



**EU FT-ICR MS**

## **Sulfur compounds characterization using FT-ICR MS: towards a better comprehension of vacuum gas oils hydrodesulfurization process**

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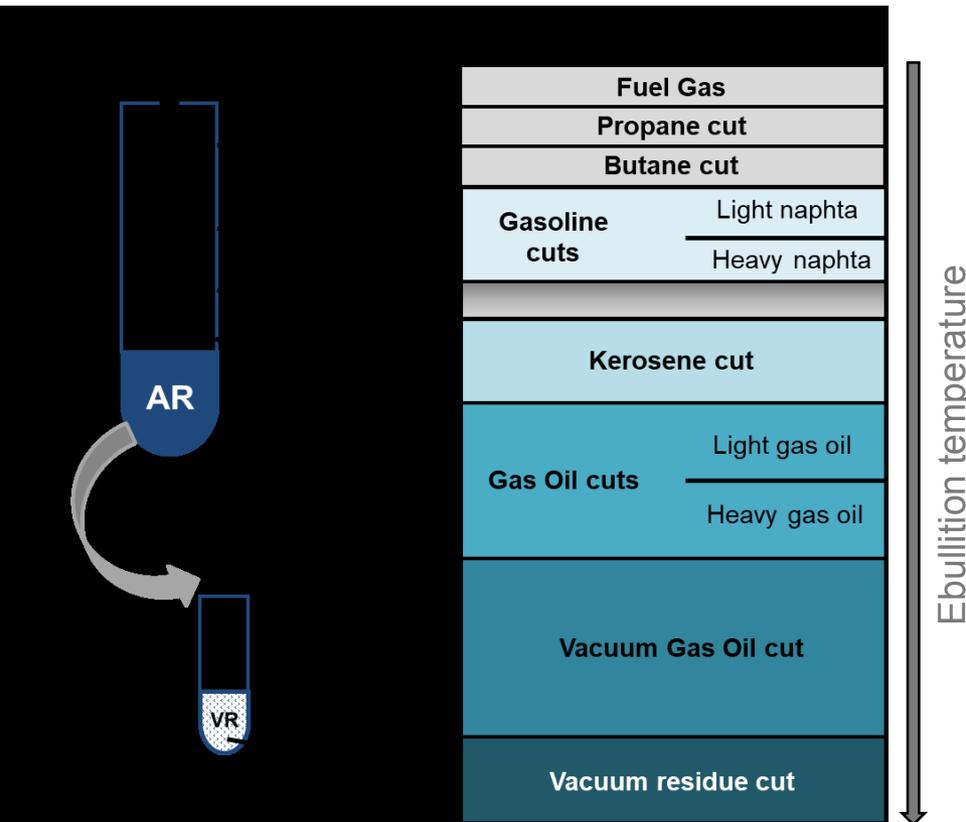
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# PETROLEUM CUTS



Depending on crude oil origin, up to 100% can contain **heavy cuts** that have a lower commercial value than light products

## ❑ How can we valorize these heavy cuts ?

VGO **conversion** into lighter cuts thanks to several **processes** using **catalysts** that might be **deactivated** by heteroatomic compounds<sup>1</sup> (N, O, S...).

## ❑ How can we improve conversion processes ?

Removal of sulfur compounds using **hydrodesulfurization** process prior to conversion processes to **improve conversion efficiency**<sup>2</sup>

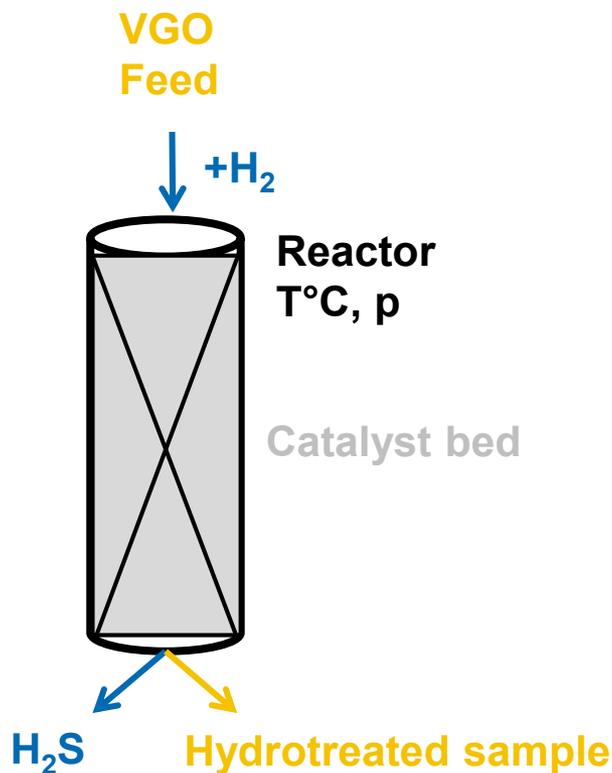


<sup>1</sup> Effects of organic nitrogen compounds on hydrotreating and hydrocracking reactions. Sau, M, *Catalysis Today*, 2005

<sup>2</sup> Hydrodesulfurization Reactivities of Various Sulfur Compounds in Vacuum Gas Oil, Ma, X, . *Ind. Eng. Chem. Res.* 1996

# HYDRODESULFURIZATION PROCESS

Main objectives: **Removing sulfur compounds** from the feed by **mixing the feed with H<sub>2</sub>** into a closed reactor at high T°C and pressure conditions with a **catalyst**



Main parameters to be changed:

- Temperature
- Pressure
- Catalyst: improve reaction efficiency
- H<sub>2</sub>/HC ratio: ratio between H<sub>2</sub> introduced and HC content
- LHSV (liquid hourly space velocity): volumic ratio between the quantity of feed and catalyst



HDS efficiency evaluated over the **total S content**  
Not enough to explain **reactivity behaviors**  
Need to monitor HDS efficiency at the **molecular level**



**Ultra-high resolution mass spectrometry: FT-ICR MS**



# SAMPLES CHARACTERISTICS

One feedstock and 6 hydrotreated samples produced using:

- Two different **catalysts**: A and B → evaluation of catalyst efficiency
- Three different **temperatures**: 1 < 2 < 3 → evaluation of temperature impact

Sample	S content (ppm)	Catalyst	LHSV (- <sup>1</sup> )	Pressure (bars)	Temperature (°C)	H <sub>2</sub> /HC (NL/L)
<b>Feed</b>	18921	-	-	-	-	-
<b>A-1</b>	1251	A	1	a	1	a
<b>A-2</b>	693	A	1	a	2	a
<b>A-3</b>	334	A	1	a	3	a
<b>B-1</b>	949	B	1	a	1	a
<b>B-2</b>	483	B	1	a	2	a
<b>B-3</b>	200	B	1	a	3	a

## FT-ICR MS sample preparation

- The feed and the hydrotreated samples were first solubilized in Toluene to 1% w/w
- The samples were diluted to 0.05% v/v in a 90%-10% Toluene-Methanol
- 6 technical replicates were prepared and analyzed in the same experimental conditions

# INSTRUMENTAL SET-UP

## FT-ICR MS

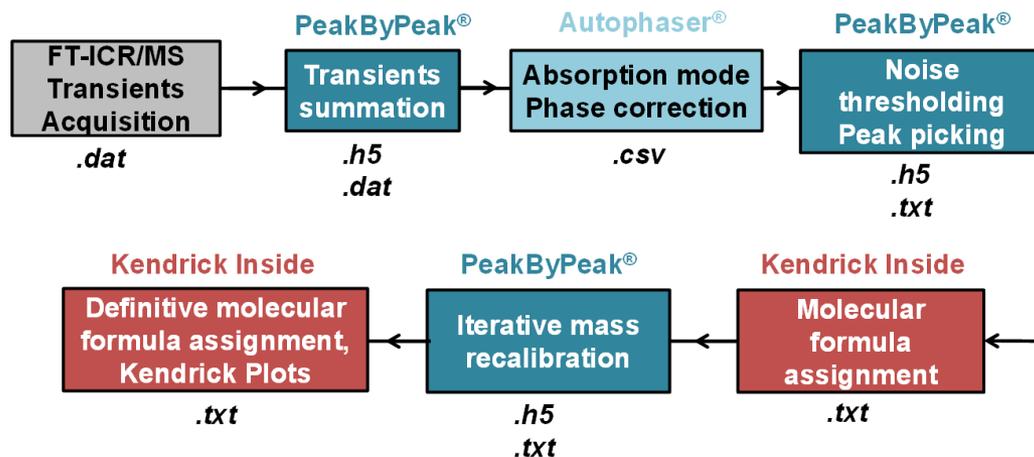


### Thermo LTQ FT Ultra 7T

- APPI ion source operated in (+) mode
- $m/z$  98 to 1000
- $R=200,000$  at  $m/z$  500
- 70 scans, 4  $\mu$ -scans, 1.6s transient
- Focus on S1 class ( $M^{+}$ )

## Data processing

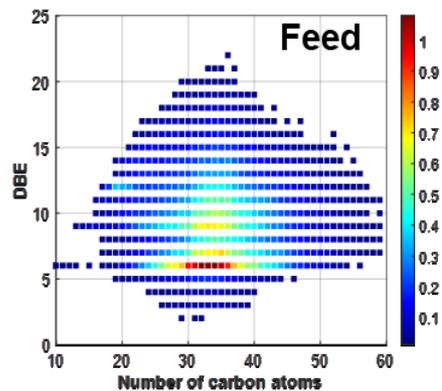
Spectroswiss



- Increased resolution of about **2.5%** for VGO samples up to **700,000**
- Mass error below **800 ppb**
- Pseudo-concentration: Relative intensity  $\times$  Sulfur content (ppm)

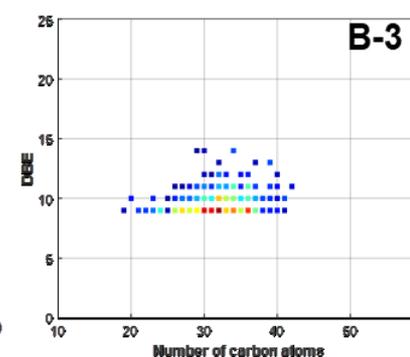
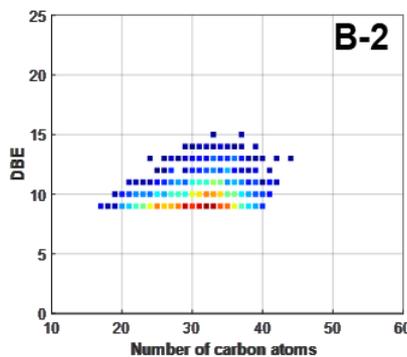
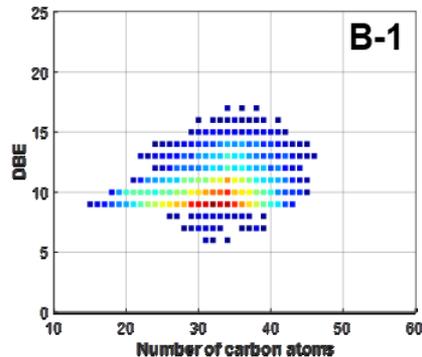
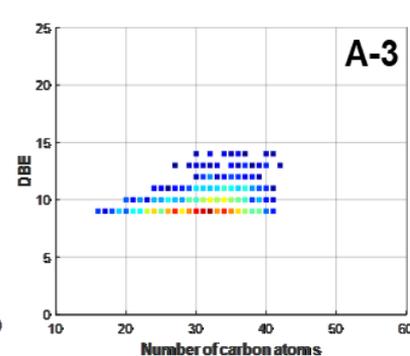
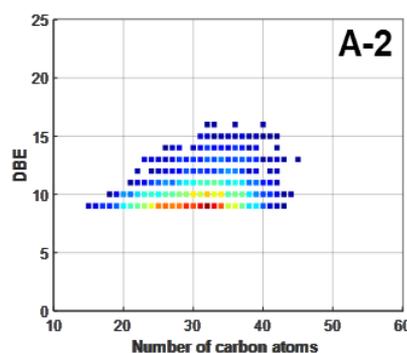
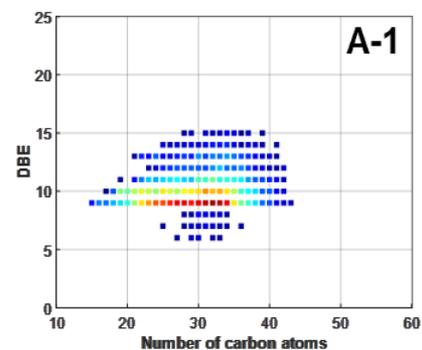
# COMPARISON OF ALL SAMPLES

- DBE=f(#C) plots: Fast evaluation of **temperature** and **catalyst** effects on the **aromaticity** and **alkylation** levels of the sulfur compounds



DBE: Number of rings +  
Double bonds

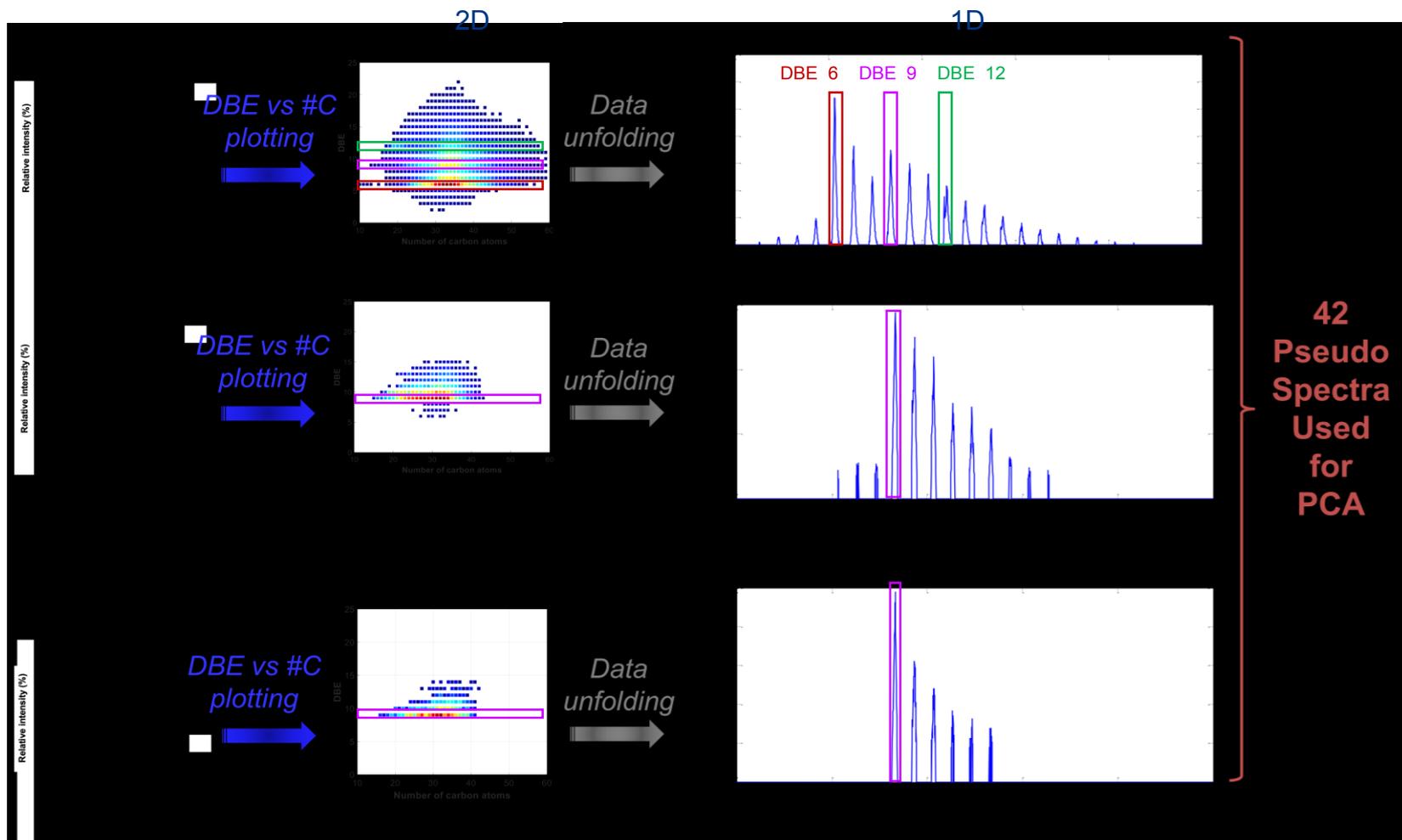
## Temperature effect



Catalyst effect

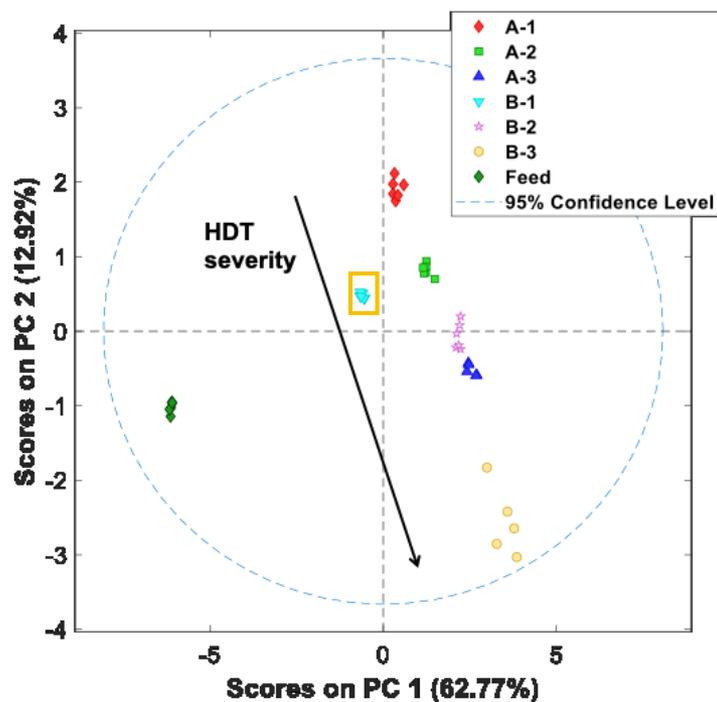
# COMPARISON OF ALL SAMPLES

- FT-ICR MS data processing for **chemometrics**: unfolding on the DBE=f(#C)

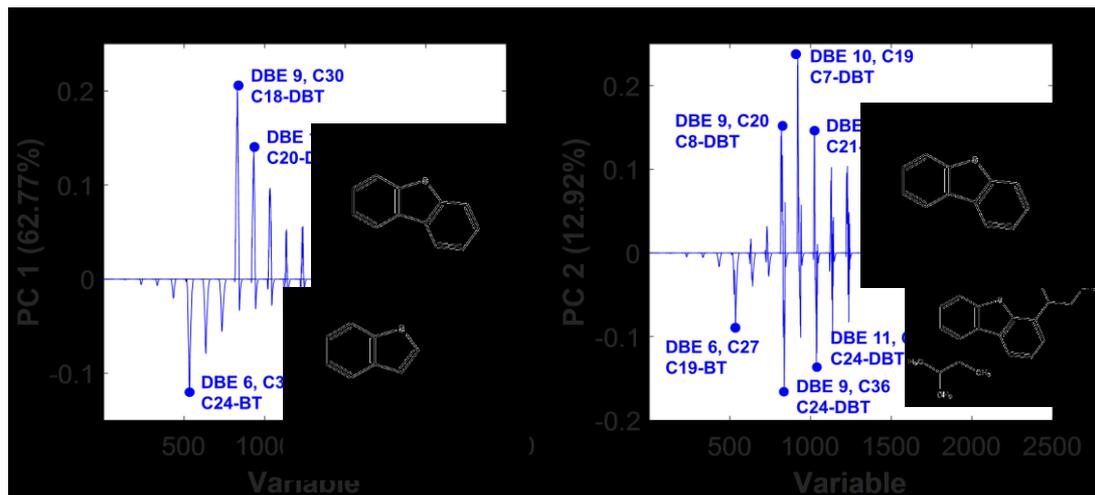


# COMPARISON OF ALL SAMPLES

Score plot



Loadings plots



- ❑ Separation of the **feed from the effluents** on PC1: linked to BT and DBT contents
- ❑ Separation of the effluents depending on the **HDT severity** on PC2: more alkylated species at high HDS efficiency
- ❑ **Atypical** projection for sample B-1 compared to A-1 ?

# COMPARISON OF ALL SAMPLES

## Low temperature case: A-1 and B-1

Activity of catalyst B is separated into **4 phases**:

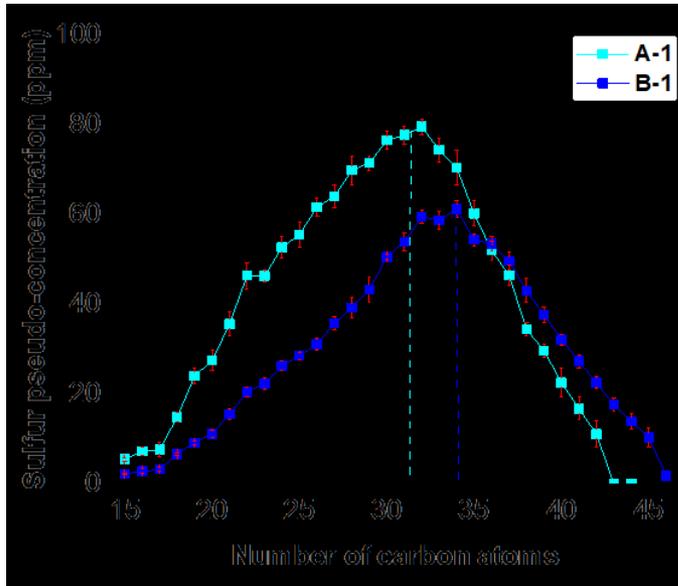
- Phase 1: both catalysts A and B have similar activity
- Phase 2: catalyst B is by far more efficient than catalyst A
- Phase 3: both catalysts A and B have similar activity
- Phase 4: catalyst A is slightly more efficient than catalyst B

- ⇒ Catalyst B is more selective towards DBT compounds (DBE 9-10-11)
- ⇒ Catalyst A is a little bit more selective towards very aromatic compounds (DBE >14)

Two possible hydrodesulfurization mechanisms ?

# COMPARISON OF ALL SAMPLES

DBE 9 case:



- ❑ DBT in sample A-1 are **less alkylated** than DBT in sample A-2
- ❑ Catalyst A: **change in alkylation level** compared to feed → catalyst A more efficient to remove very alkylated species
- ❑ Catalyst B: **no change in alkylation level** compared to feed → catalyst B more efficient to remove less alkylated species

Two possible hydrodesulfurization mechanisms ?

# CONCLUSIONS AND PERSPECTIVES

## Global comparison

- FT-ICR MS is a very powerful tool to **monitor the hydrodesulfurization mechanism**
- The effects of **temperature** and **catalyst** over the global HDS efficiency were studied
- The main **refractory** compounds were identified: **dibenzothiophenes** family

## Aromaticity

- The DBT with a **DBE equal to 9** were shown to be the **most refractory** compounds
- At the lowest HDS severity, both catalysts were shown to present **different selectivity**

## Alkylation

- The carbon atoms distribution of the DBE 9 compounds was relatively large (**C15-C42**)
- The hydrogenation of poorly alkylated species was **slower at low temperature**
- At the lowest HDS severity, both catalysts were shown to present **different selectivity**



**Perspectives: ion mobility analysis to identify the most refractory isomers, DBT ?**

*Thank  
you!*



- ❑ **PhD supervisors:** Alexandra Berlioz-Barbier, Florian Albrieux, Luis Pereira de Oliveira, Marion Lacoue-Nègre, Jean-François Joly, Ludovic Duponchel and Jérémie Ponthus
- ❑ **IFPEN MS team**
- ❑ **Brice Bouyssièrè**
- ❑ **EU FT-ICR MS committee**

**Thank you for your attention !**

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**EU FT-ICR MS**



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