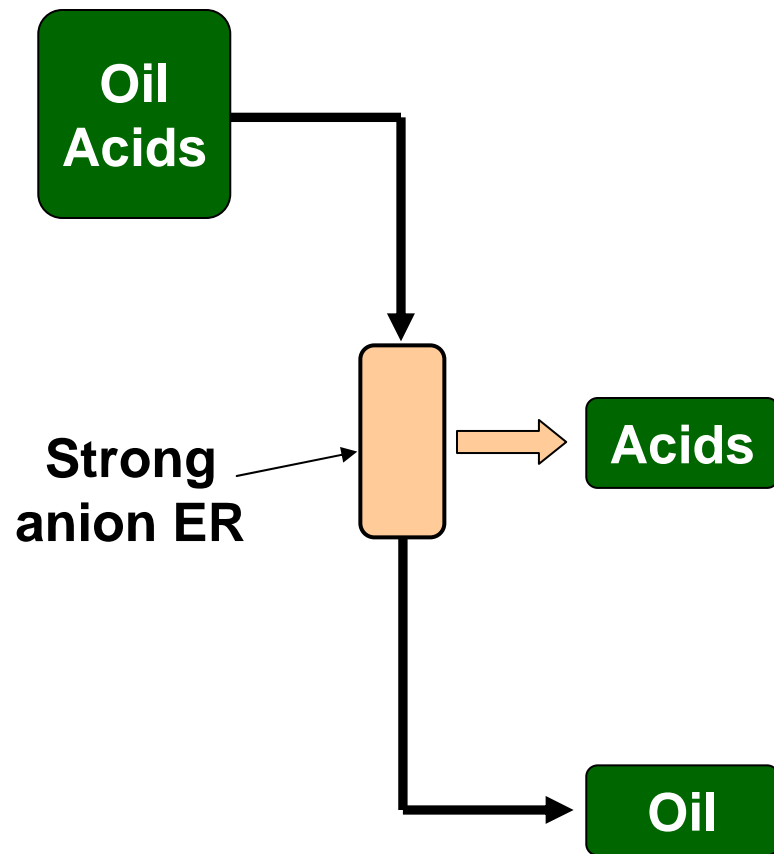


Natural Resources
Canada

Ressources naturelles
Canada



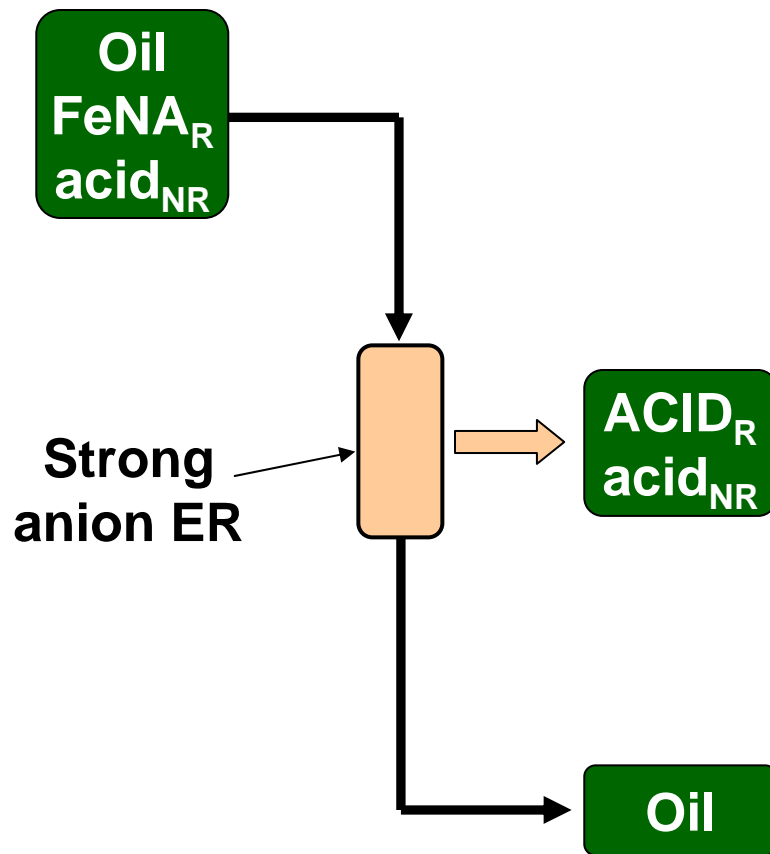
Acid-IER Method (Statoil)



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



Acid-IER Method (Statoil)



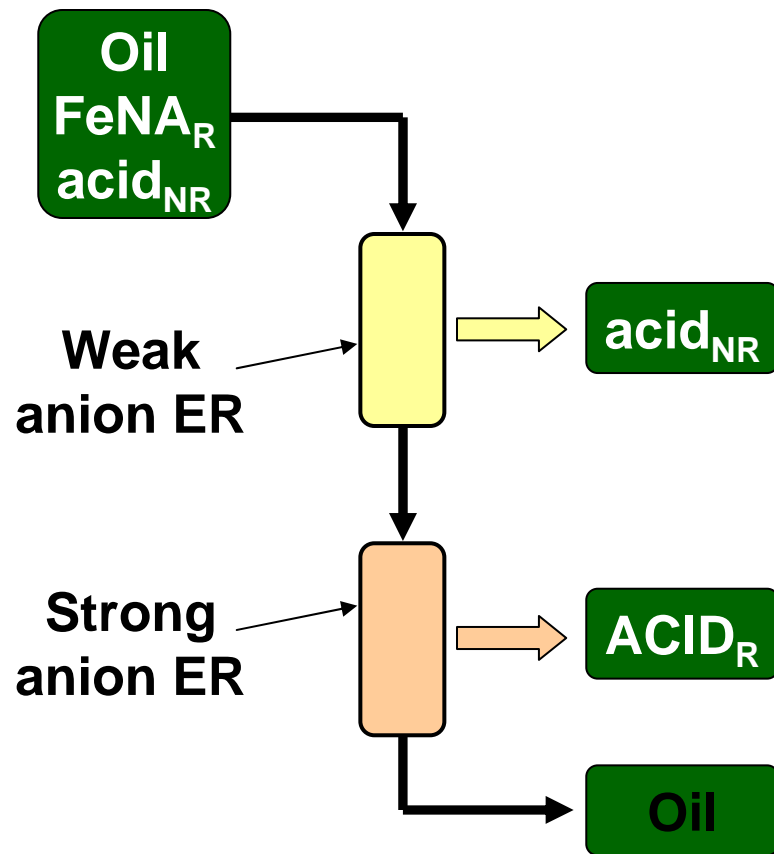
- Selective Isolation of Carboxylic Acids from Crude Oils using QAE Sephadex A-25 IER (Strong Anion ER)
- ER absorbs not only Acids but also FeNA



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



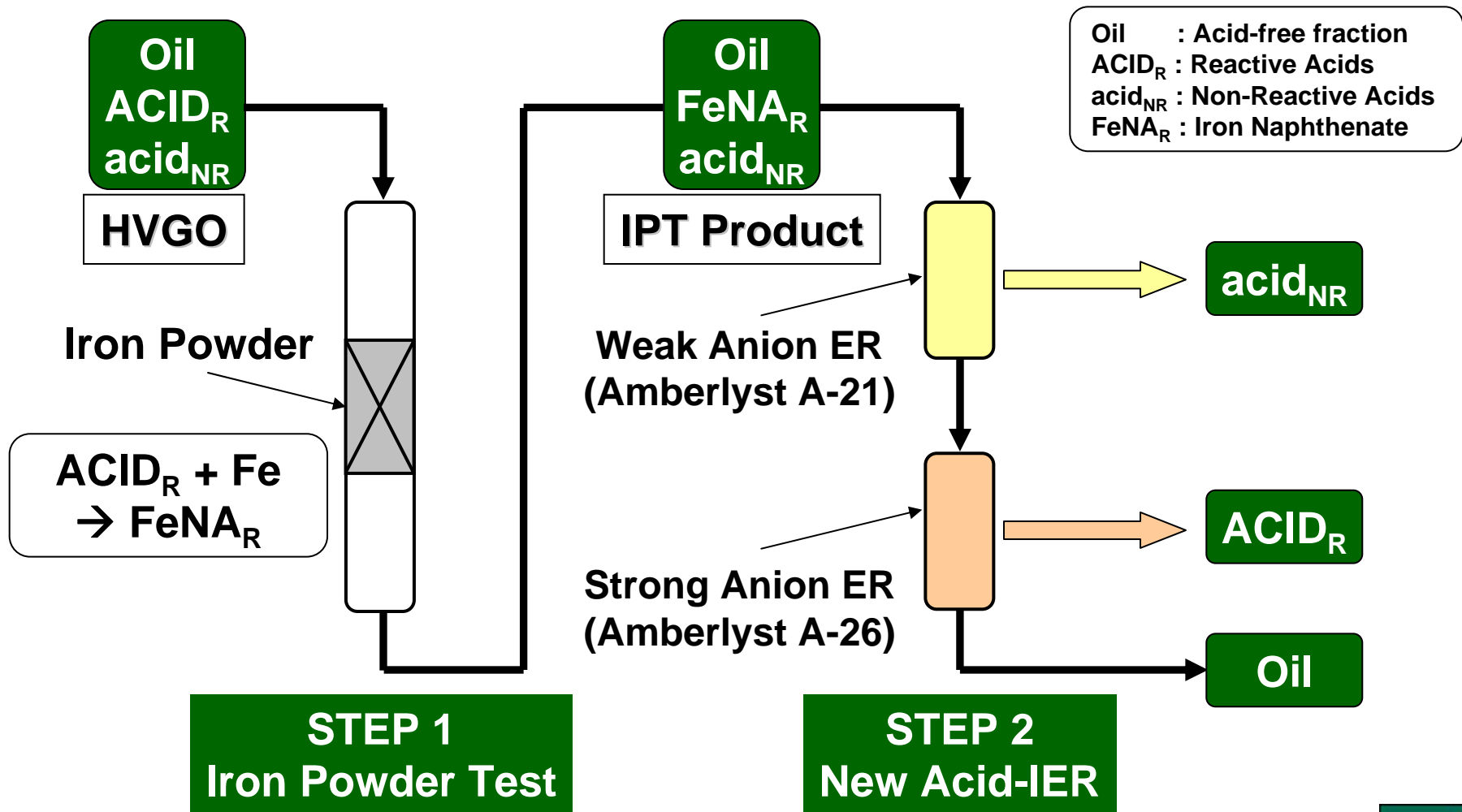
New Acid-IER Method



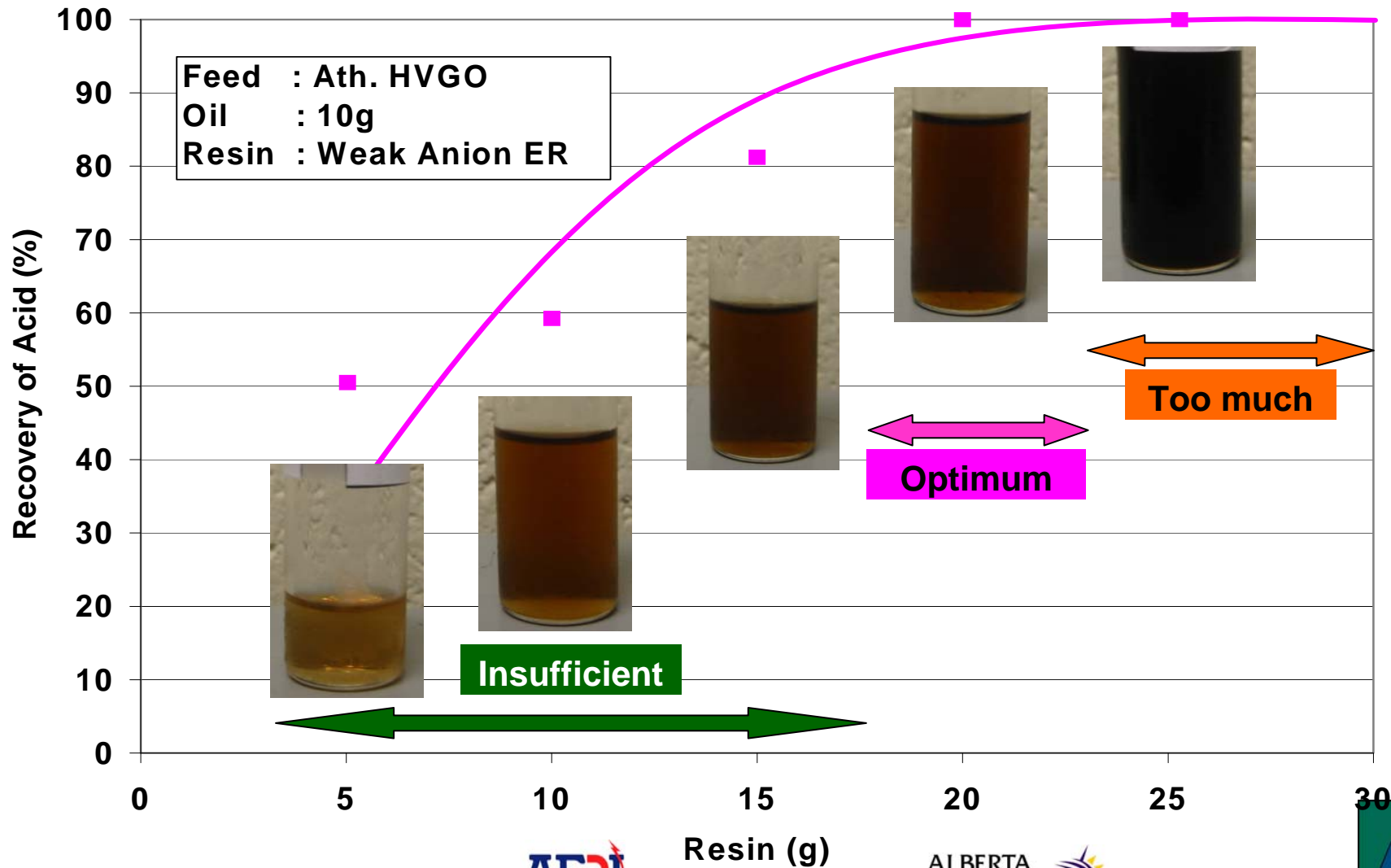
- Selective Isolation of NA and FeNA from IPT product using 2 types of resins
- Weak anion ER isolates only Non-Reactive Acids
- Strong anion ER adsorb FeNAs, and Reactive Acids can be released by formic acids



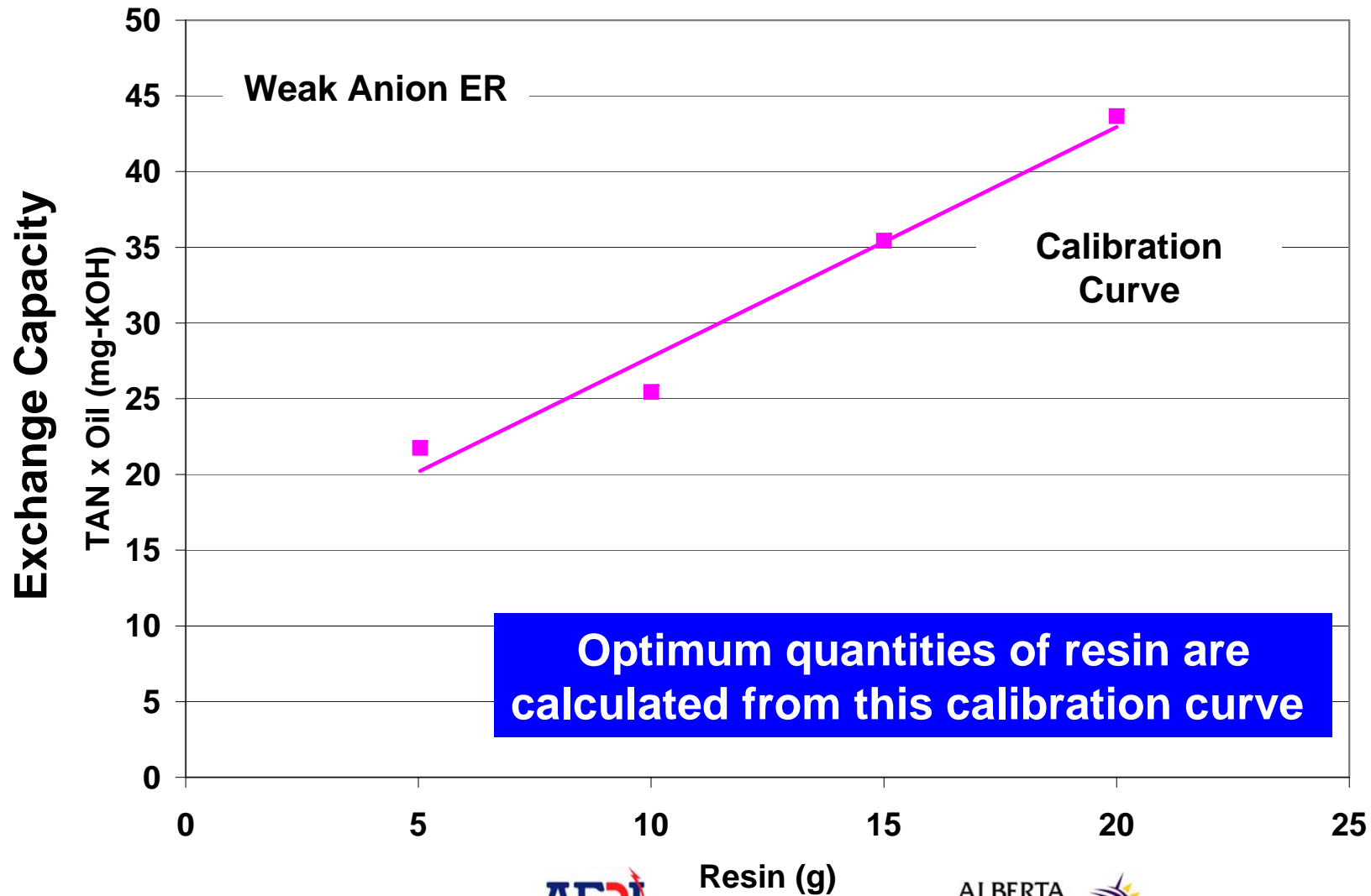
Procedure of Separation



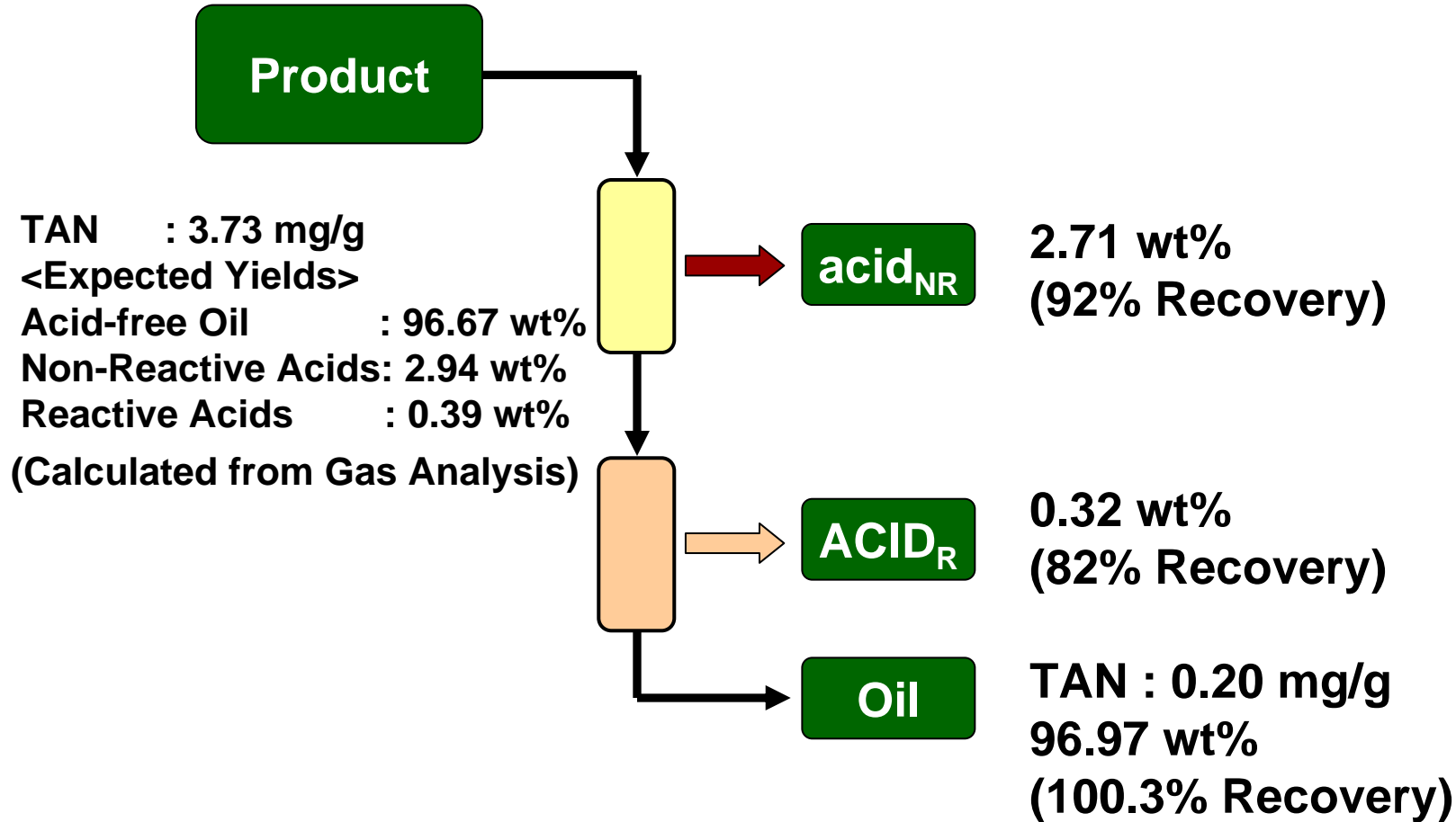
Optimum Quantity of Resin



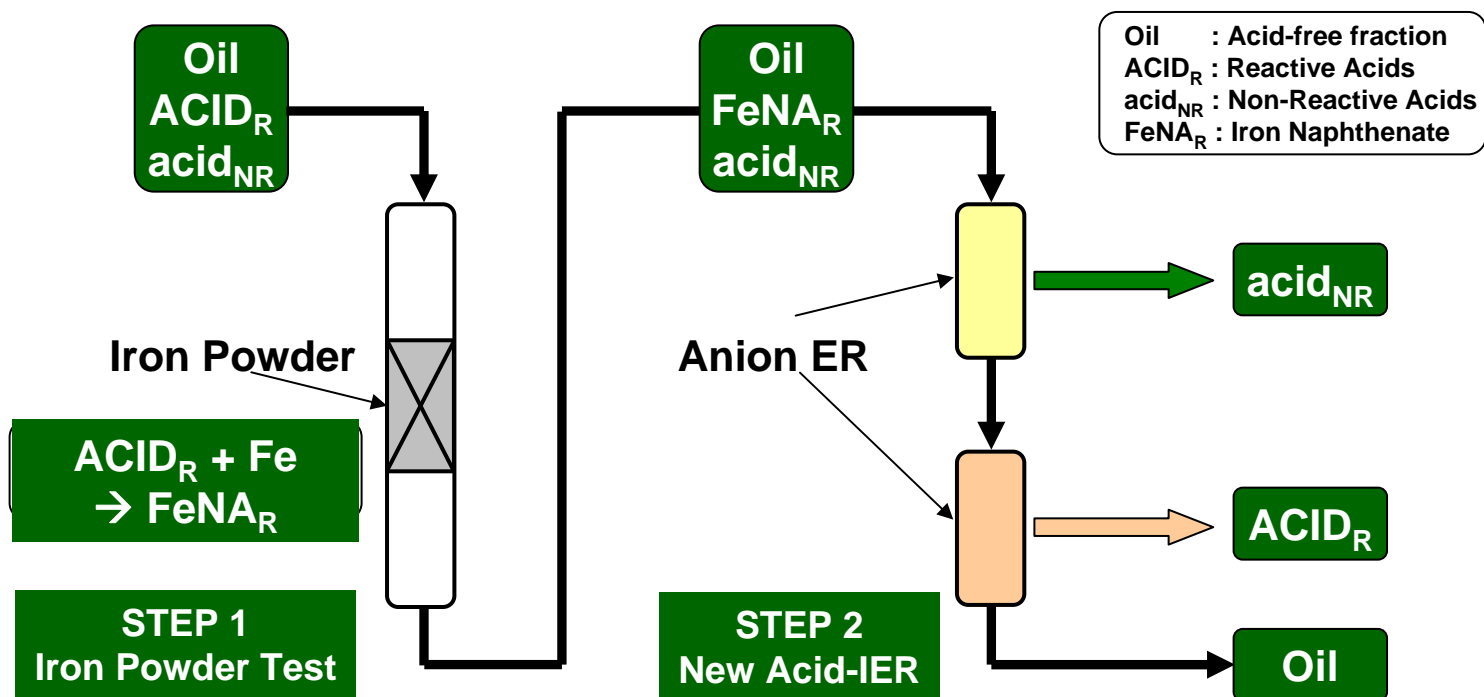
Optimum Quantity of Resin



Results of Acids Separation



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



Natural Resources
Canada

Ressources naturelles
Canada



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]



Natural Resources
Canada

Ressources naturelles
Canada



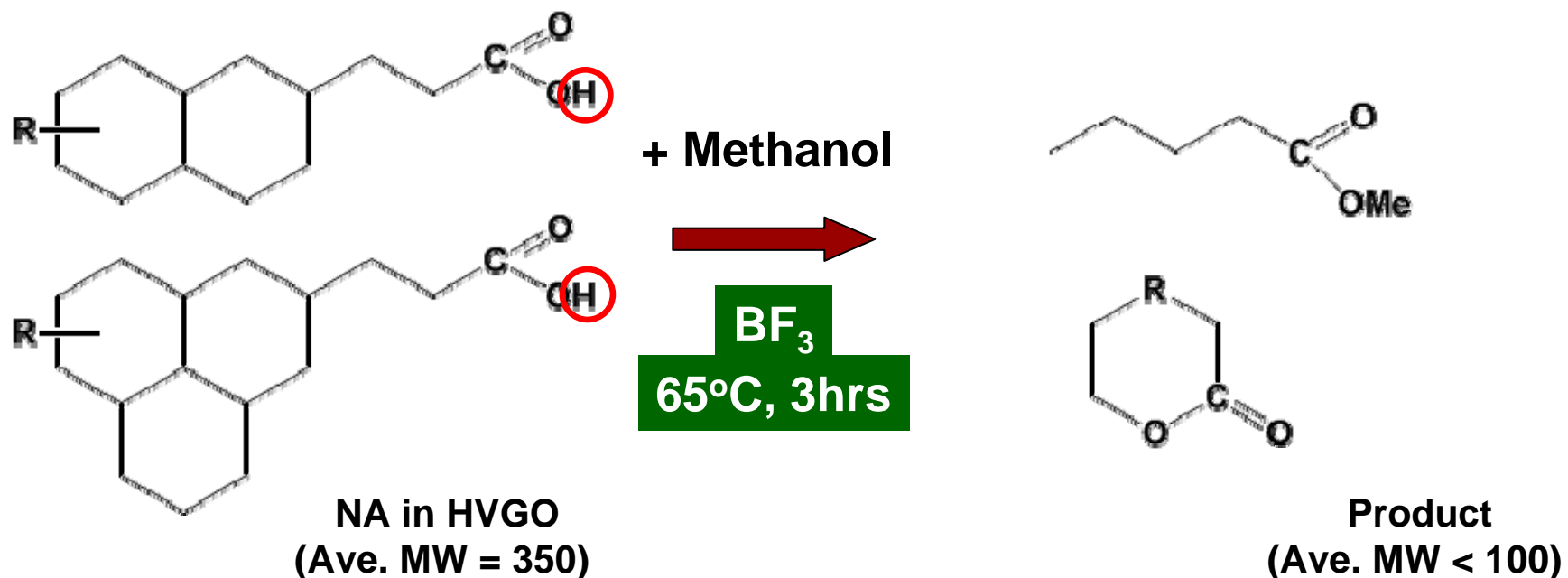
Methylation of NAs

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)]



Methylation of NAs



Chemical bonds were broken
Side reactions occurred

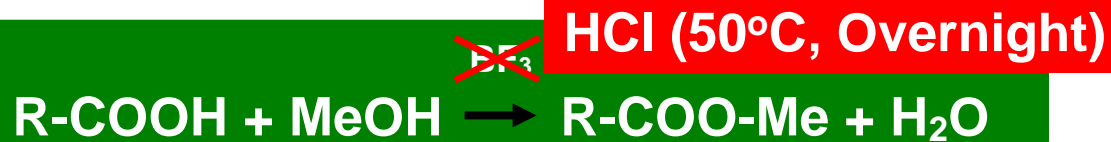
BF_3 is too strong acid



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 [Morrison, W.R. (1964)]



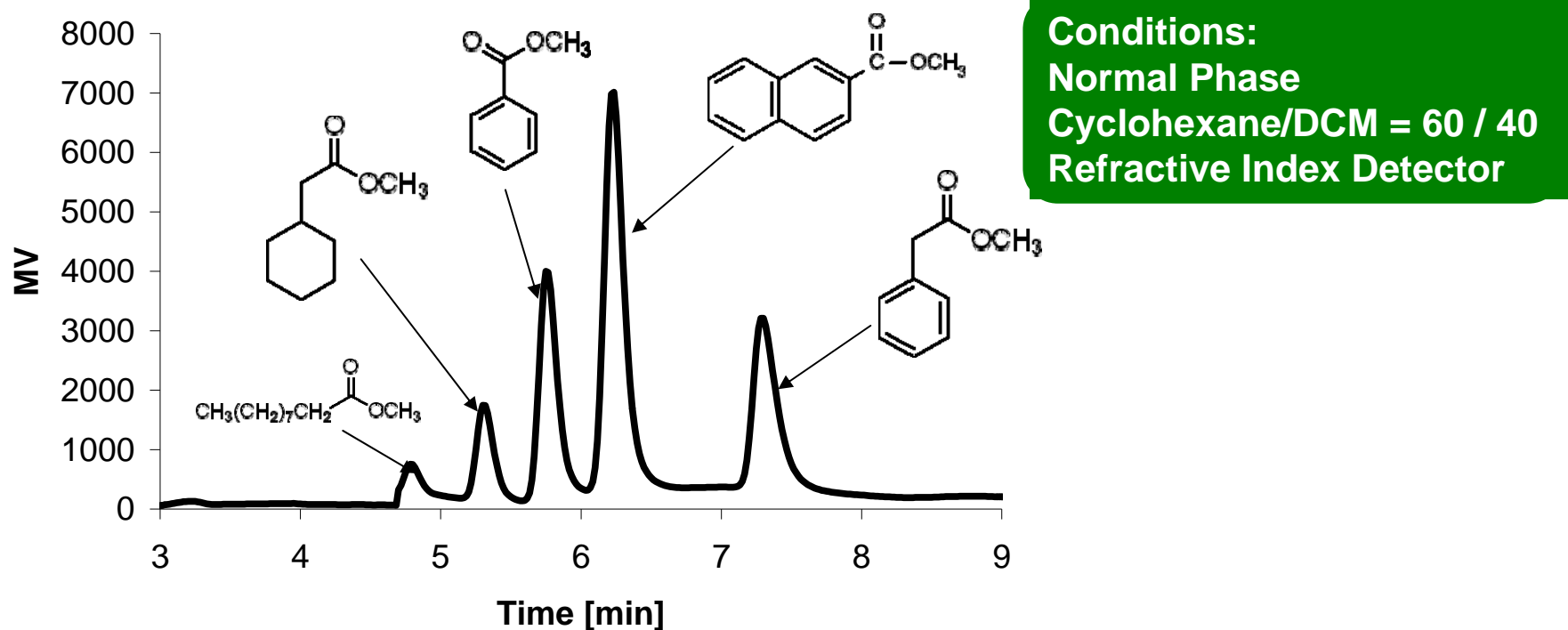
- But BF_3 is so strong Lewis acid catalyst, it broke the structure of NA, or caused side reaction
- Apply an improved methylation method which use HCl as acid catalyst [Christie, W.W. (1993)]

This method may not cause above problems!



Analytical Results (HPLC)

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



The performance of separation was good



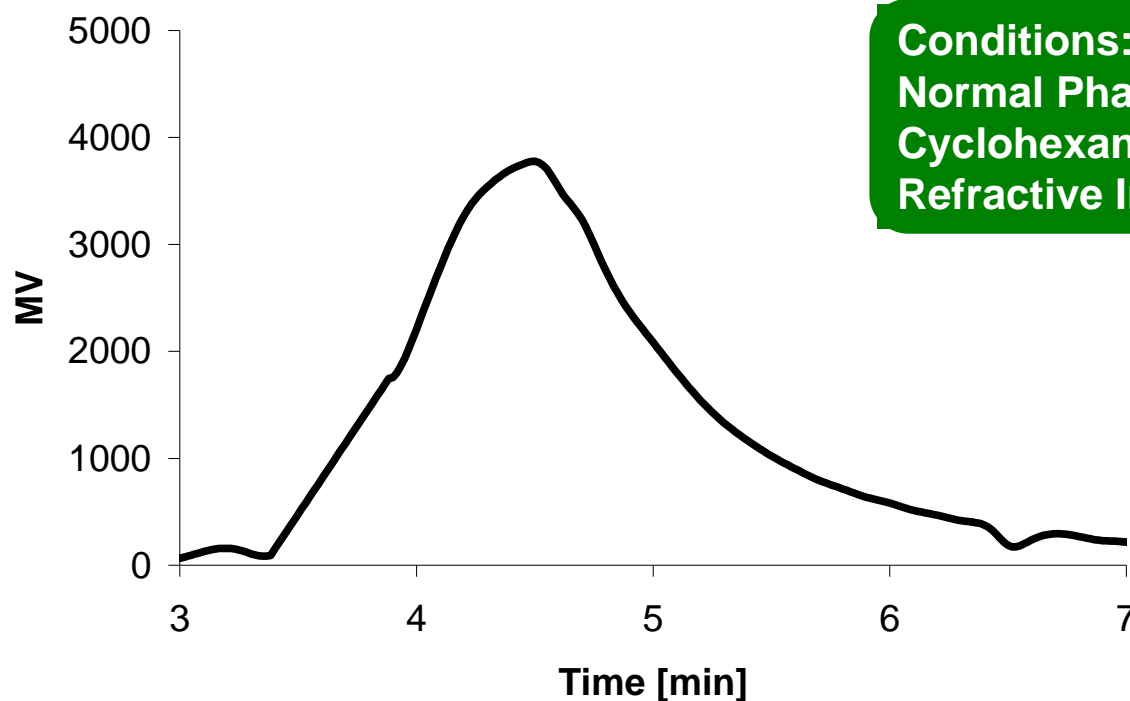
Natural Resources
Canada

Ressources naturelles
Canada



Analytical Results (HPLC)

Methylated NAs in Athabasca HVGO



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



Natural Resources
Canada

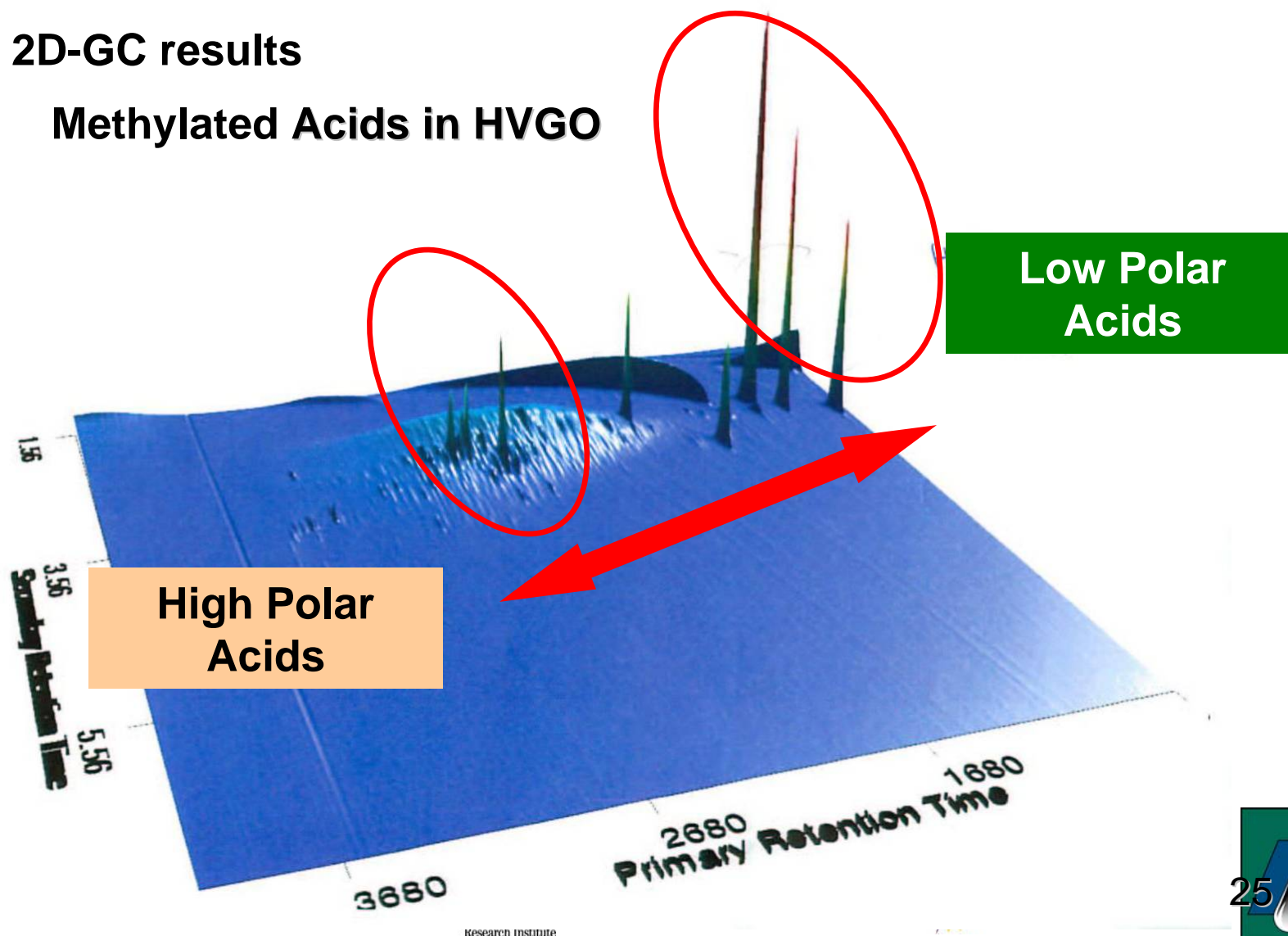
Ressources naturelles
Canada



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**



Natural Resources
Canada

Ressources naturelles
Canada



27