ASMS 2024, WP 804

Graphical Data Analysis and Sample Comparison of Complex Mesophase Pitches

Mark A. Arnould[1], Aparna Annamraju[2], Frederic Vautard[2] and Ercan Cakmak[3]

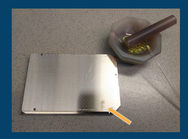
[1]Bruker Daltonics Inc., 40 Manning Road, Billerica, MA 01821, USA. [2]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. [3]Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

Mesophase Pitch:

- Mesophase pitch develops during the thermal treatment of pitches containing different planar aromatic molecules
- Molecular components are polynuclear aromatic compounds (think PAH) with planar configurations generated by condensation of lower molecular weight components from the isotropic phase
- No extensive structural rearrangement is required during graphitization, mesophase's orientational order is crucial to produce high quality carbon fiber
- Using mesophase pitches from model compounds has recently gained ground
- Difficulty of high quality, tailored production of carbon materials arises from:
  - incomplete understanding of the underlying reaction mechanisms during processing
  - insufficient compositional and structural knowledge of the raw pitches, the critical intermediates and the final products

Autoflex maX

Solid Sample Preparation



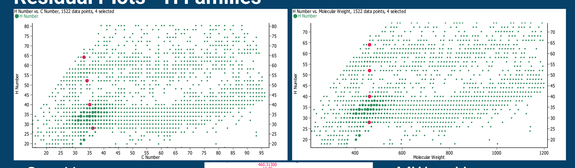
Sample Preparation:

- Grind a small amount of the solid sample on the target surface using a spatula
- Scrape off excess leaving a thin layer on the target
- Unused solid was blown off with clean compressed air

Data Processing:

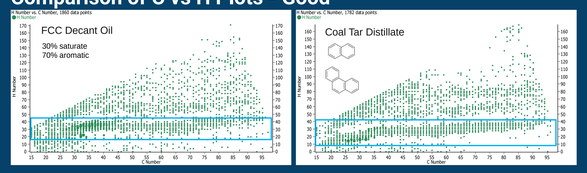
- Graphical data analysis was accomplished using **Investigator** from **Sierra Analytics**

C vs H or MW vs H Plots Display the Data Similar to the Residual Plots - H Families

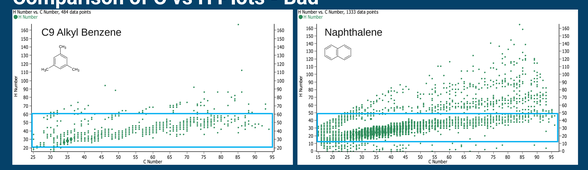


- C vs H
  - H increasing by 12 going up
  - C decreasing by 1 to the left
- MW vs H
  - H increasing by 12 going up
  - The line is vertical because the mass differs only in the decimal place

Comparison of C vs H Plots - Good



Comparison of C vs H Plots - Bad



- The good samples have a longer continuous carbon skeleton with little change in the hydrogen count
  - Lower hydrogen to carbon ratio indicative of high percentage of aromatic structure
  - Presence of some methyl (CH3) groups as side chains
  - Higher proportion of aromatic rings versus alkyl substituents
  - Presence of a highly fused non-flexible aromatic structure
- The bad samples have either no continuous carbon skeleton or increasing hydrogen count with increasing carbon
  - Higher hydrogen to carbon ratio indicative of lower percentage of aromatic structure
  - Presence of higher number of methyl (CH3) groups as side chains and lower aromatic rings
  - Presence of linear flexible structure

Good ☺

FCC Decant Oil

Mass	Calculated Mass	Formula	Relative Frequency
24.00174	24	C2	100
12.00349	12	C	97
26.01017	26.01565	C2H2	91.9
50.01308	50.01565	C4H2	88.1

Coal Tar Distillate

Mass	Calculated Mass	Formula	Relative Frequency
24.00103	24	C2	89
26.00611	26.01565	C2H2	85.6
50.00722	50.01565	C4H2	80.9
12.00171	12	C	67.6

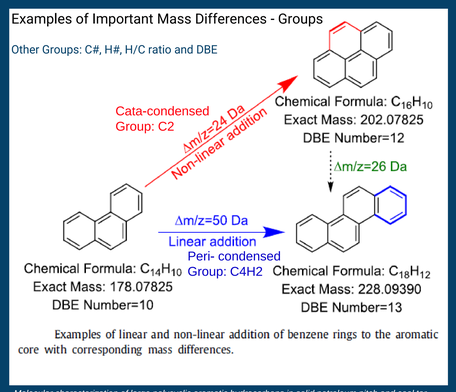
Bad ☹

C9 Alkyl Benzene

Mass	Calculated Mass	Formula	Relative Frequency
11.99771	12	C	67.4
26.01267	26.01565	C2H2	53.8
23.99977	24	C2	22.9
50.01083	50.01565	C4H2	6.1

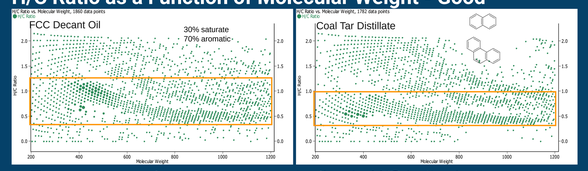
Naphthalene

Mass	Calculated Mass	Formula	Relative Frequency
12.00239	12	C	97.9
24.00564	24	C2	94.3
26.0056	26.01565	C2H2	91.7
50.0109	50.01565	C4H2	87.4



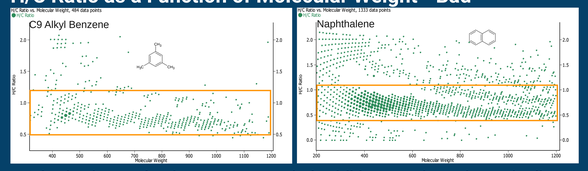
Molecular characterization of large polycyclic aromatic hydrocarbons in solid petroleum pitch and coal tar pitch by high resolution MALDI TOF MS and insights from ion mobility separation. Wen Zhang, Jan T. Andersson, Hans Joachim Räder, Klaus Müllen

H/C Ratio as a Function of Molecular Weight - Good



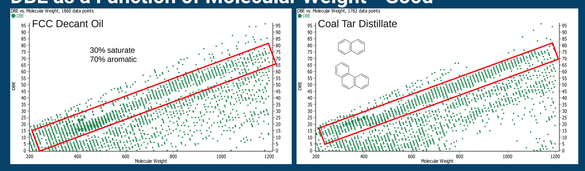
- The good samples have a steep decline in H/C in the in the main distribution as well as going to higher masses

H/C Ratio as a Function of Molecular Weight - Bad



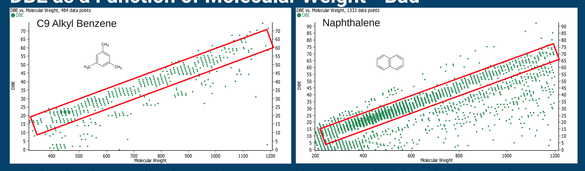
- The bad samples have more methyl additions and no sharp decline in the H/C in the main distribution or at higher MW

DBE as a Function of Molecular Weight - Good



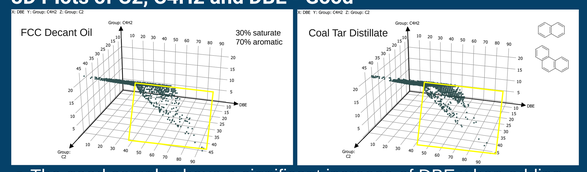
- The good samples have a steep increase in DBE in the in the main distribution as well as going to higher masses

DBE as a Function of Molecular Weight - Bad



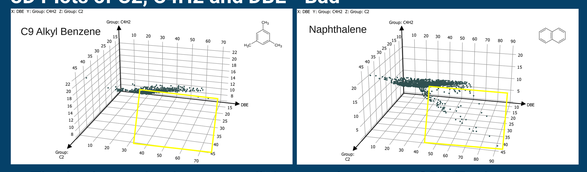
- The bad samples have less steep increase in DBE in the main distribution as well as going to higher masses

3D Plots of C2, C4H2 and DBE - Good



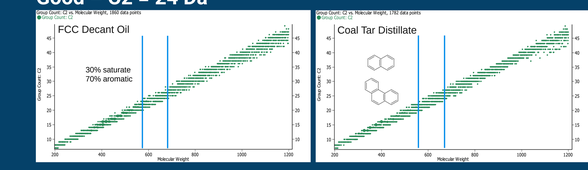
- The good samples have a significant increase of DBE when adding C4H2 then C2

3D Plots of C2, C4H2 and DBE - Bad

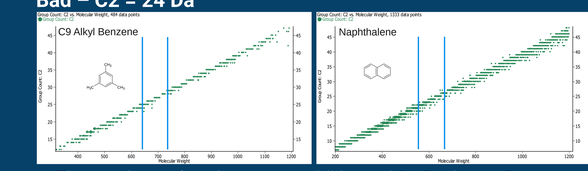


- The bad samples have very little to no increase of DBE when adding C4H2 then C2

Mass Differences as a Function of Molecular Weight – Good – C2 = 24 Da

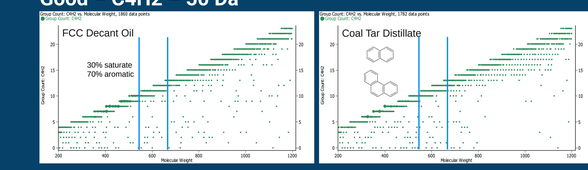


Mass Differences as a Function of Molecular Weight – Bad – C2 = 24 Da

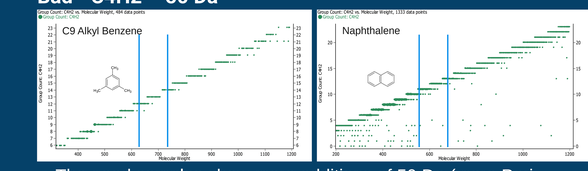


- The good samples show more additions of 24 Da (more Cata-condensed structures) as a function of MW when compared to the bad samples

Mass Differences as a Function of Molecular Weight – Good – C4H2 – 50 Da

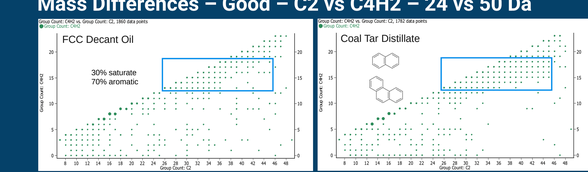


Mass Differences as a Function of Molecular Weight – Bad– C4H2 – 50 Da

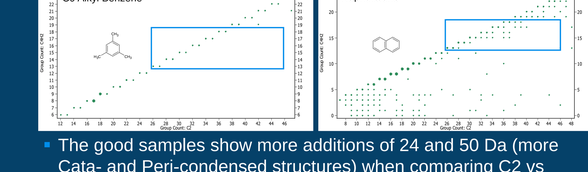


- The good samples show more additions of 50 Da (more Peri-condensed structures) as a function of MW when compared to the bad samples

Mass Differences – Good – C2 vs C4H2 – 24 vs 50 Da



Mass Differences – Bad – C2 vs C4H2 – 24 vs 50 Da



- The good samples show more additions of 24 and 50 Da (more Cata- and Peri-condensed structures) when comparing C2 vs C4H2
- The molecules in the good samples are condensing using both additions to form planar highly conjugated molecules

- If we use graphical and statistical analysis to investigate these types of samples, it could be possible to determine more about the microstructure, faster.
- Screen materials before test spinning
- If we add in CCS values and higher resolution mass accurate data (TIMS-TOF), then we would have definitive information about how the molecule is connected – long flexible chains or highly conjugated ring systems (PAH) while distinguishing isomers
- We need to collect as much MS data as possible and start mining the data differently to fully understand what we observe – patterns
- Feed this data to AI/ML