Recent Advances in Heavy Oil Processing Technology

*Presented by: **Dr. Opinder K. Bhan***

CRITERION CATALYSTS & TECHNOLOGIES

Presentation Overview

- Heavy Oil Upgrading Challenges
- Making the Right Chemistry Happen in your Residue Upgrading Unit
- Composition & Characterisation of Heavy Oil
- New Innovative Methods for Characterising Heavy Oils
- Conclusions & Takeaway Message

Heavy Oil Upgrading Challenges

Impact on Fixed Bed and Ebullated Bed Residue Upgrading Units

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Challenge #1: Make more cleaner transportation fuels by higher conversion of heavier Residue and with lower emissions of greenhouse gases

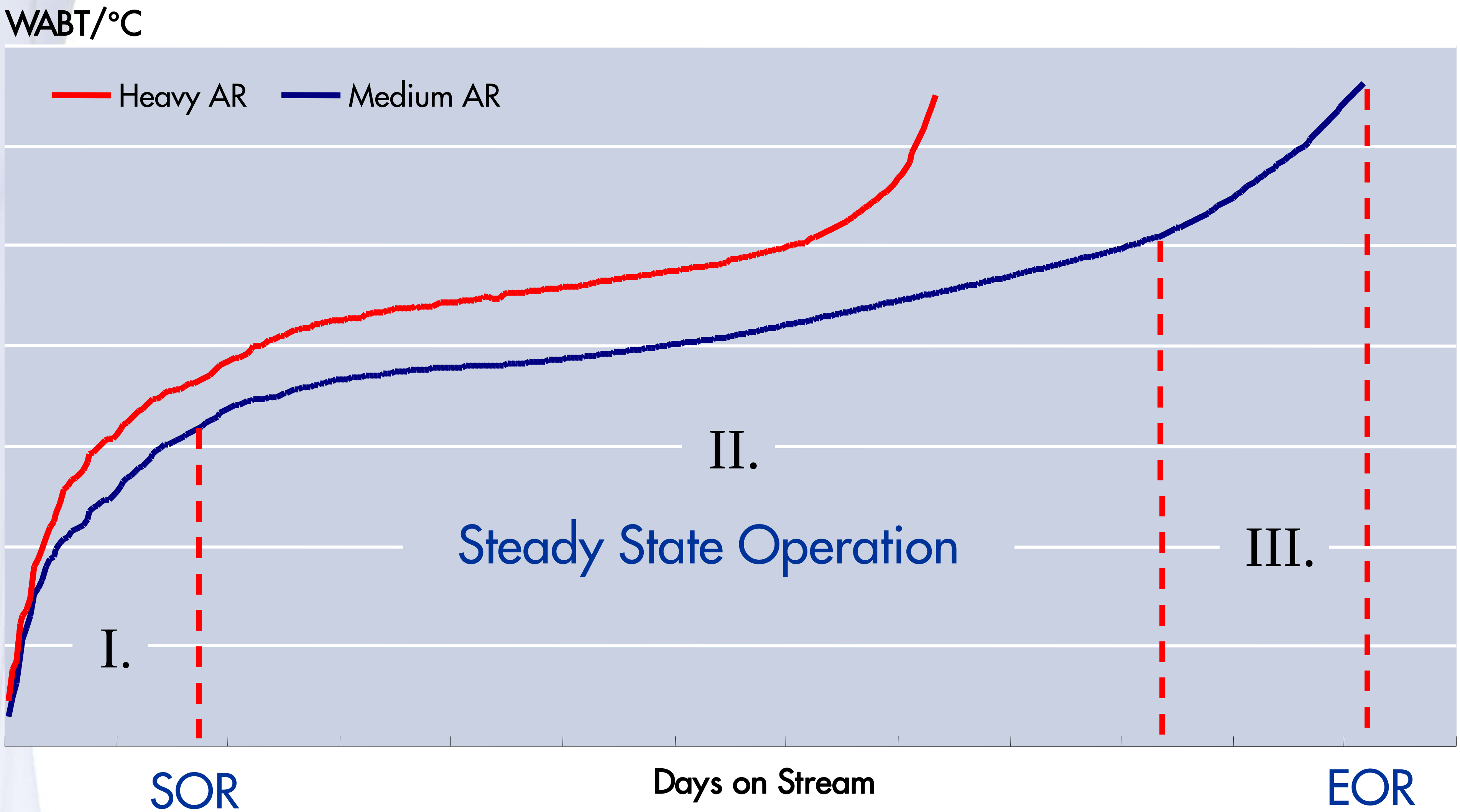
3 Hard Truths

1. Increasing demand for Energy!

2. Days of Easy Oil are over!

3. CO_2 constrained world is here!

Challenge #2: Balance conversion, deactivation rate, cycle-length, (un)planned shut-downs, turnaround time and schedule, product quality, blending economics, etc.

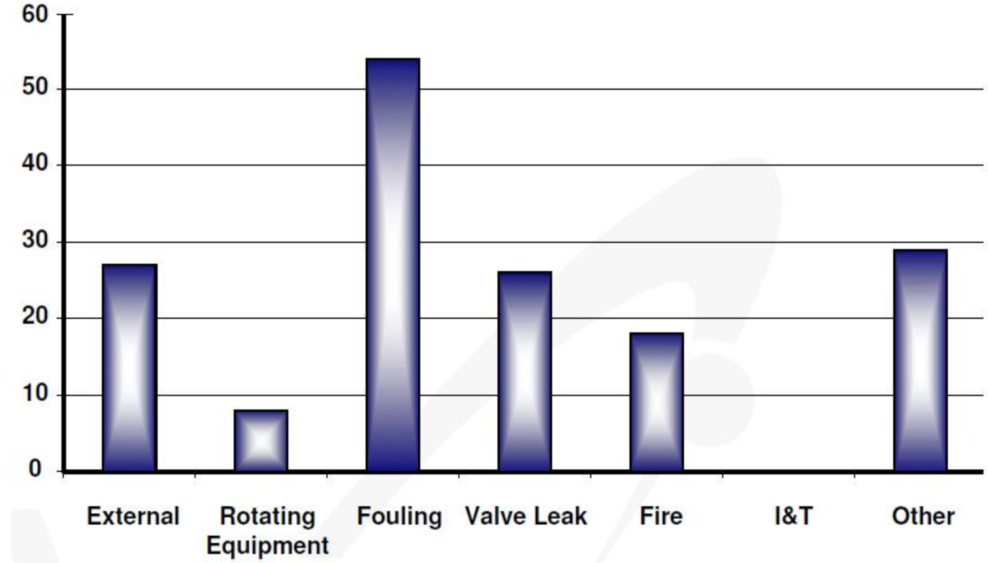


I. *Fast initial coke laydown*

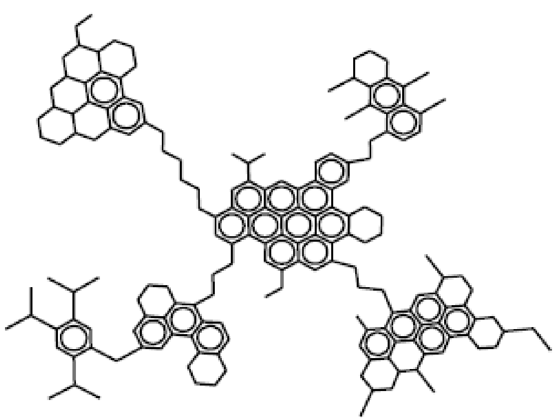
II. *Equilibrium-based deactivation*

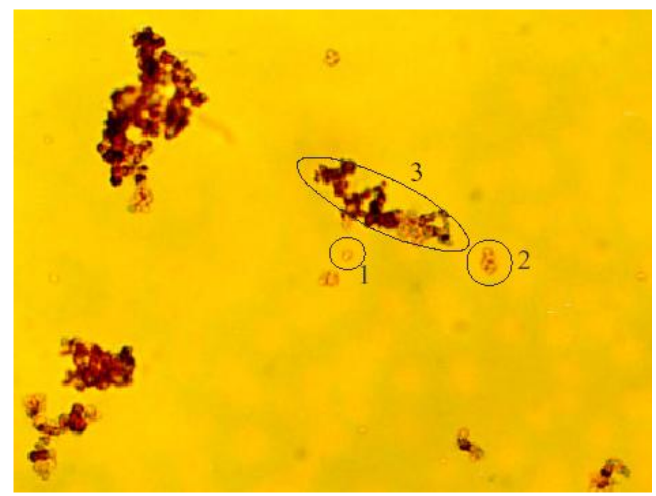
III. *Coke+Metals deactivation*

Challenge #3: Maintain "operability" in Residue Upgrading while higher conversion of heavier oil brings increased fouling of downstream hardware and products



Fouling is the main cause for downtime

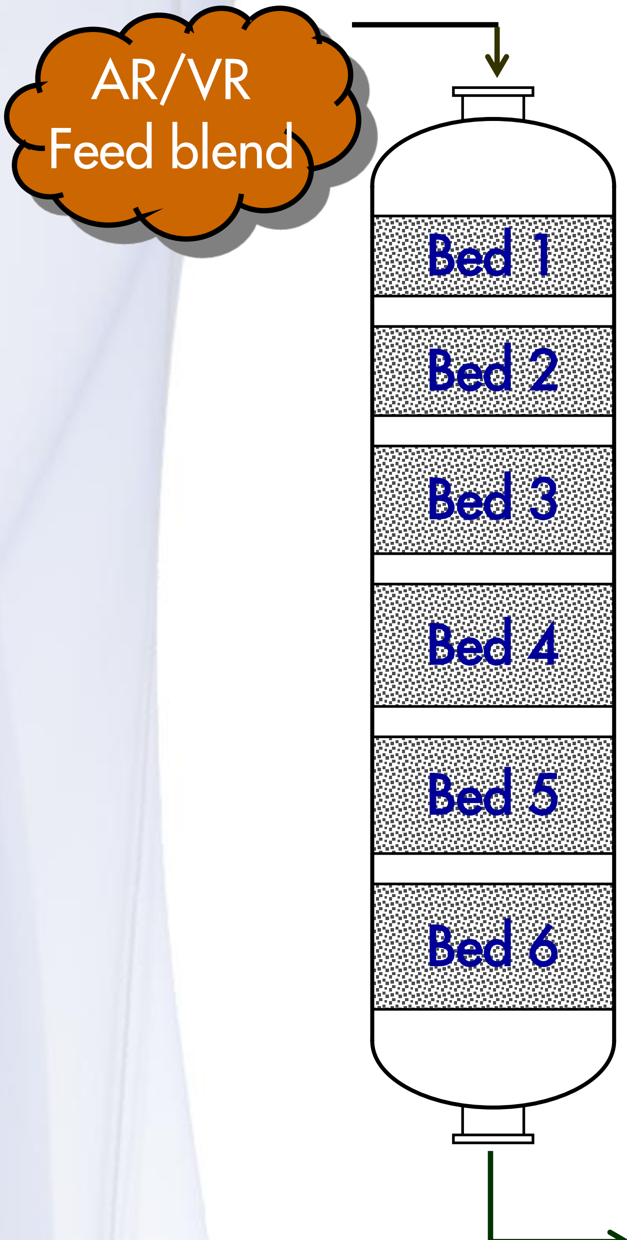




Left photo taken from the Axens-NA presentation: "Process Options available to EB Hydrocrackers for controlling Sediment & Stability," given at the Criterion 2006 EB Residue Upgrading Workshop, Mexico, November 2006

Figure taken from Axens presentation:"H-Oil$_{RC}$ Process : Mitigating Fouling through Design and Understanding" given at Criterion EB Users Workshop, Kananaskis, Canada, June 2008

Customising catalysts for heavier oil processing in Fixed Bed Resid (ARDS/RDS/VRDS) Units

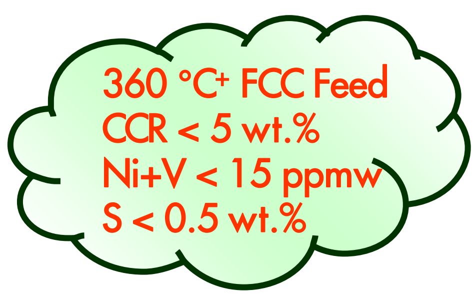


Chemistry *(HDM/HDS/HDCCR/HDAsp ..)*

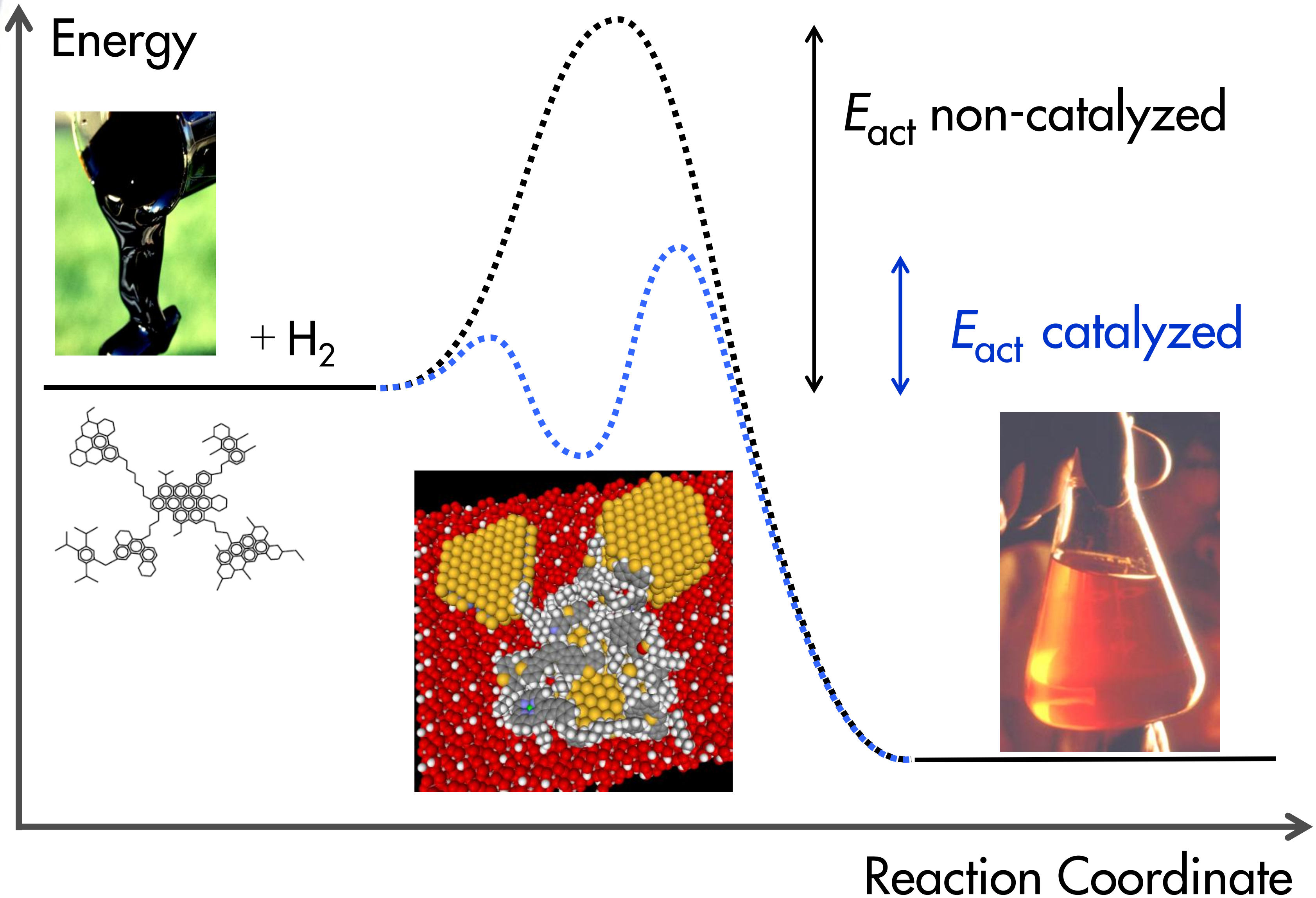
Composition (AR/VR *Quality* (SARA)/*% in blend)*

Conditions *(Unit operation & limitations)*

Catalyst (Activity, Stability, Shape & Selectivity
Bottoms H_2 Selectivity of active sites to help keep Asphaltenes in solution)

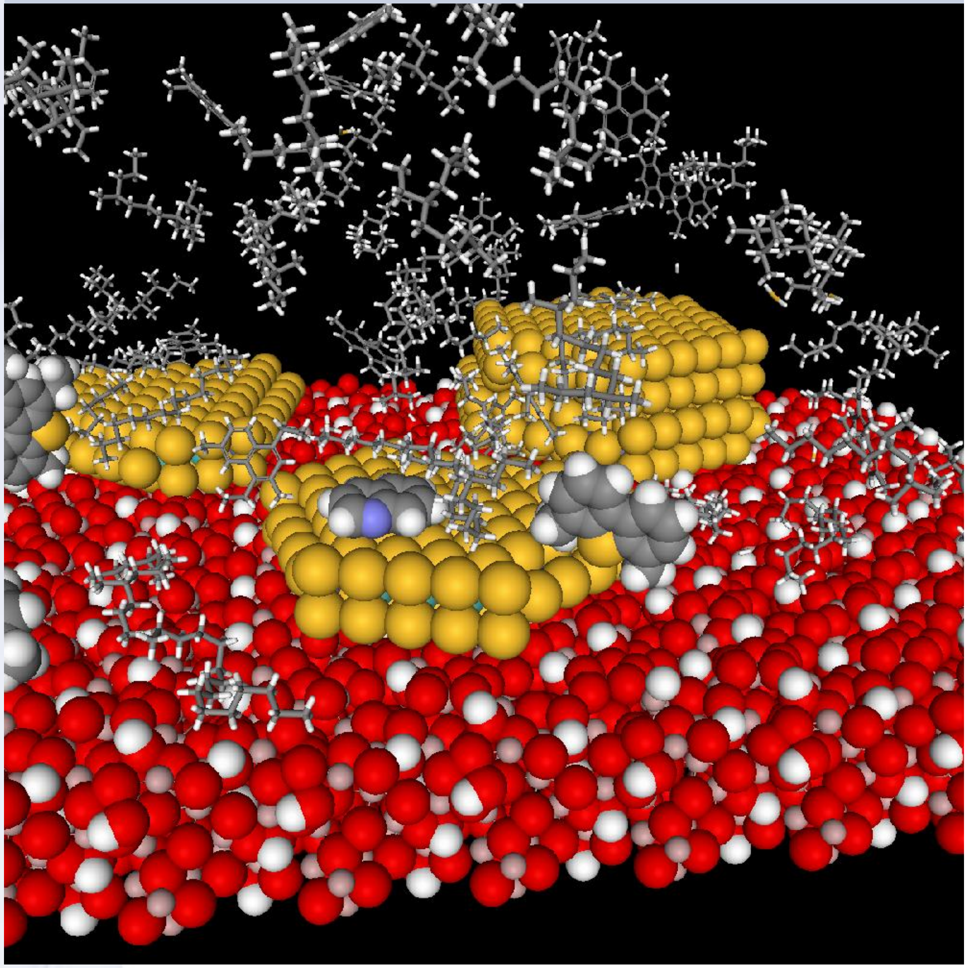


Customised Catalyst – “Bringing together” of Heavier Oil feedstock & Residue Upgrading Process

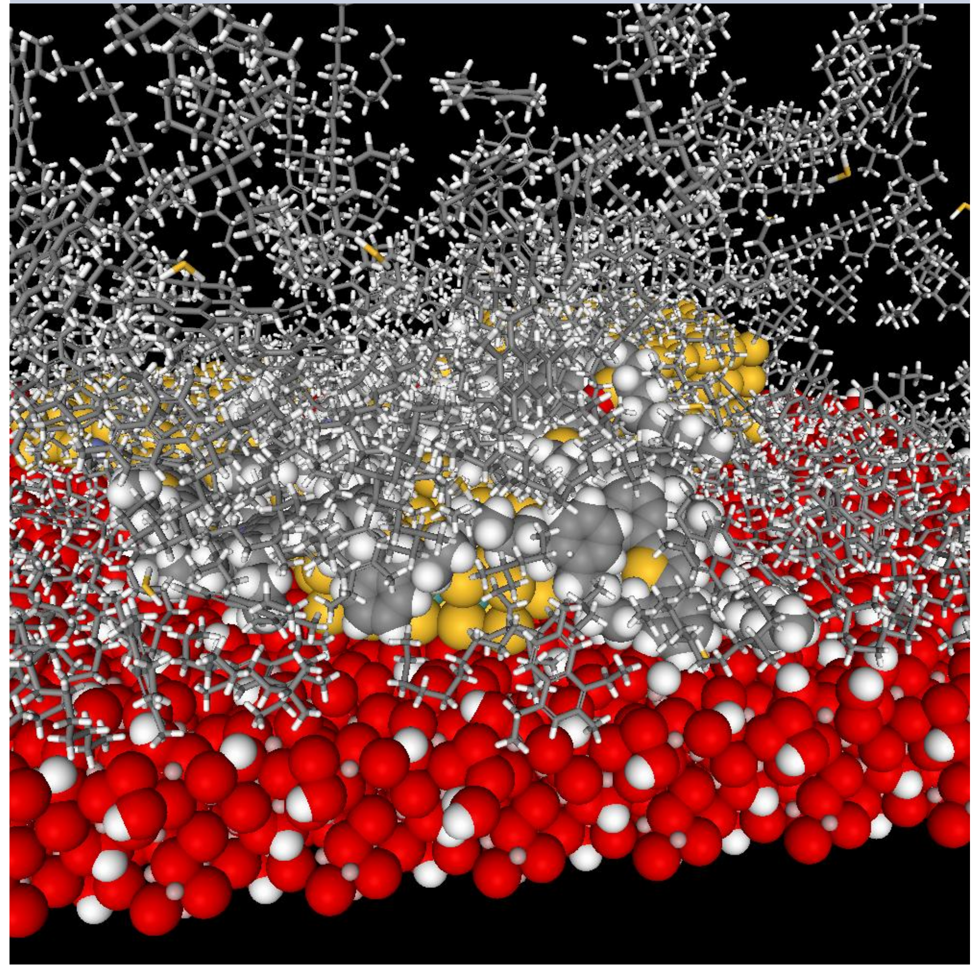


The More Complex Chemistry of Heavy Oil Upgrading compared to Ultra Low Sulfur Diesel

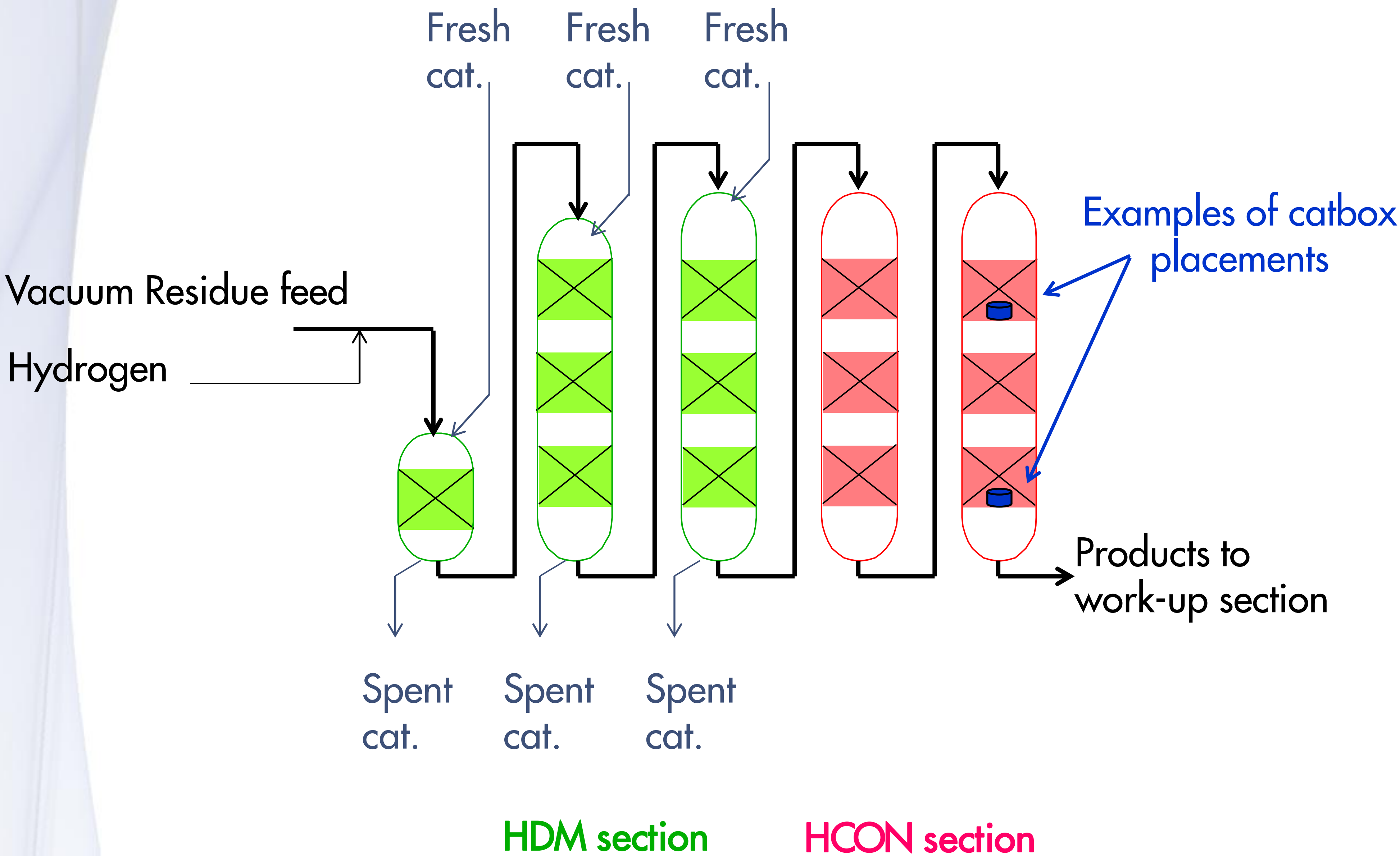
Catalyst surface processing Diesel



Same surface processing Atm. Resid

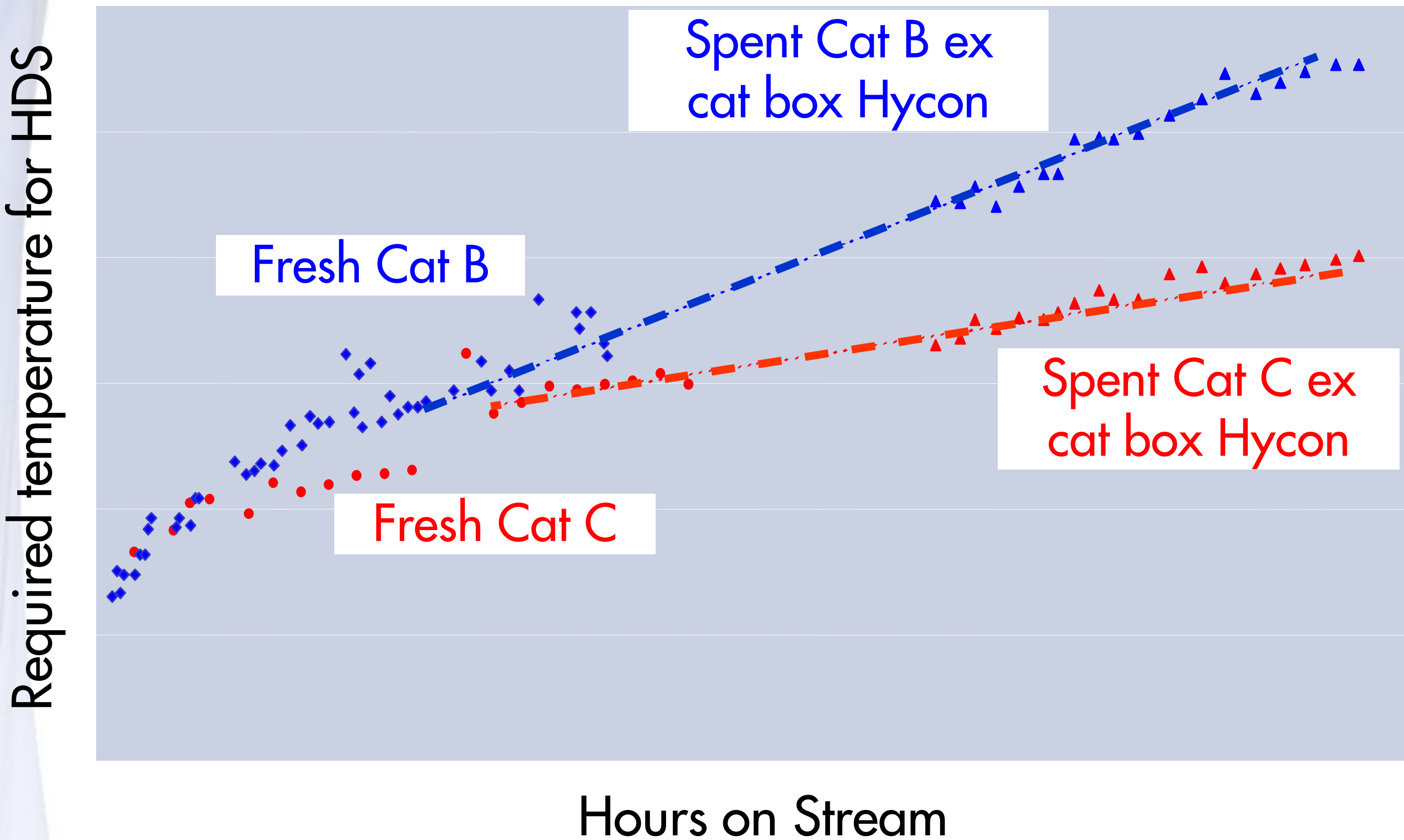


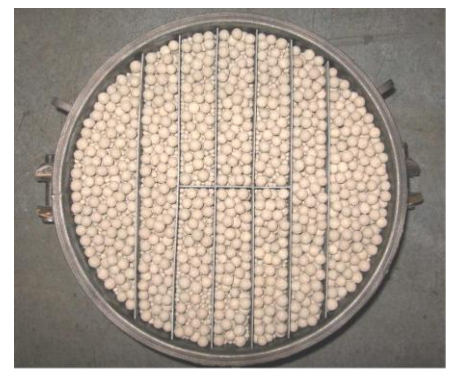
Overview of the Shell Pernis Hycon unit reactor section



EOR Catalyst Stability performance advantage of customised catalyst (Catalyst C) measured through using catboxes loaded in commercial unit

Catalyst B not suitable for a 22 month cycle





Ebullated Bed Operators adjust severity for various feeds to maintain low sediment/fouling rates and a stable operation

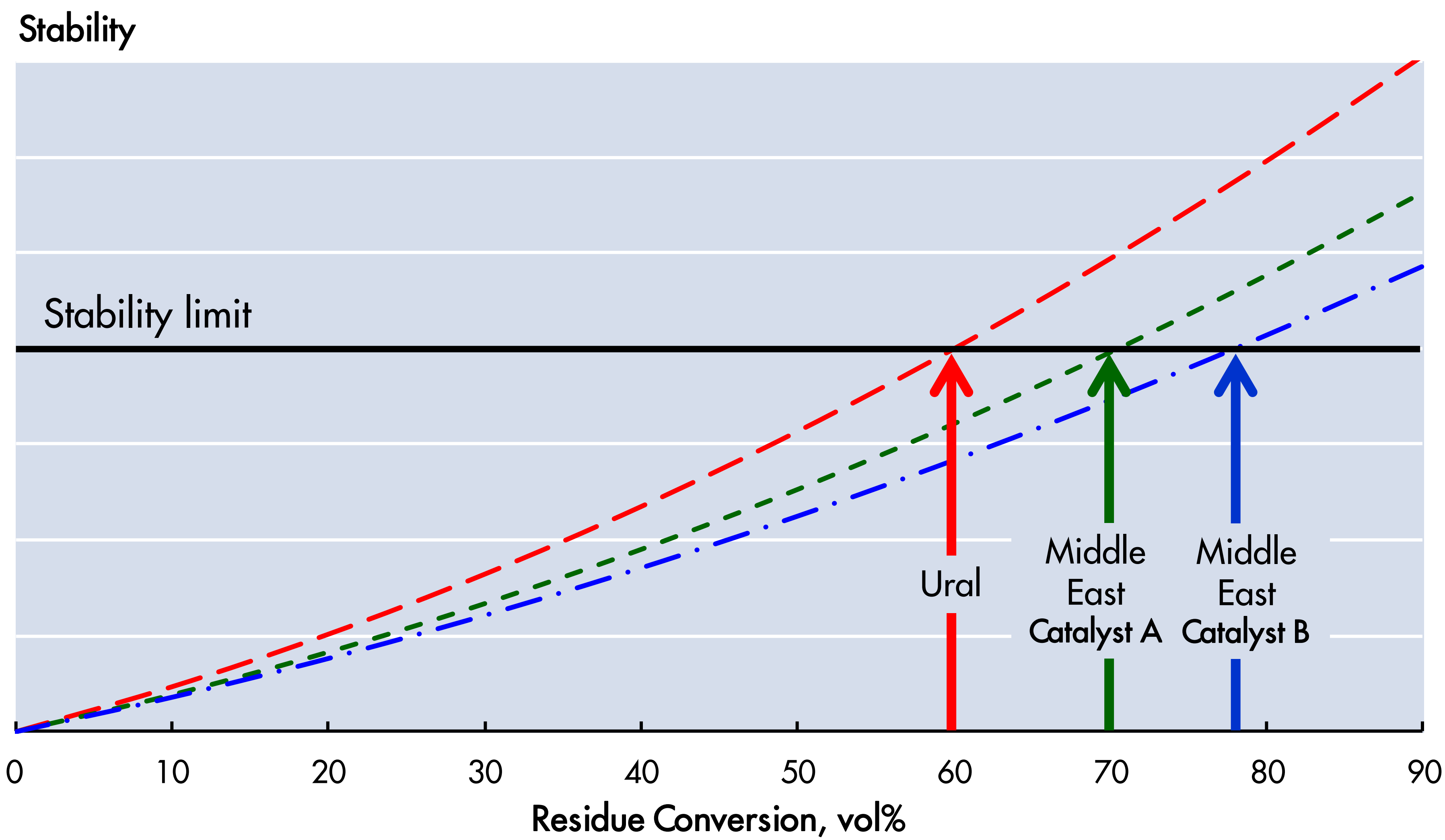


Figure courtesy of AXENS N.A.

Characterising Heavy Oil is no simple task because of Asphaltenes

- Heavy Oil consists of ~10^6 molecules held together in a SARA matrix
- The relative distribution of the SARA matrix species varies widely with crude type
- Asphaltenes are the most complex & least characterised of all the heavy oil macromolecules given their tendency to self-associate & flocculate during reaction
- In Resid upgrading operation the delicate solute *(asphaltene)* / solvent *(aromatic oil)* SARA compatibility balance has to be maintained to avoid sediment-induced fouling

```
      s   s   s
   s   a   a   a   s
 s  a  R R R  a  s
s  a  R A A R  a  s
s  a  R A A R  a  s
 s  a  R R R  a  s
   s   a   a   a   s
      s   s   s
```

A = Asphaltenes (Solute)

R = Resins (Dispersant)

a = aromatics (Solvent)

s = saturates (Non-solvent)

	Wt.%	Ni/ppmw	V/ppmw	S/wt.%
S. American Crude	----	38	114	3.2
Pitch	100	100	300	5.6
s	18	0	0	4.3
a	17	0	0	4.8
R	40	110	260	5.7
A	**25**	**230**	**740**	**6.5**

So what exactly are Asphaltenes ??

- Asphaltenes are defined as the toluene soluble fraction that precipitates when a large excess of n-heptane or pentane is added to oil.
  [Heavy Oil Characterisation, Irv Wiehe, Soluble Solutions]
- They represent the least soluble fraction in Heavy Oil ($538\ ^{\circ}C+$)
- High in concentration of heteroatoms: S, N, O and Metals
- Molecular weight around 700–1000 g/mol;
  association increases molecular weight to 2000–5000 g/mol
- Molecular sizes ranging form 30–100 Å.
  Associated molecular structures 500 Å
- Asphaltenes are colloidially dispersed in the SARA matrix characterising Heavy Oil
- Asphaltene structure becomes more condensed (lower H/C ratio) with increasing bottoms conversion level

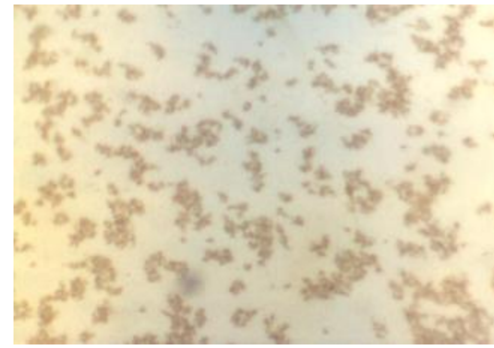
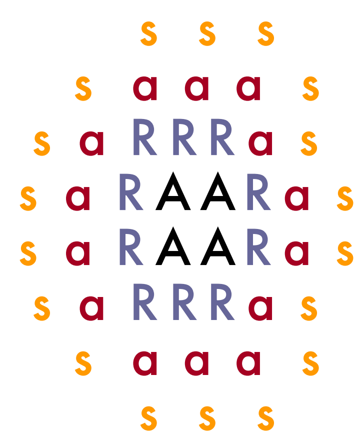
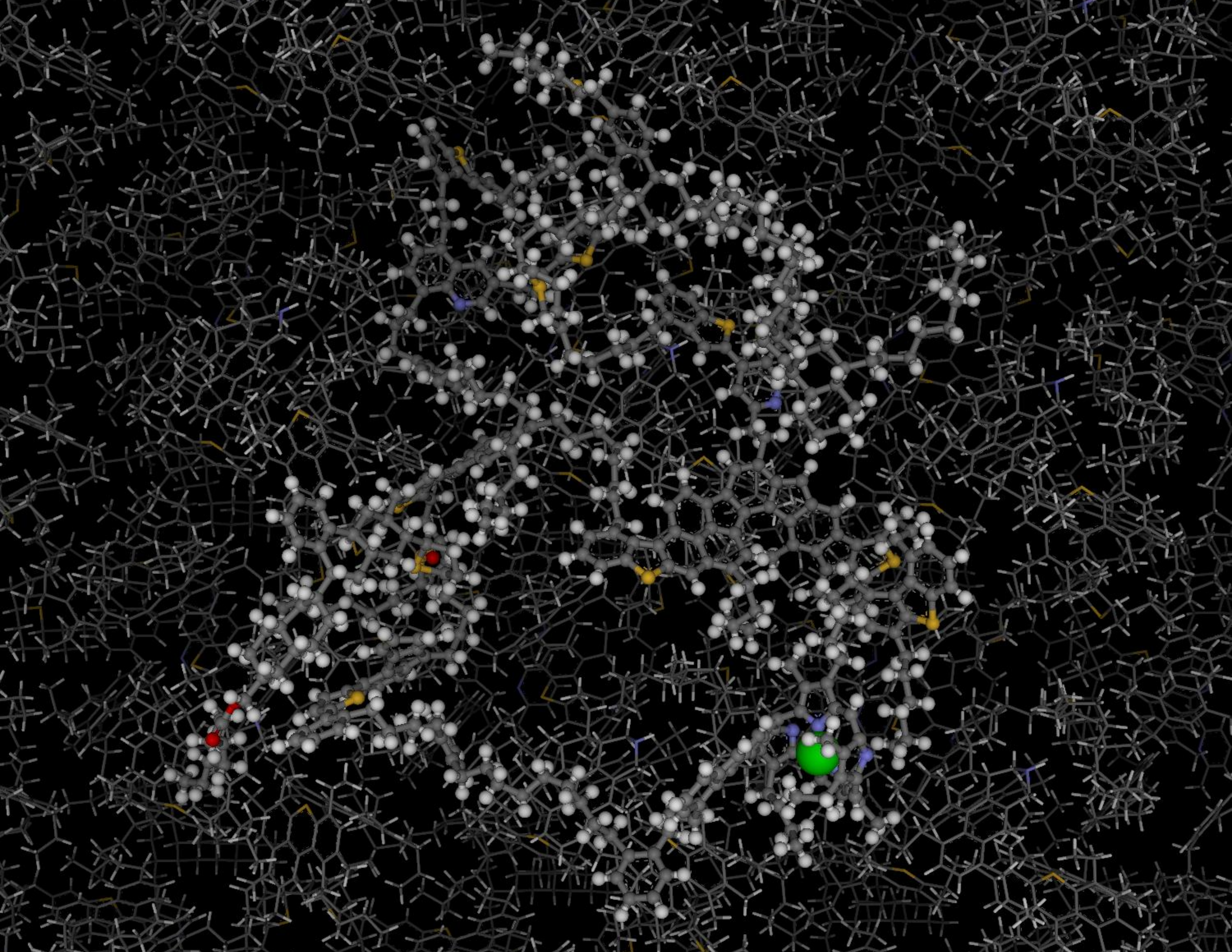
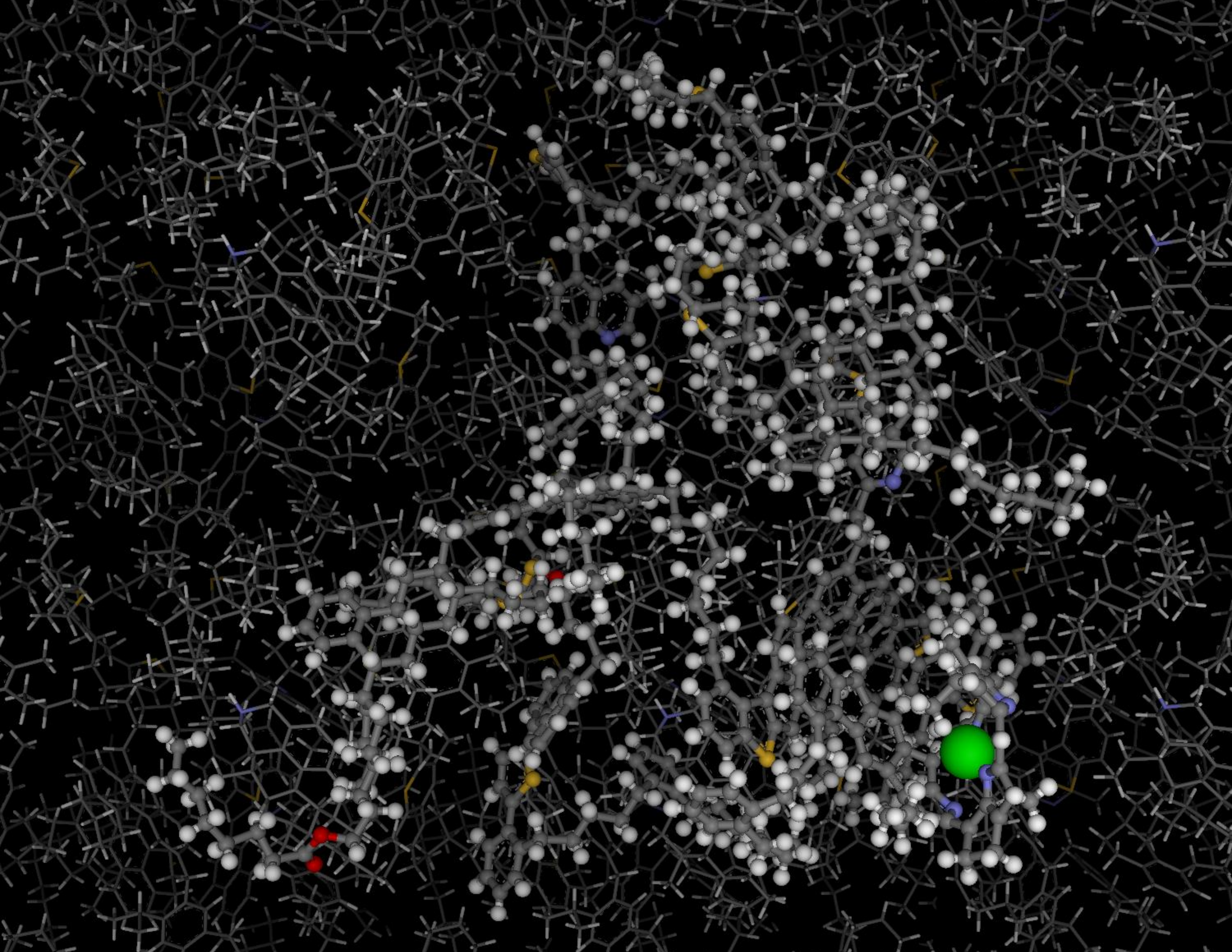
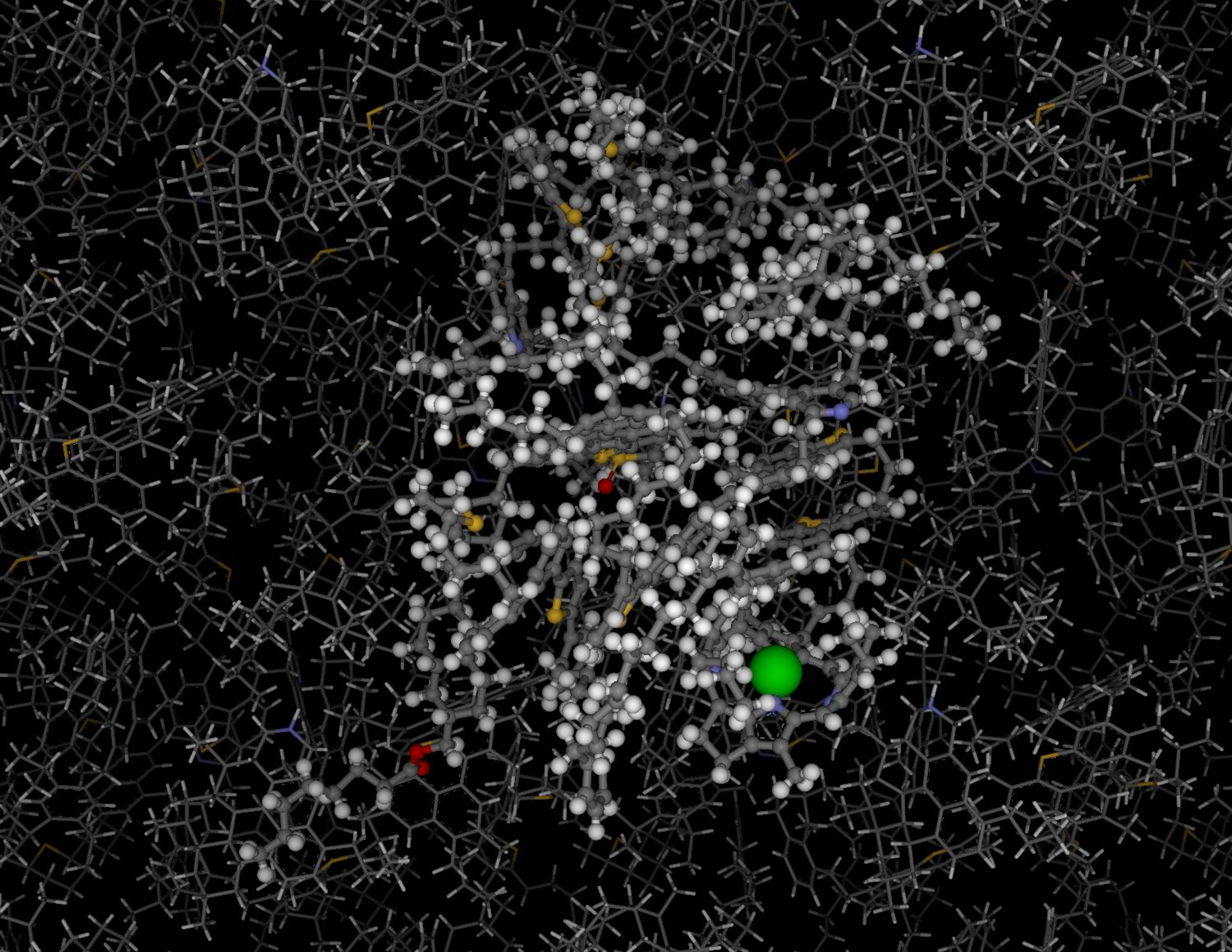


Photo courtesy of
Soluble Solutions







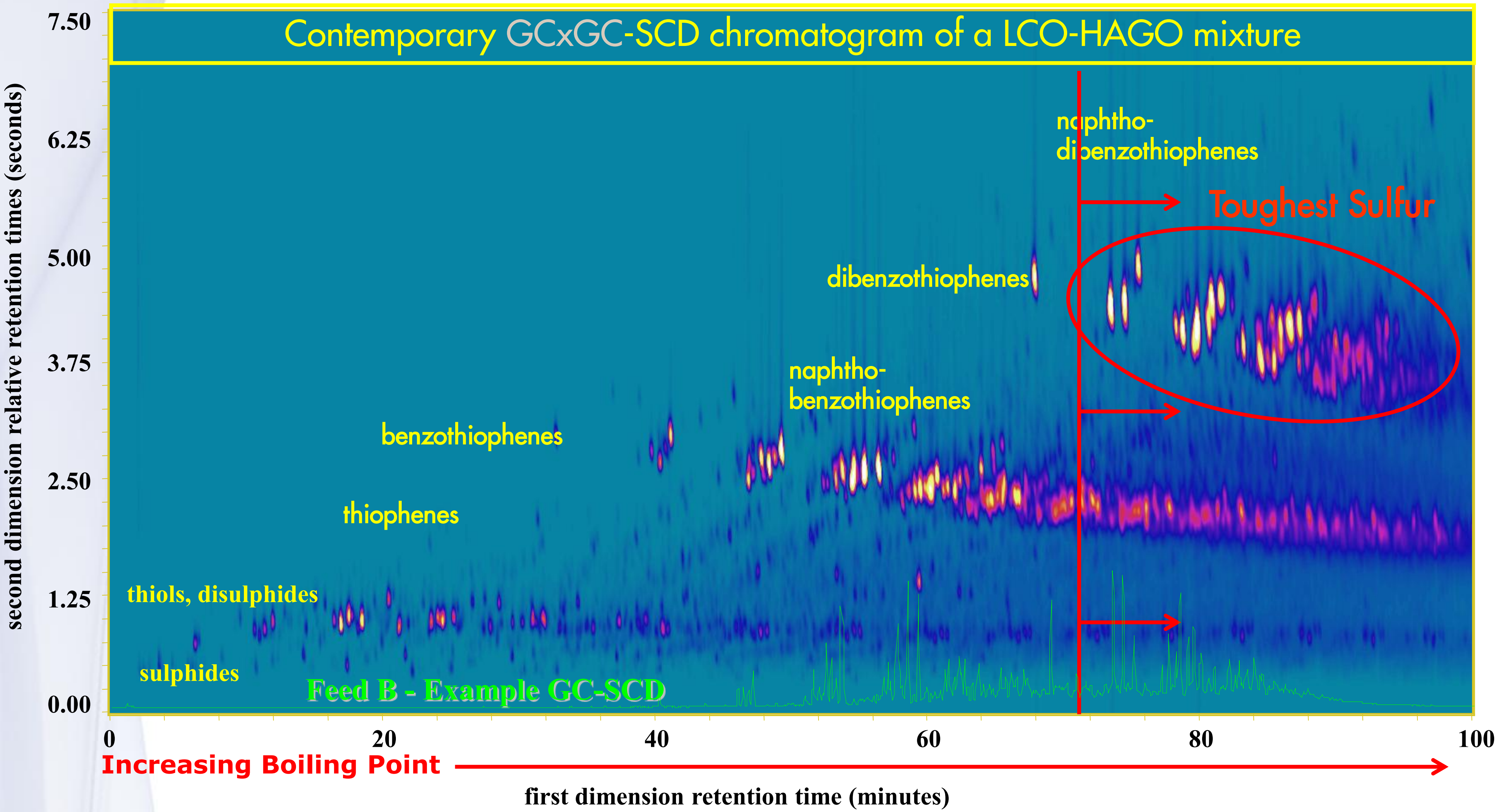


Atmospheric Residue feeds properties without advanced analysis

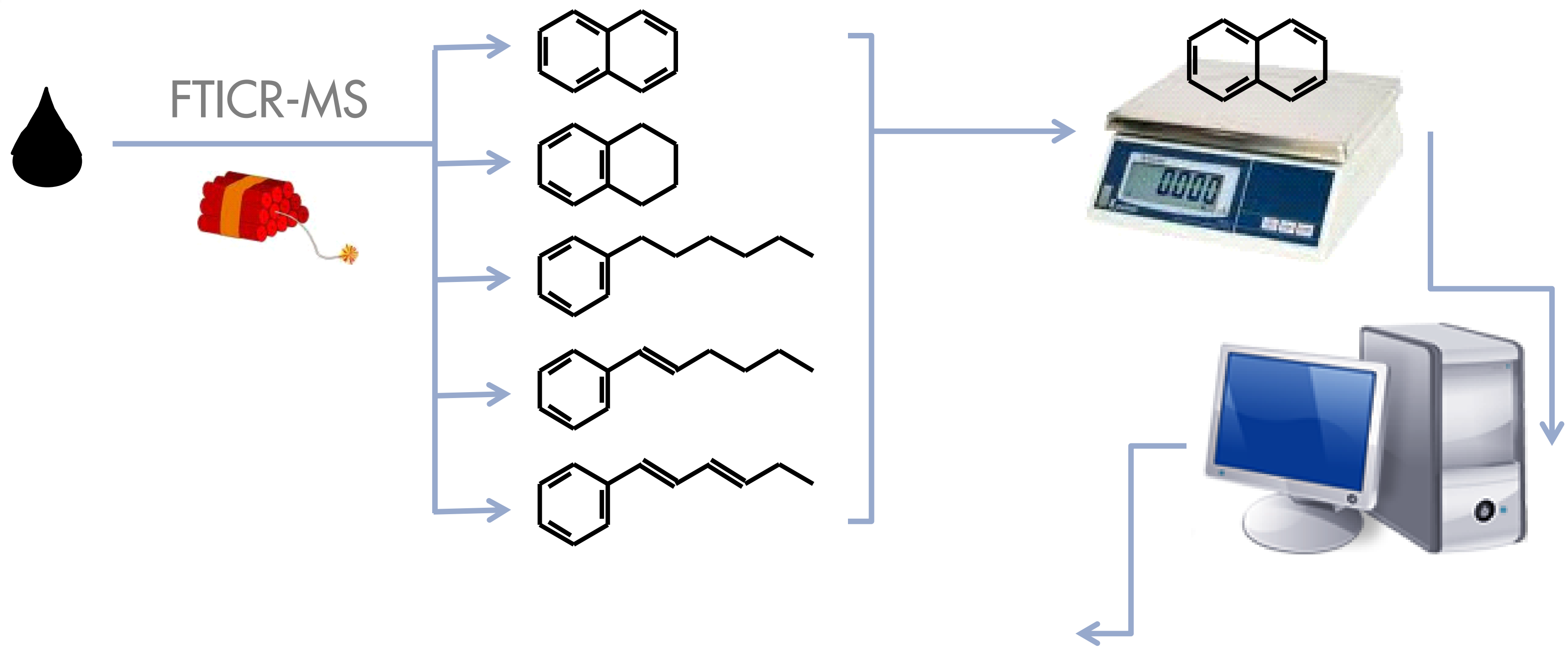
	FEED A-1	FEED A-2	VARIATION	
Density @ 15 °C	0.9808	0.9819	**0.0011**	g/ml
H (wt.%)	11.02	11.02	**0**	%
C (wt.%)	84.04	84.07	**0**	%
N (wt.%)	0.267	0.260	**–3**	%
S (wt.%)	4.536	4.575	**0.9**	%
Ni (ppmw)	21	20	**–3**	%
V (ppmw)	65	70	**7**	%
Metals (ppmw)	85	90	**6**	%
MCR (wt.%)	12.0	12.1	**0.8**	%
1000 F+ (wt.%)	51.3	49.8	**–3.0**	%
C_7 asph (wt.%)	6.0	5.5	**–9.1**	%

Not consistent with increased heaviness of current feed:
incorrect characterisation technique?

In USLD applications, GC*GC helped unravel the chemistry at molecular level



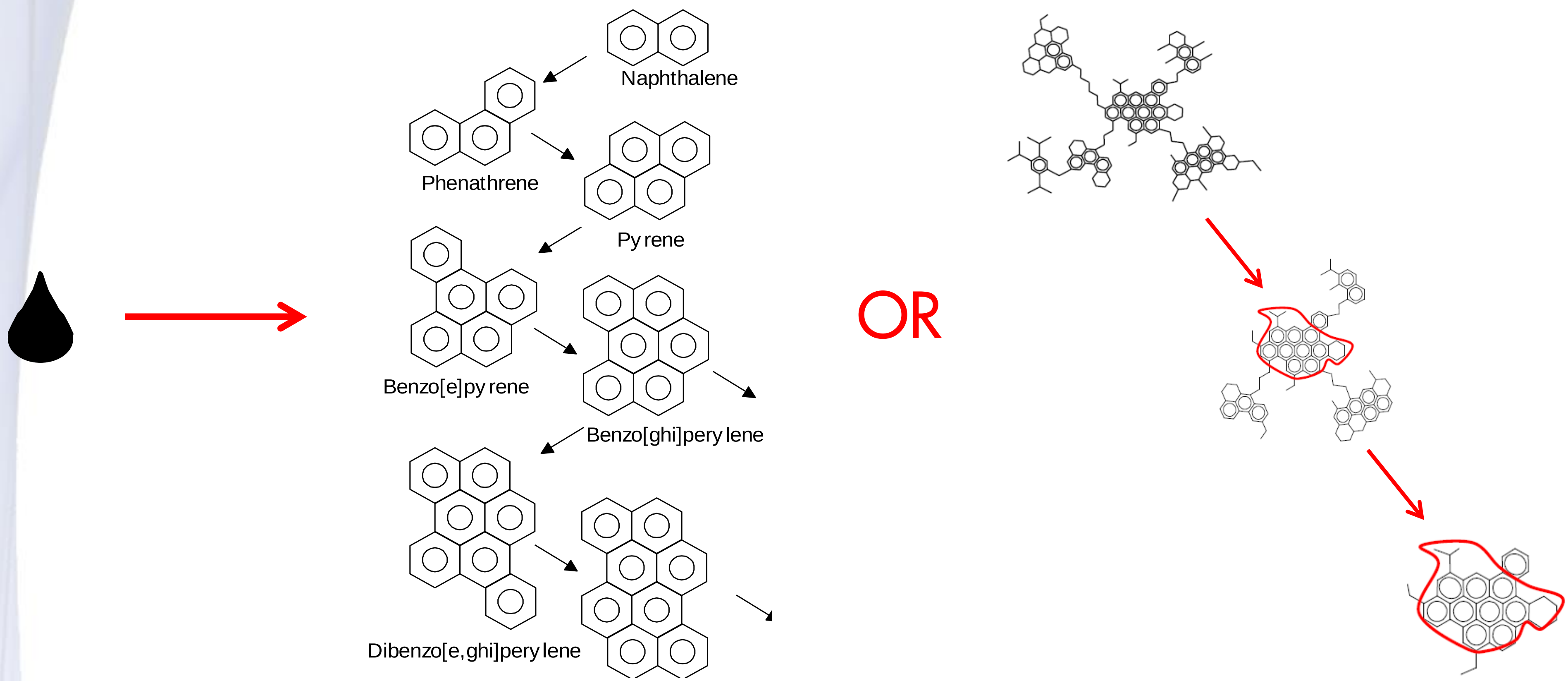
For Residue Upgrading – Fourier Transform Ion Cyclotron Resonance Mass Spectroscopy represents a 1st step in the same direction



Peak No.	Mol. Weight	Intensity	C	H	N	O	S	Molecular Type
2317	185.0419	0.002698	12	9	0	0	1	S1
1902	345.0337	0.002386	27	5	0	1	0	O1
2171	352.0342	0.001922	26	8	0	0	1	S1
1442	345.0703	0.002413	28	9	0	0	0	HC
1911	341.0291	0.002588	24	7	1	0	1	N1 S1
2285	384.0690	0.001925	29	8	2	0	0	N2

4000 – 8000 components

Fourier Transform Ion Cyclotron Resonance-Mass Spectrometry can be used to qualitatively follow Residue Upgrading reactions



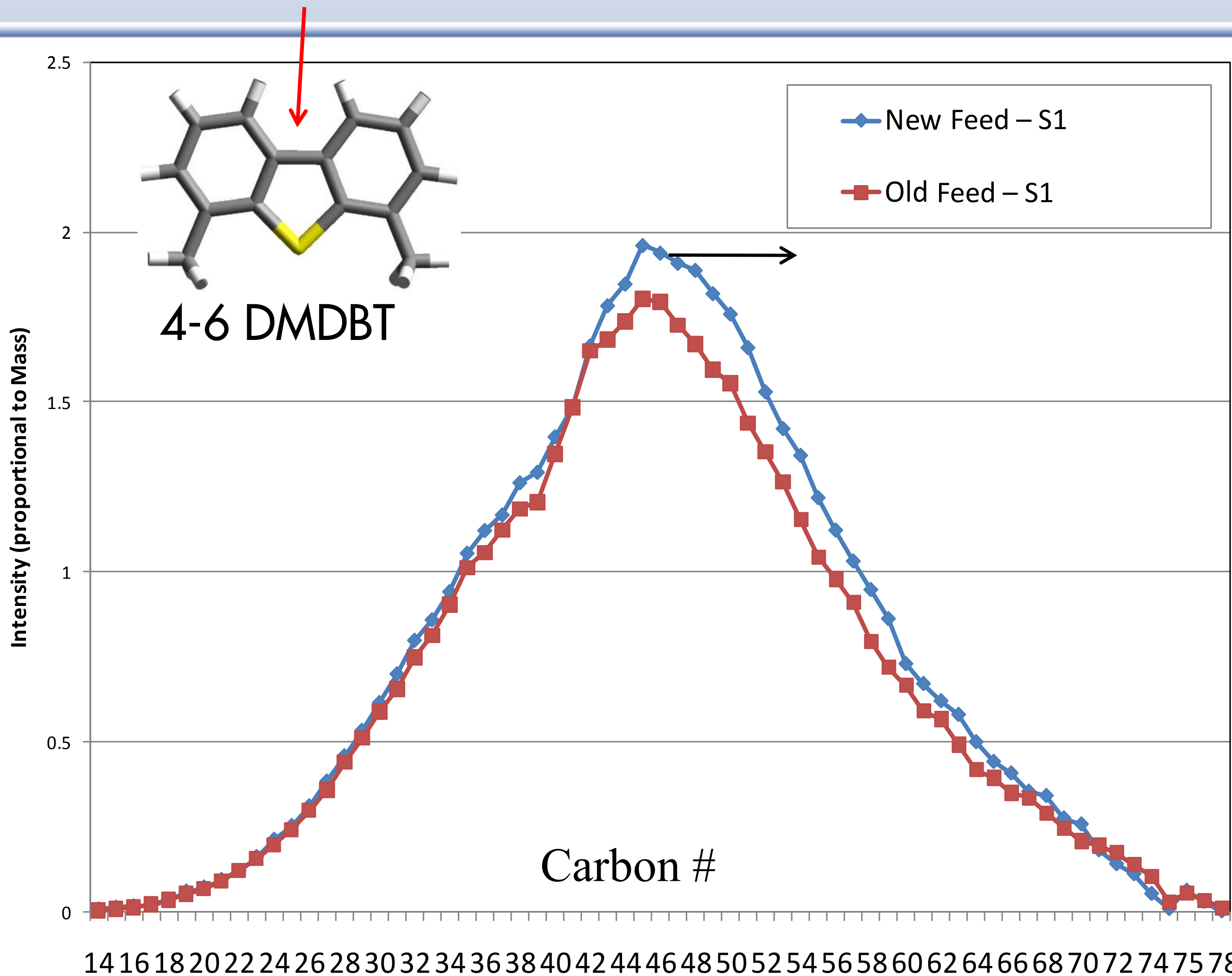
Coke formation

Asphaltene conversion

- Ability to look at individual molecules in Residue feedstocks (4000–8000 species per sample)
- Leads to improved understanding as to which catalysts work on which molecules
- Gives a clearer picture of how the molecules change during the Residue Upgrading process

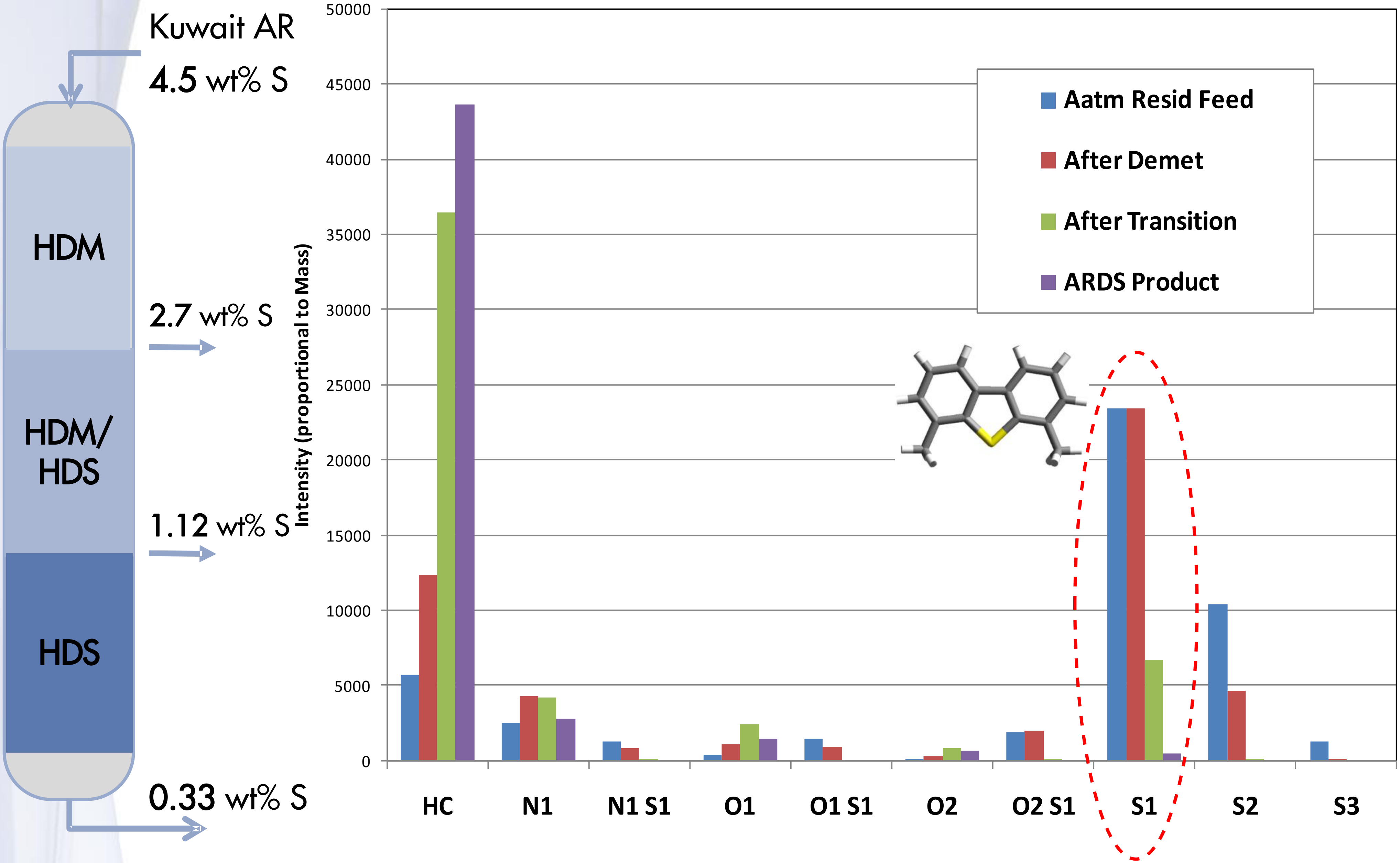
S1 Species are the most difficult Sulphur molecules to convert

Example of S1 molecule in diesel which can be found in the front end of an AR fraction

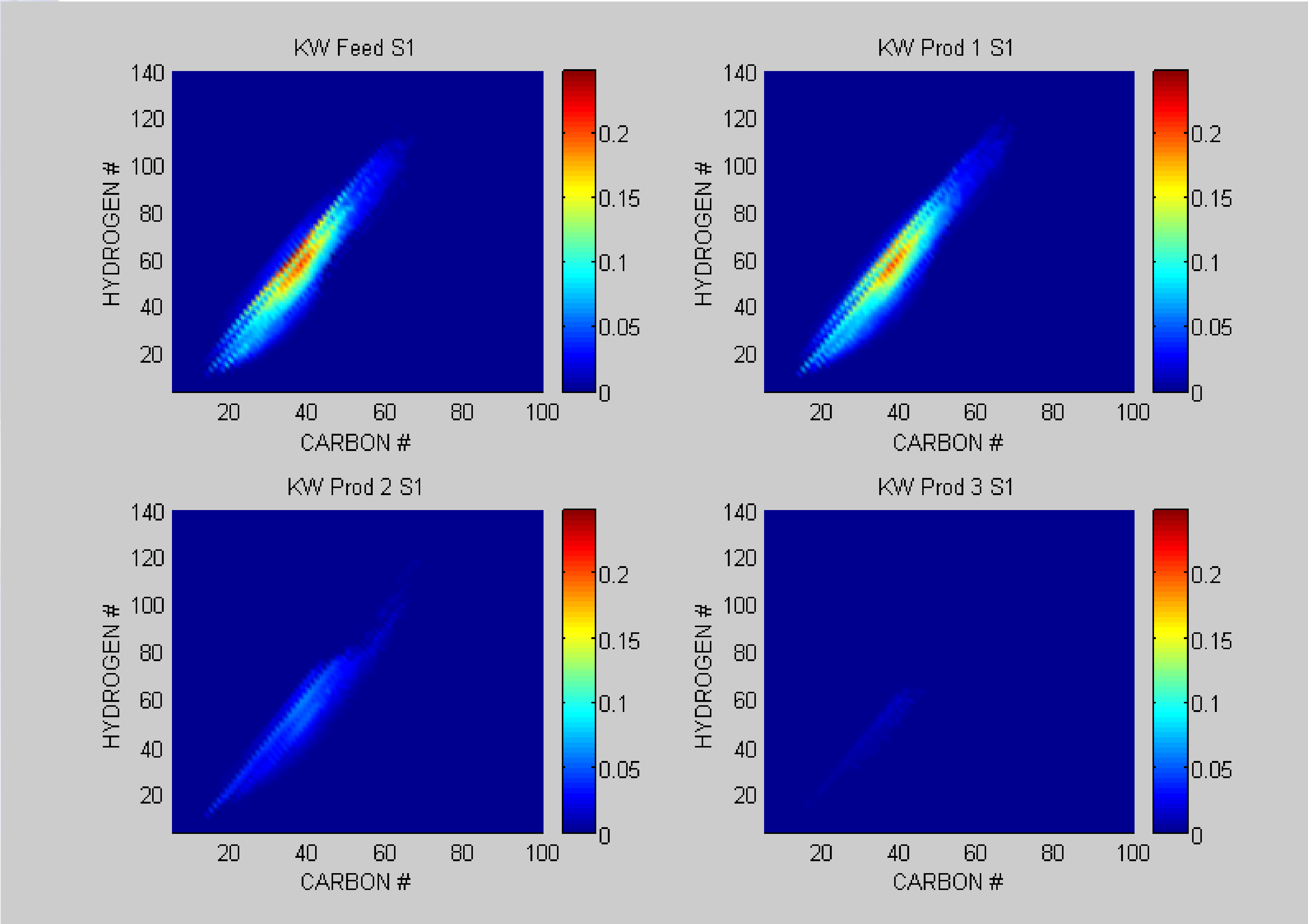


New feed has more and heavier S1 species

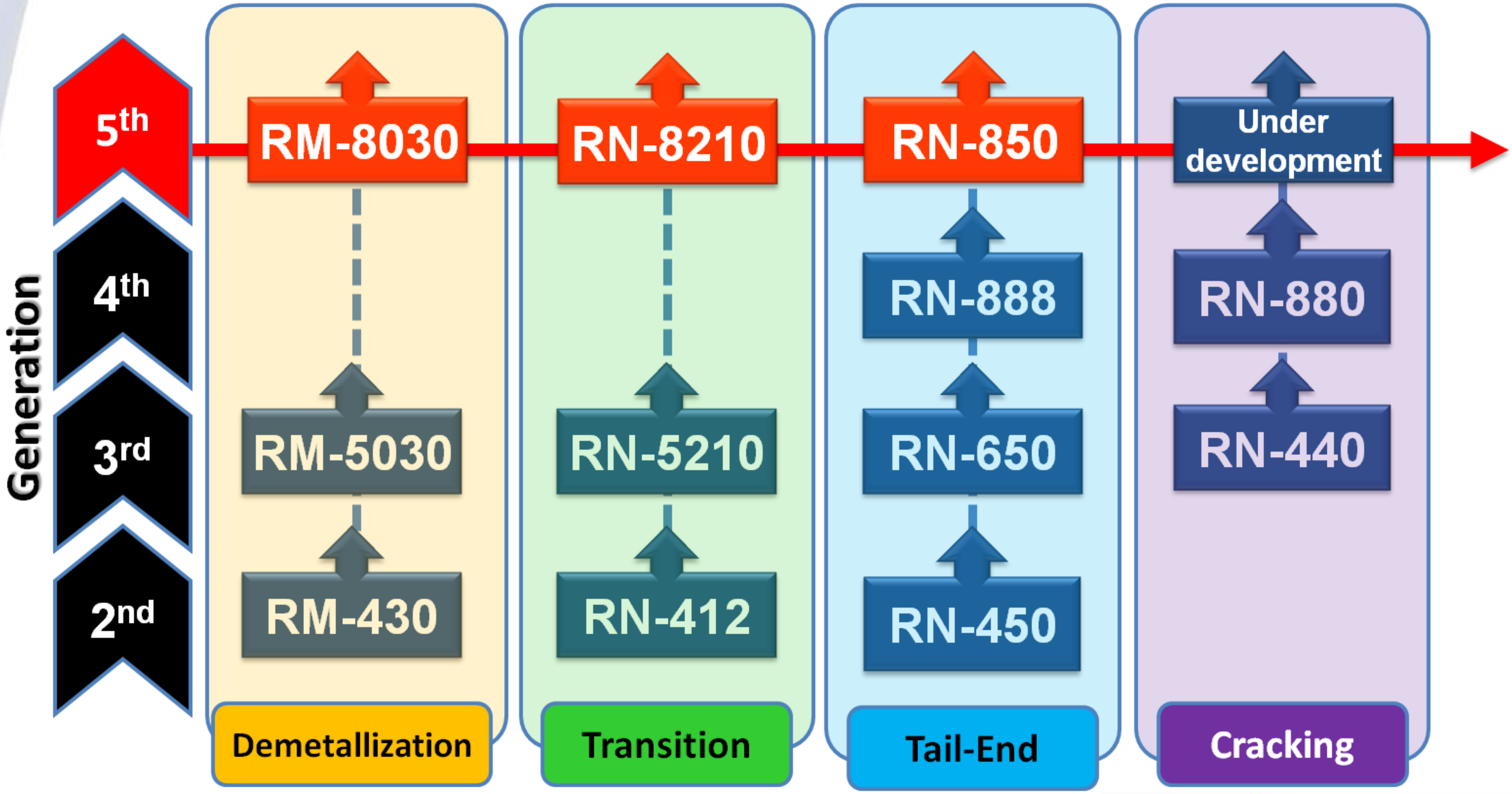
Examples of using FTICR-MS to distinguish different families of compounds present in AR & track their respective conversion rates



Output charting removal of S1 Molecules in each stage as a function of Carbon & Hydrogen content



Using data from Molecular based Characterisation techniques such as FT-ICR MS contributes to new generation catalyst development



Using Innovative Catalyst Technology to Overcome Processibility Barriers

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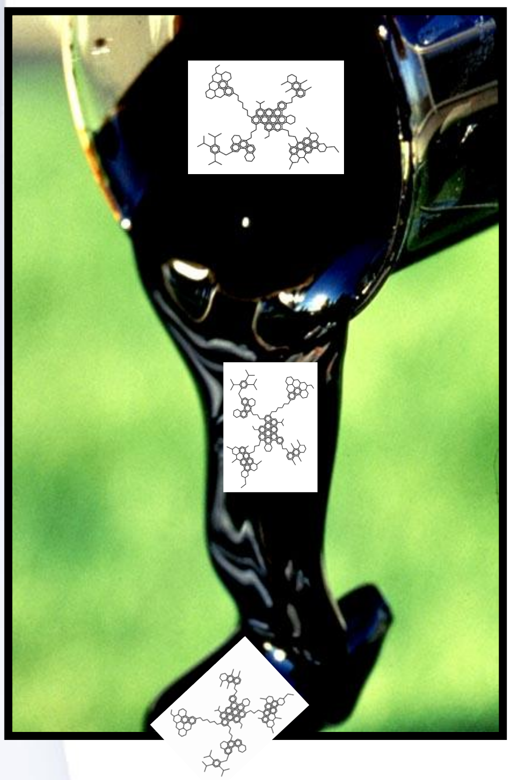
Takeaway Message

Meeting the future Heavy Oil upgrading challenge in your Residue Upgrading unit starts with broader Feed Characterisation as part of making the right

SEDEX SARA

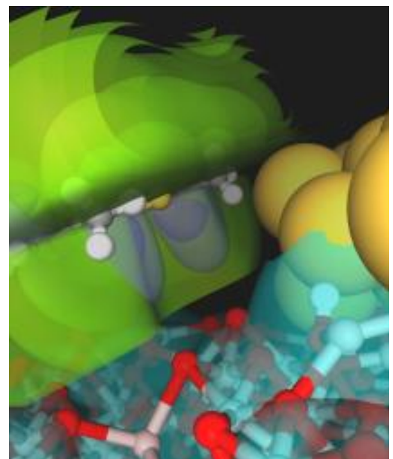
FT-ICR MS

SHFT



HTSD

C_5 Insolubles



CHEMISTRY

happen!!

Acknowledgements

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