Report on the 2015 ASMS Conference Workshop "Advanced MS and Separation Approaches for Biofuels and Petroleum"

Patrick G. Hatcher and Mark P. Barrow

The workshop was held on Monday, June 1 in Room 132 at 5:45 – 7:00 PM. Dr. Barrow moderated the workshop speakers and discussion after a short introduction by Dr. Hatcher. The following organization was prepared to spur discussion:

- Mark Barrow (University of Warwick, UK)
  - ❖ Introduction
- Florian Albrieux (IFPEN, France)
  - ❖ "Real world" areas of research
  - ❖ Experimental methods
  - ❖ Discussion
- Janne Jänis (University of Eastern Finland)
  - ❖ Data analysis and validation
  - ❖ Structure
  - ❖ Discussion

Slides for each of the speakers are included in this report and these served to stimulate abundant discussions in which a significant proportion of the 75-100 participants stepped up to make comments. Those attending represented a range of academic and commercial establishments, and the active discussion lasted the full duration of the available time.

It became quite clear in these discussions that we need better strategies to characterize both bio-oils and petroleum-derived oils. We also need to find ways to standardize the vast amounts of data being gathered for these materials. Along this line, we need to find approaches to better quantify products for which authentic standards are scarce or unavailable. In the case of biofuels, an important question is how do we utilize the MS approaches to predict pyrolysis product quality. In the areas of both petroleomics and biofuels, some important questions arose regarding:

- Chemical structure of molecules for which only elemental formulas are obtained
- The need to combine other characterizations methods (NMR, spectroscopy) with MS to obtain a more comprehensive view of sample composition
- Data analysis needs to be more automated and incorporate statistical treatment of large datasets
- Understanding of the chemistry will require the development of structural databases
- Can better progress be made by limiting the focus of examination to the 10 or 20 most abundant compounds or is it vital to include all of the minor components?

Overall, much discussion ensued on these topics with the hope that such discussion would promote added focus of research efforts and guide the work to be presented at future ASMS meetings.

Emerging topics and challenges

Advanced MS and Separation Approaches for Biofuels and Petroleum

Discussion

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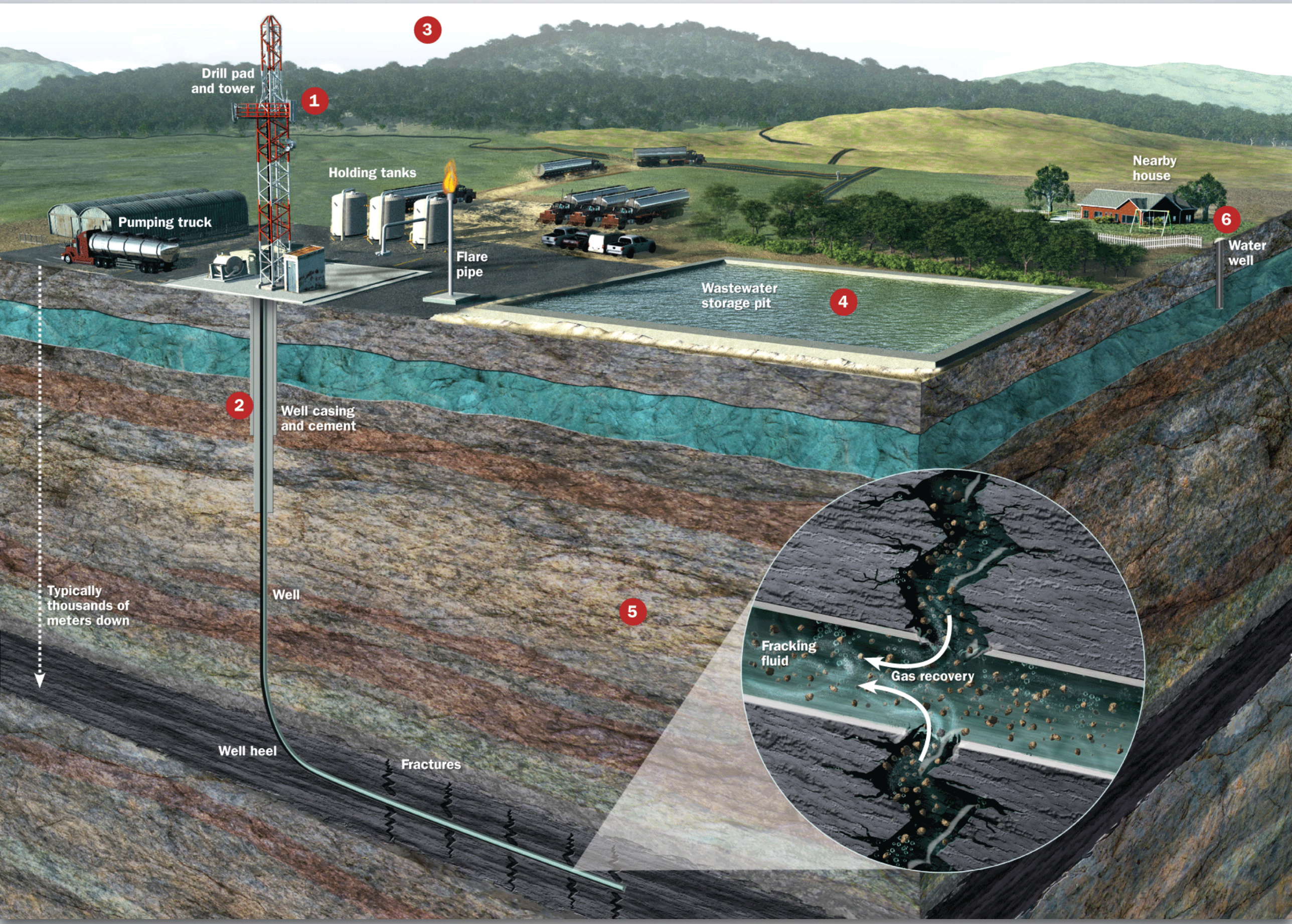
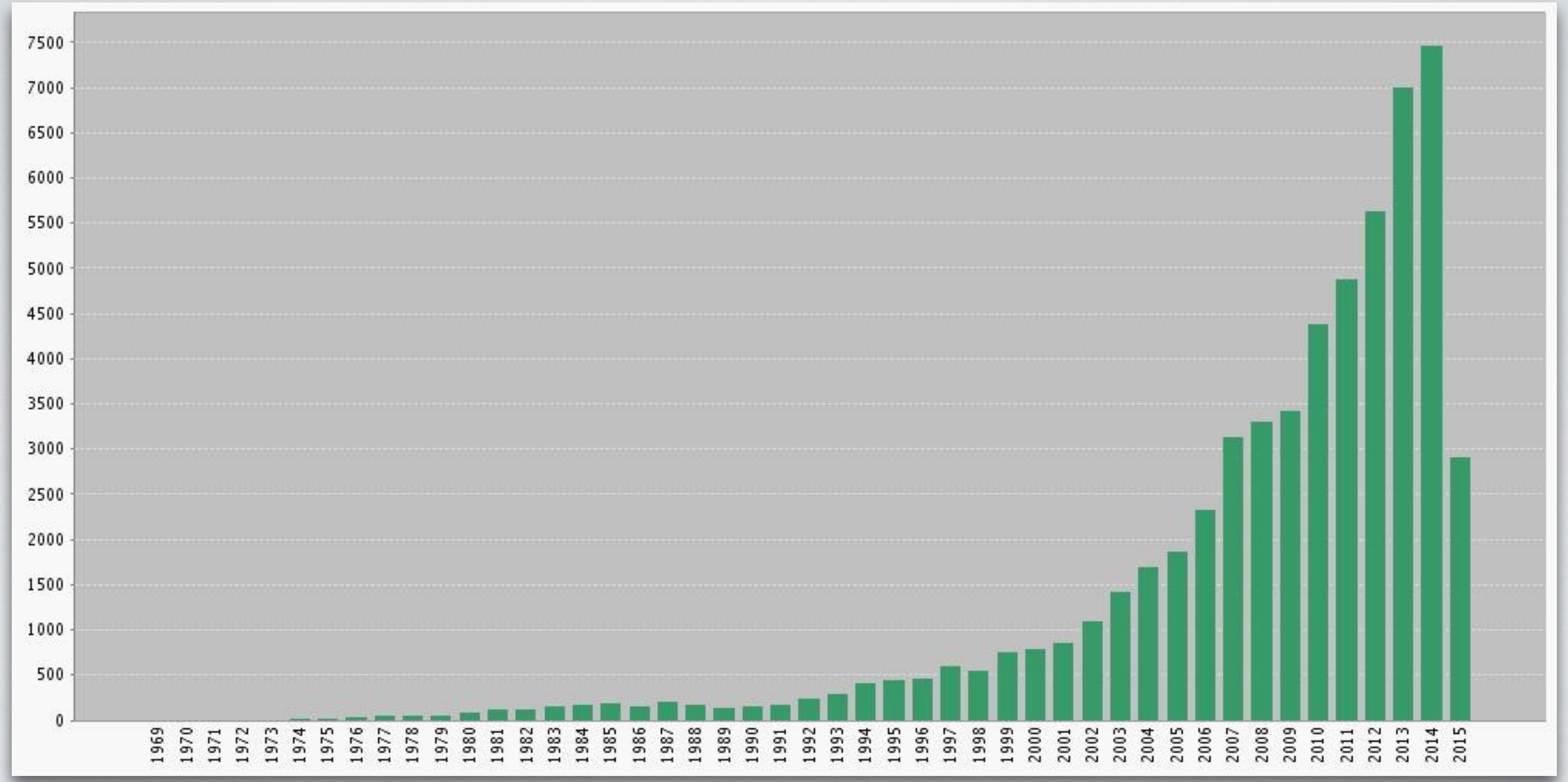
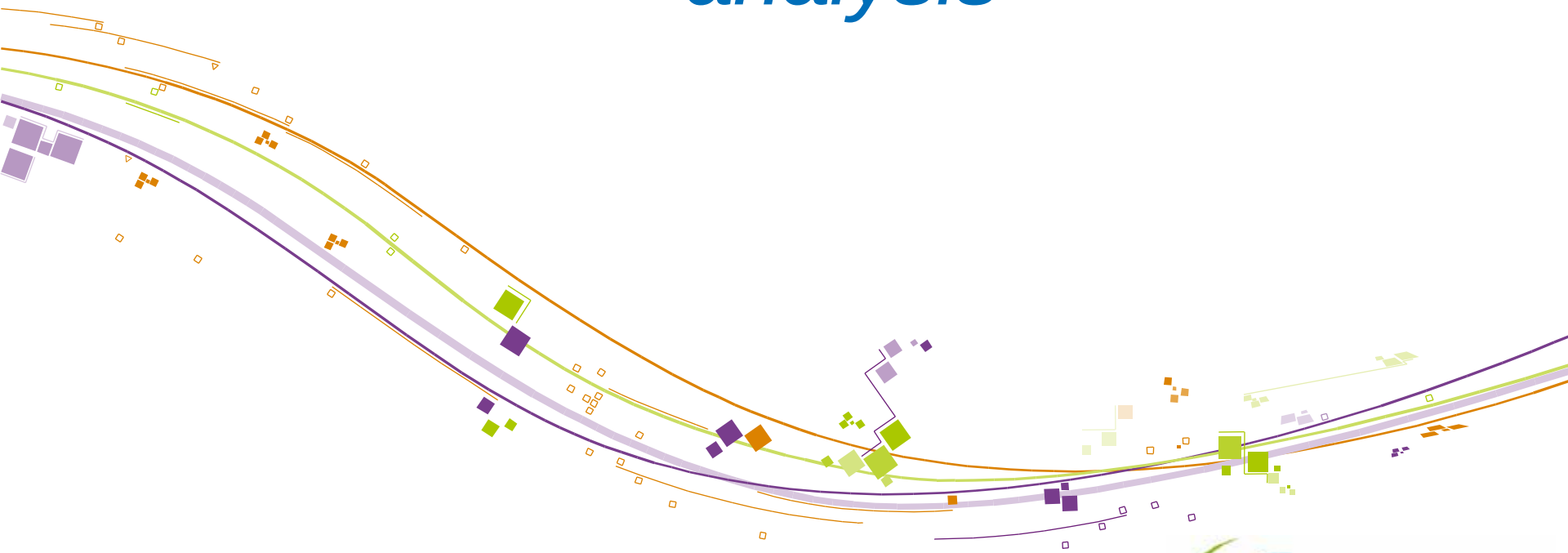

Drill pad and tower
1
3
Holding tanks
Pumping truck
Flare pipe
Nearby house
6
Water well
Wastewater storage pit
4
2
Well casing and cement
Typically thousands of meters down
Well
5
Fracking fluid
Gas recovery
Well heel
Fractures

Citations for “petroleum” and “mass spectrometry”



Source: Web of Science

Petroleum and Biomass analysis



Problematics in molecular characterization

- **Tools for molecular description at structural level**
  - **GC*GC/MS (TOF, Orbitrap, EI, CI, FI) è volatile products**
  - **FT-ICR/MS and Orbitrap-MS è medium and heavy products**
  - **LC and LC*LC/MS, IM-MS and SFC/MS è Add a separative dimension and for Ion Mob gives conformational informations**

Future challenges

- **Better characterization of heavy products to valorize the maximum of crude oil (ressources diminution)**
- **Better understanding of HDT process è Development of more efficient catalysts**
- **Development of new startegies to charcaterize ex biomass products (bio-oils and upgrading products, biomass feeds in petrochemistry)**
- **Standarisation of data acquisition**

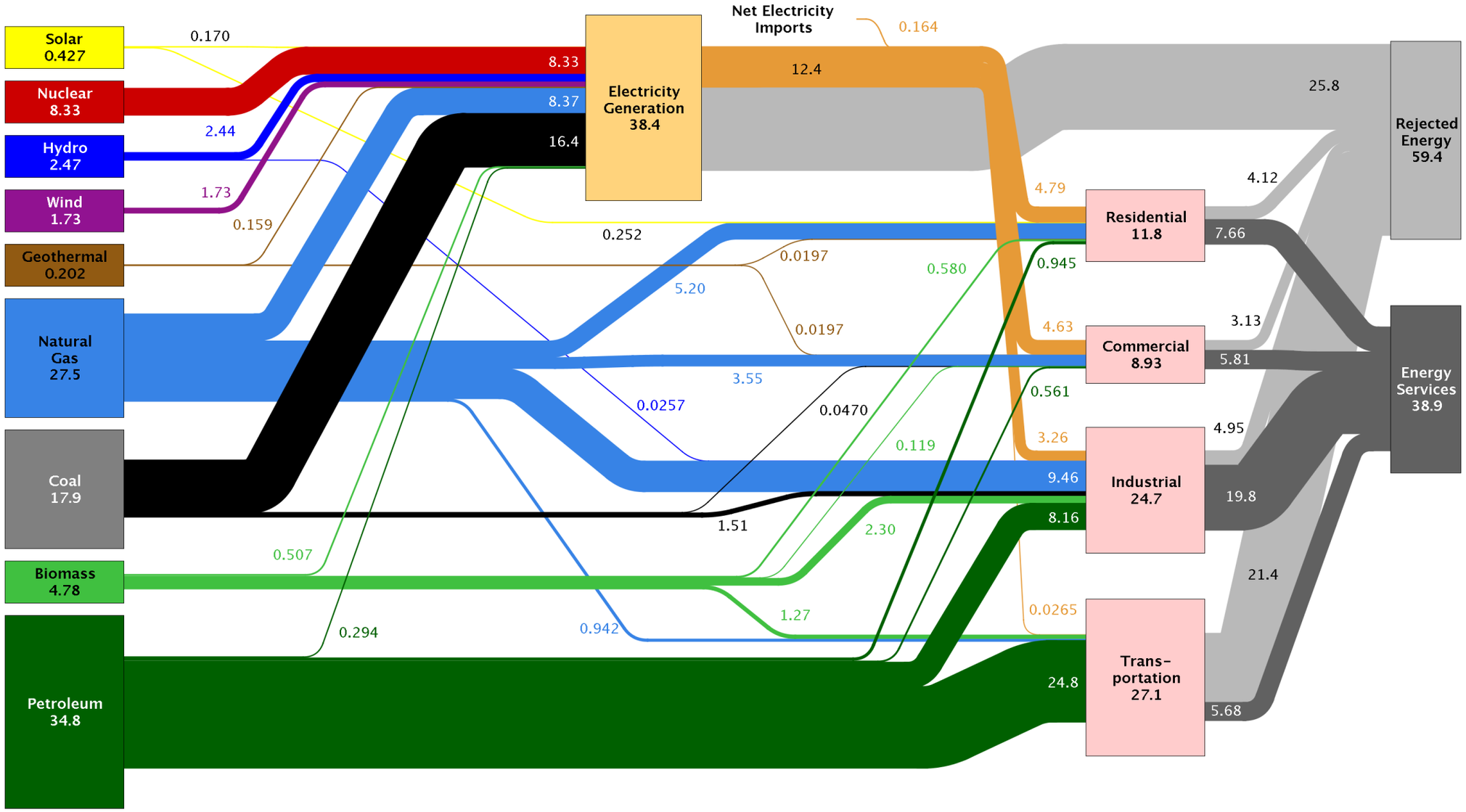
Petroleomics — why and *how*?

Janne Jänis
UEF Chemistry

ASMS Workshop 2015

Estimated U.S. Energy Use in 2014: ~98.3 Quads

Lawrence Livermore National Laboratory



Source: LLNL 2015. Data is based on DOE/EIA-0035(2015-03), March, 2014. If this information or a reproduction of it is used, credit must be given to the Lawrence Livermore National Laboratory and the Department of Energy, under whose auspices the work was performed. Distributed electricity represents only retail electricity sales and does not include self-generation. EIA reports consumption of renewable resources (i.e., hydro, wind, geothermal and solar) for electricity in BTU-equivalent values by assuming a typical fossil fuel plant "heat rate." The efficiency of electricity production is calculated as the total retail electricity delivered divided by the primary energy input into electricity generation. End use efficiency is estimated as 65% for the residential and commercial sectors 80% for the industrial sector, and 21% for the transportation sector. Totals may not equal sum of components due to independent rounding. LLNL-MI-410527

Crude oil spa in Azerbaijan

"Petroleomics is the identification of the totality of the constituents of naturally-occurring petroleum and crude oil using high resolution mass spectrometry. In addition to mass determination, petroleomic analysis sorts the chemical compounds into heteroatom class (nitrogen, oxygen and sulfur), type (degree of unsaturation, and carbon number)"

http://en.m.wikipedia.org/wiki/Petroleomics

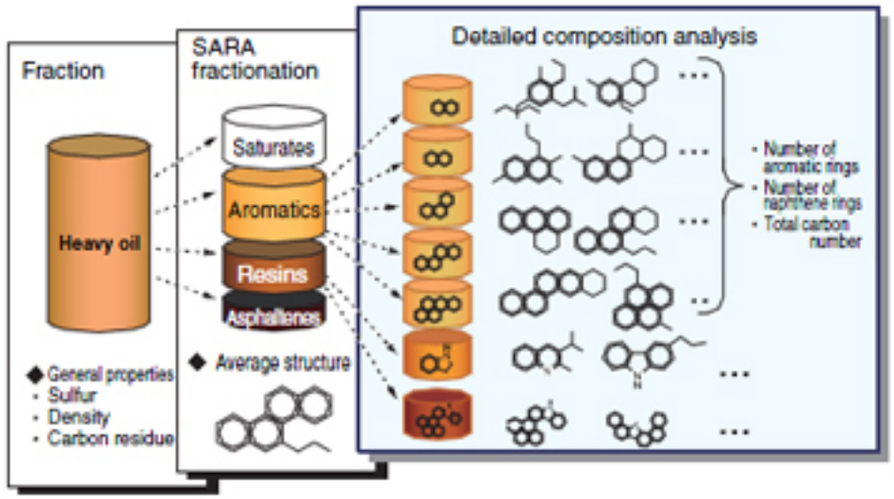


Figure 1 Pre-fractionation processing for detailed composition analysis of heavy oil

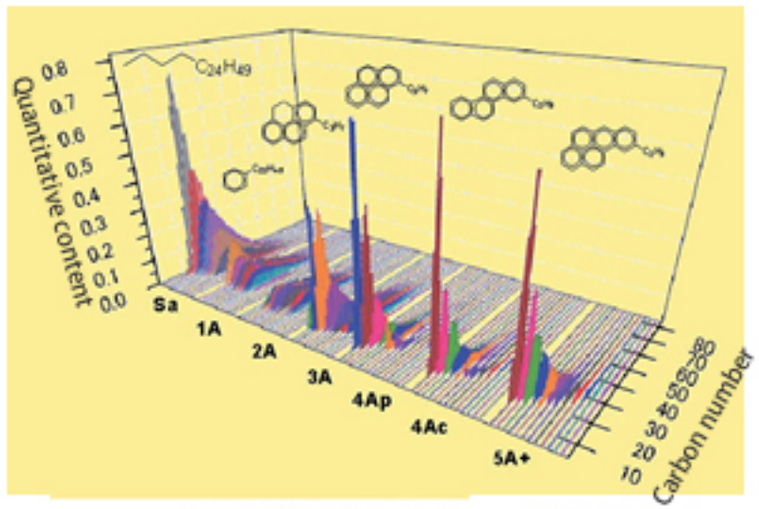


Figure 2 Detailed composition analysis of atmospheric residue (by way of example)

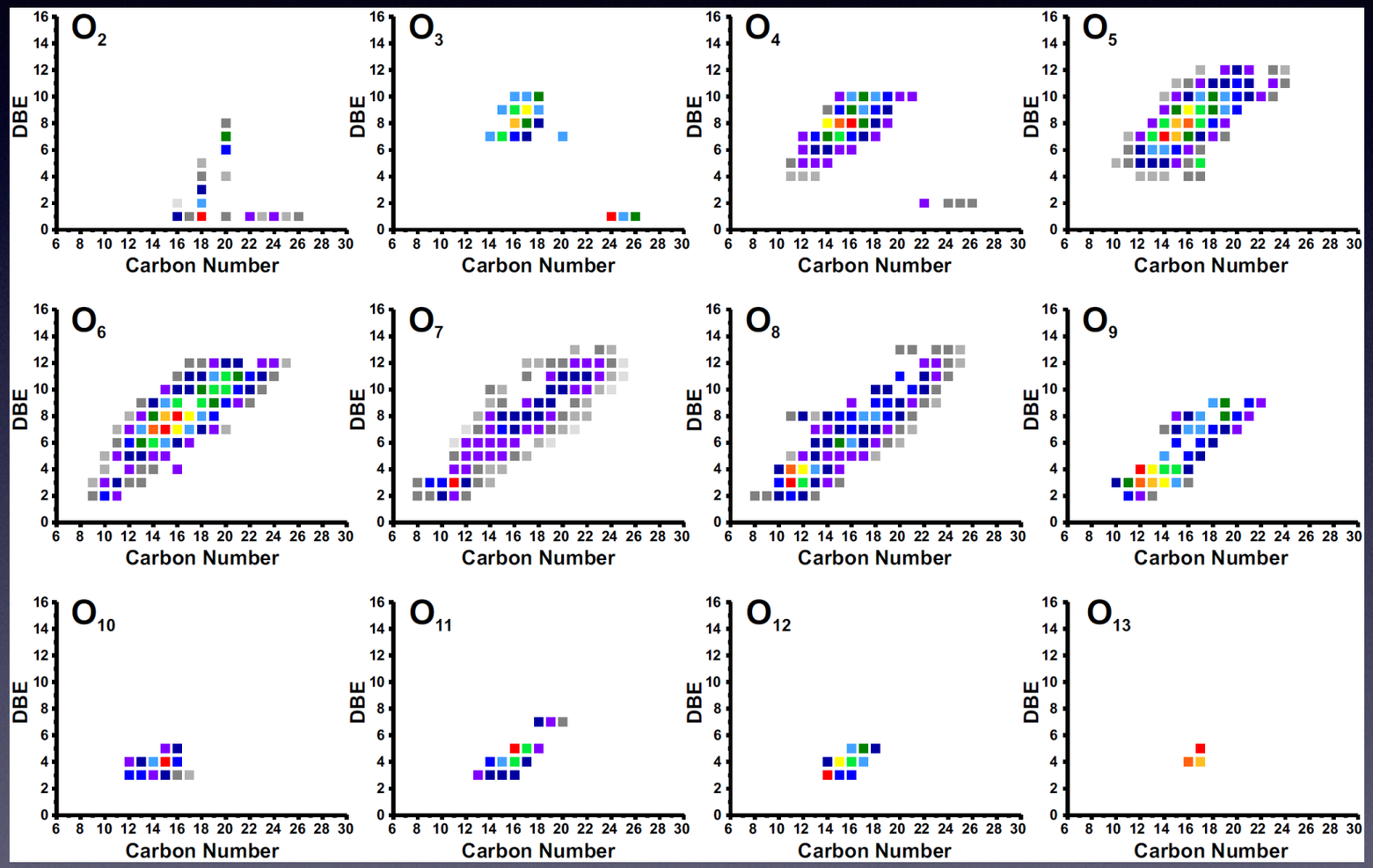
The needs?

- Instrumentation? Does MS give comprehensive view (totality)? Needs for improvements — instrument-wise? Can it be quantitative? Should MS be combined with other methods — which? Isomer separation?

- Data analysis? More automated, streamlined applications *that do everything*? Statistics of large petroleomics data sets similar to other branches of chemistry? Validity? General guidelines?

- Understanding chemistry? Elemental formula = chemical structure? Databases, repositories? Arising needs due to shift to biofuels?

Understanding chemistry — the case of wood based pyrolysis oil



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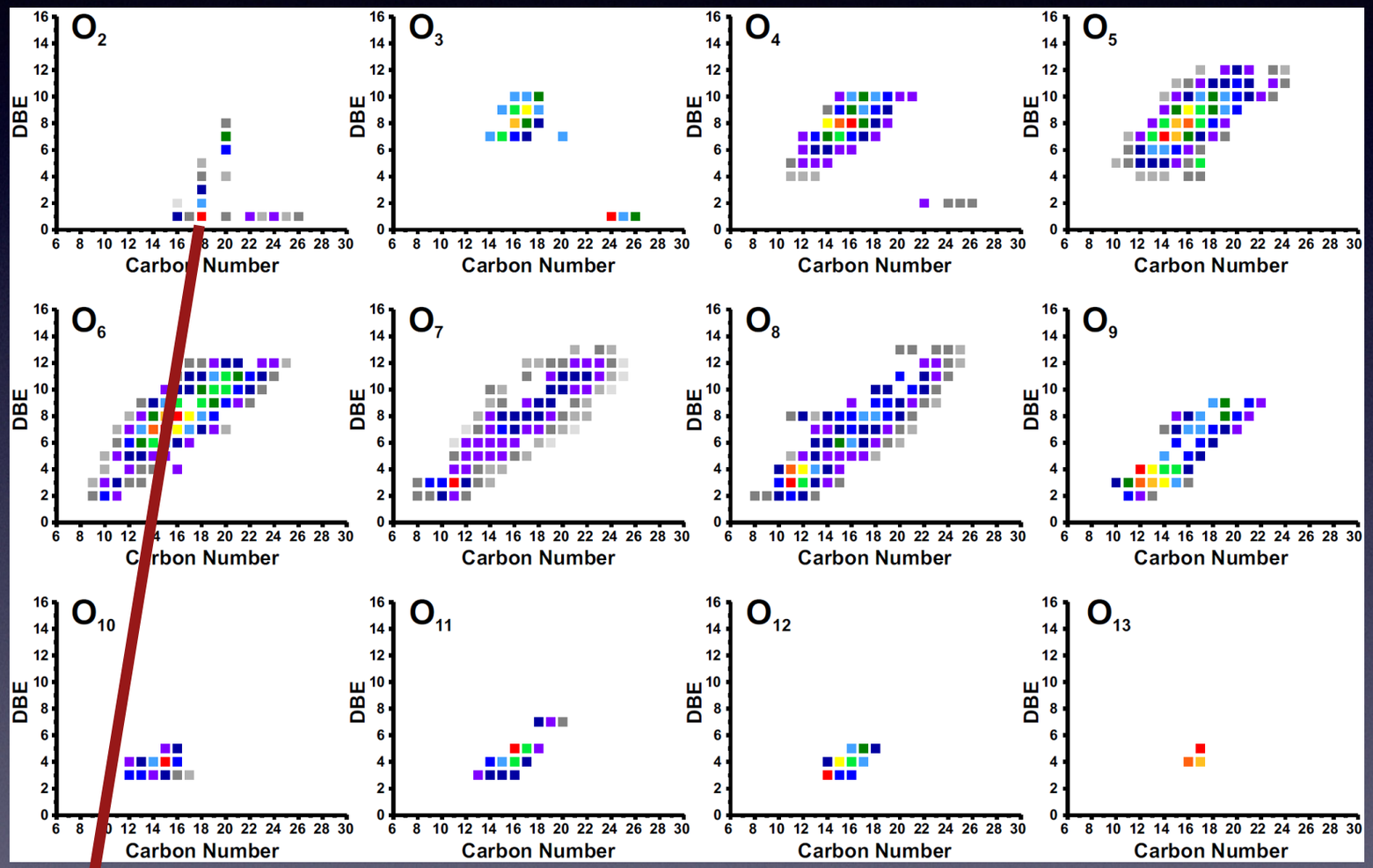

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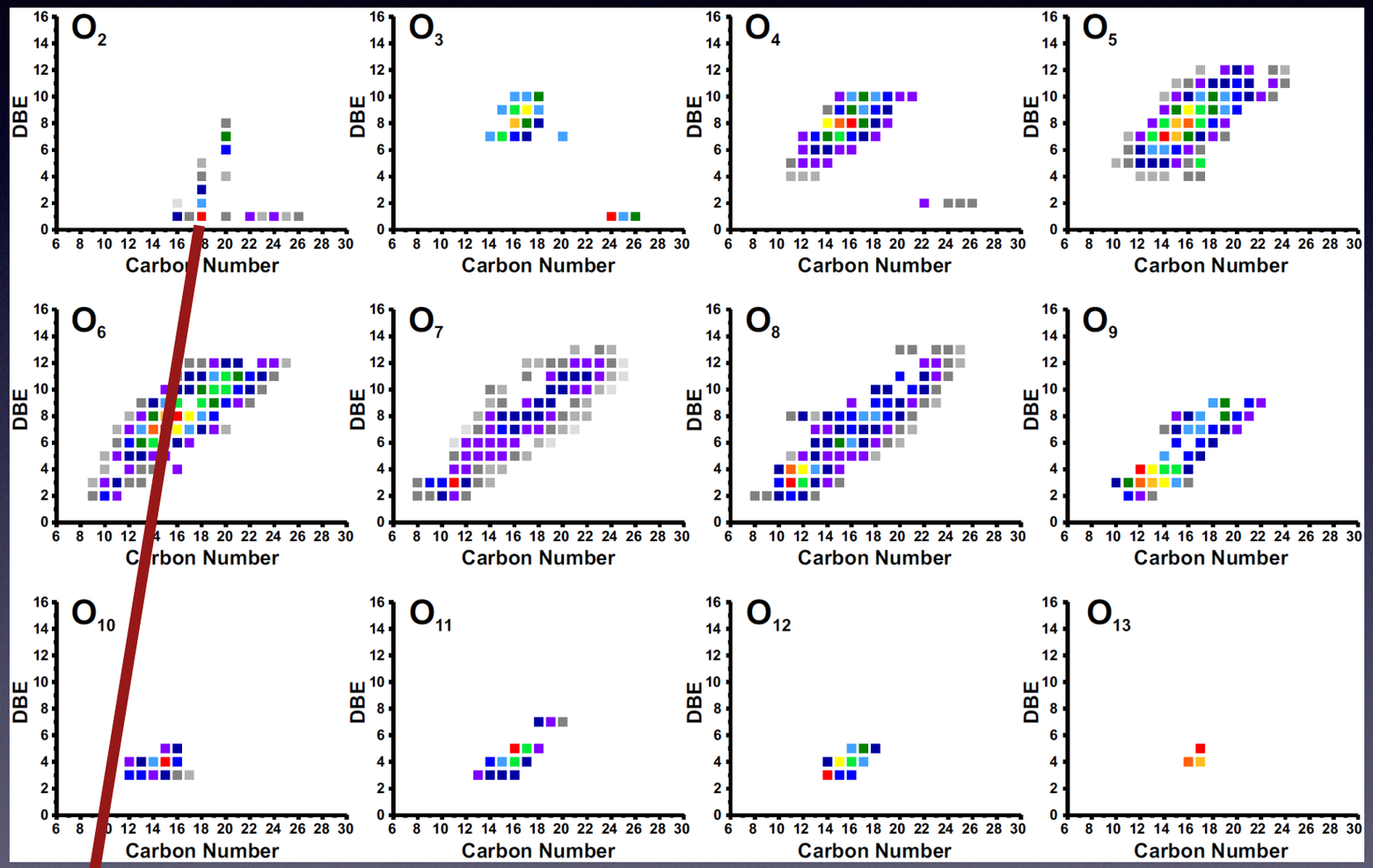

$C_{18}H_{36}O_2$ (DBE = 1)

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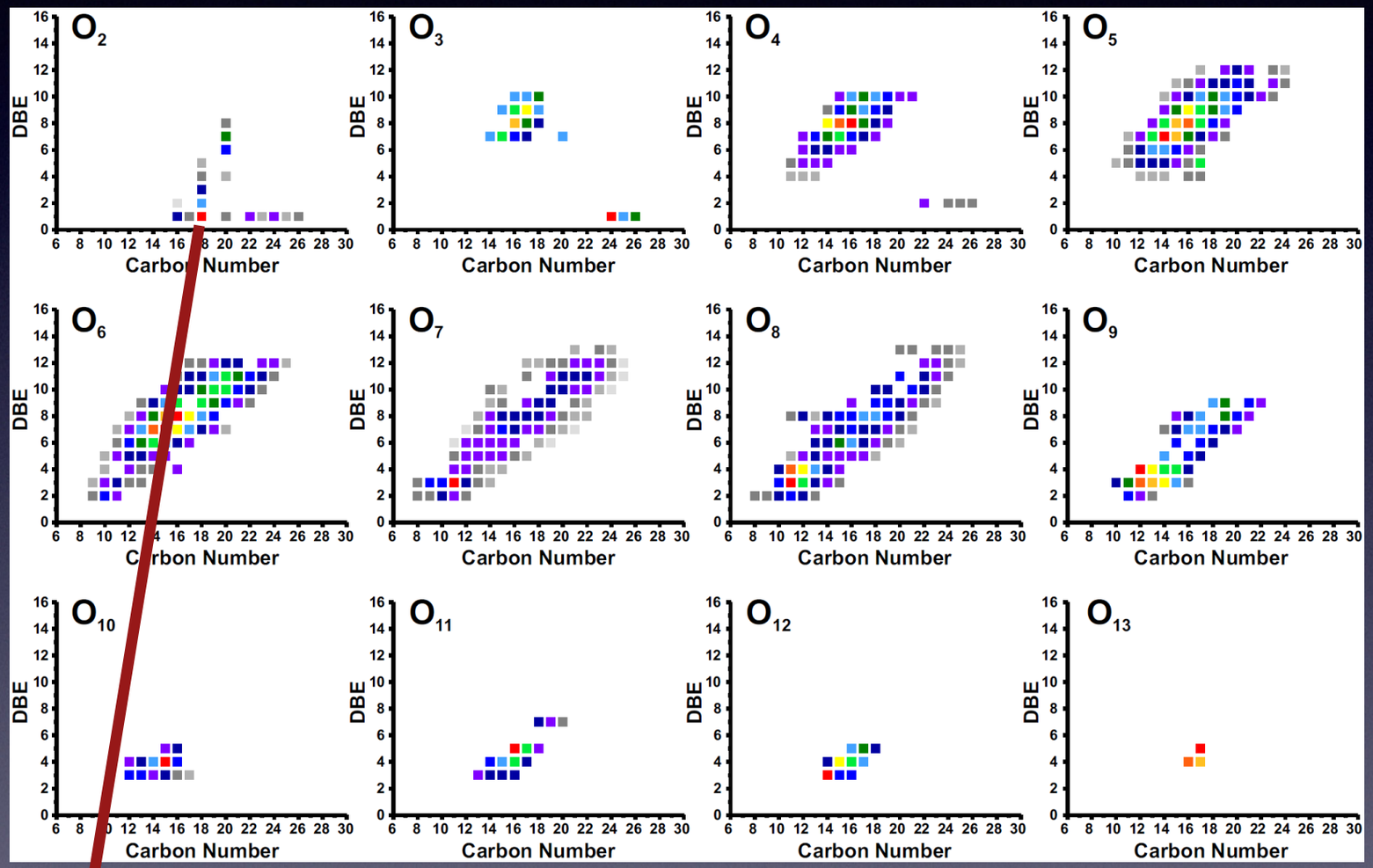

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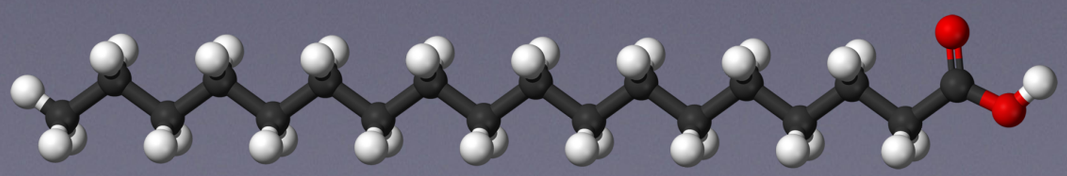

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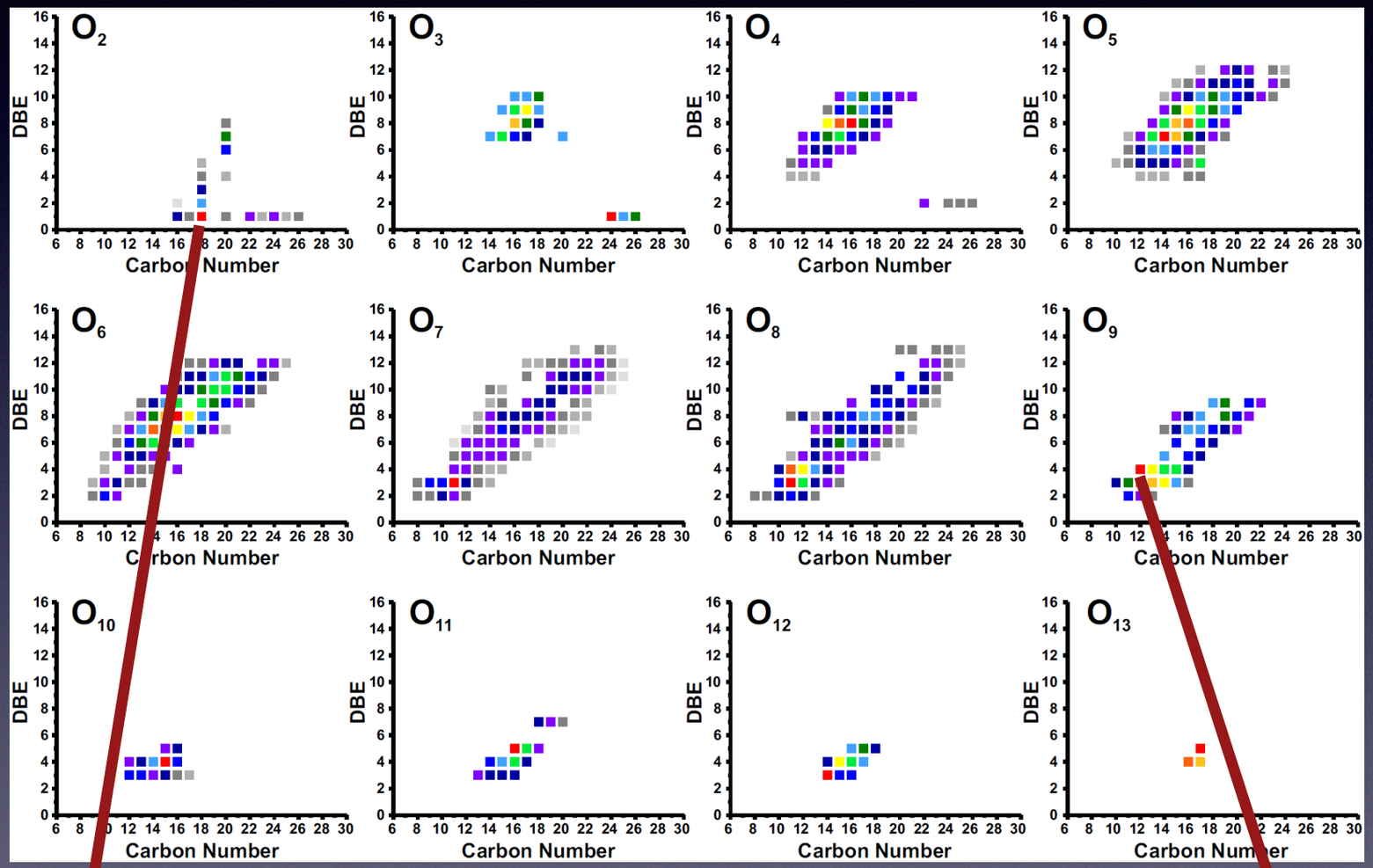

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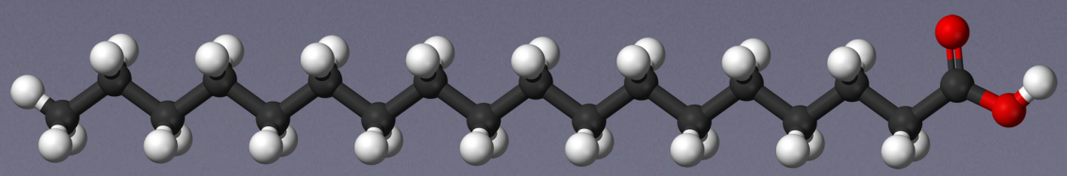

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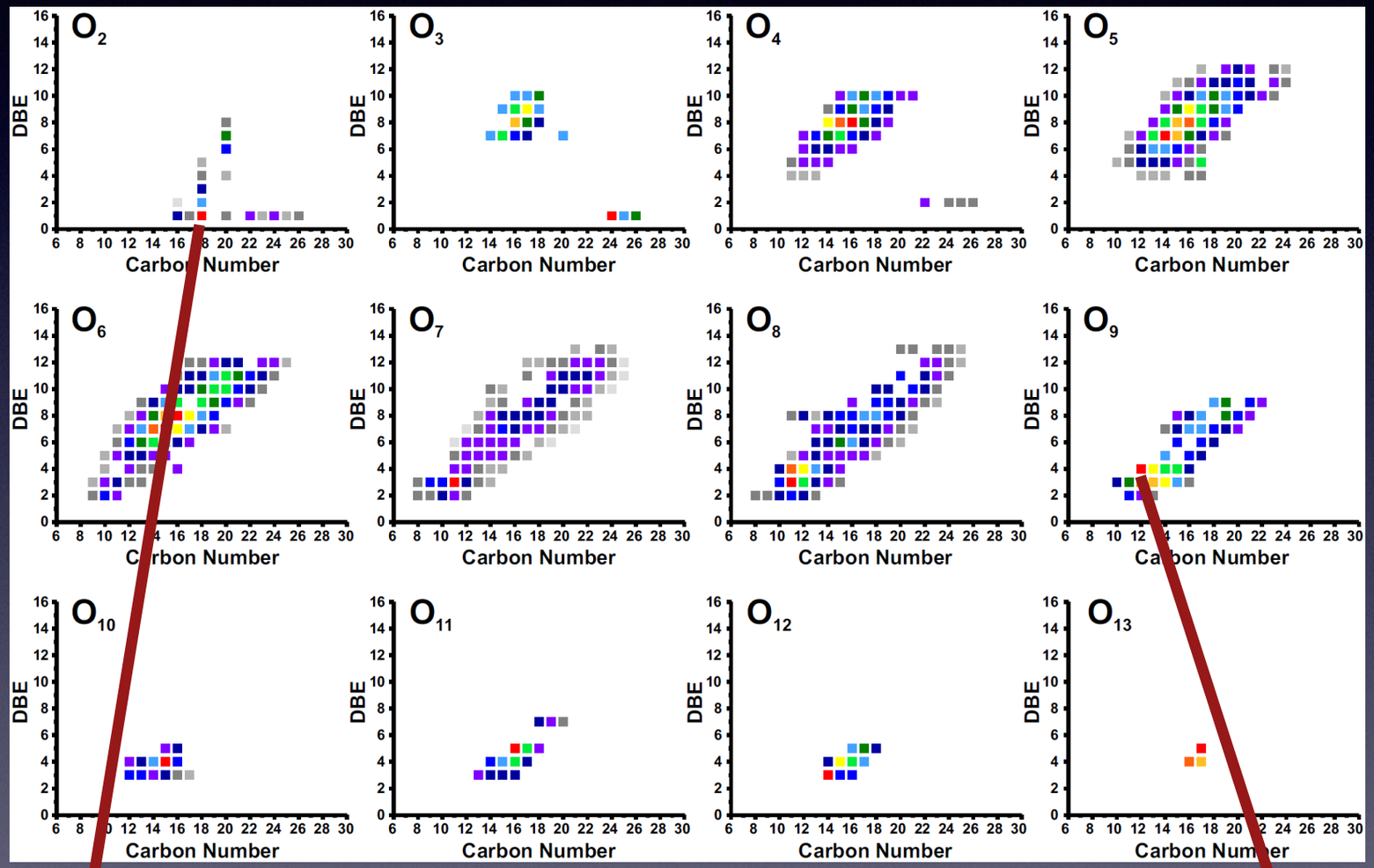

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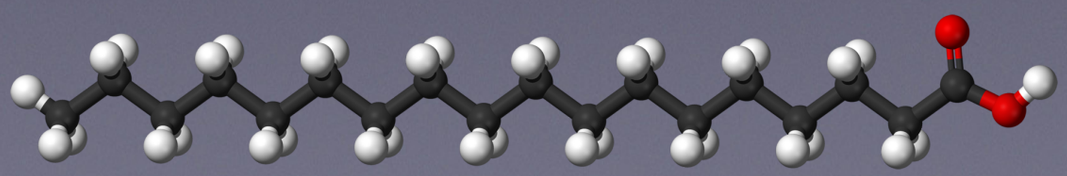

$C_{12}H_{18}O_9$ (DBE = 4)

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