concawe

ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

PETROLEUM SUBSTANCES

WORKSHOP ON SUBSTANCE IDENTIFICATION AND SAMENESS

Helsinki 7 October 2014

Foreword

"**P**etroleum **S**ubstances" (**PS**) in the context of this presentation refer only to those substances which are derived from Crude Oil (Petroleum) or Natural Gas Condensates and for which Concawe prepares the joint part of the REACH registration dossiers.

More than 4,000 registrations have been made by more than 800 Legal Entities for approximately 200 PS.

Other substances derived from Crude Oil and Natural Gas Condensates are managed by specific REACH Consortia, e.g. Petroleum Gases, Stream-cracked products, Hydrocarbon Solvents, Petrochemicals, etc. The discussion in this presentation does not necessarily apply to these substances.

Outline

- Refining processes → variable and complex substances.
- Category approach to avoid underestimating hazard
- Substance ID assignment and use of EC numbers
- Concawe sameness controls and guidance
- Specific Challenges
  1. Classification variations ("Notes")
  2. Composition: Analytical Methods and Challenges
  3. Describing Manufacturing Processes
  4. Blended Fuels
- Summary

Refining

Crude oil

- Is a naturally occurring very complex and variable mix of compounds, primarily hydrocarbons with a wide range of carbon number and molecule type. Crude oil itself is exempt from registration.

"Refining"

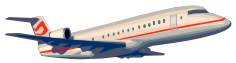
- Is the generic name for the processes used to obtain many different substances from crude oil.
- Distillation is used to separate the crude oil into product-related fractions.
- Chemical treatments and further cycles of fractionation are applied to some streams.
- Finished petroleum products (fuels, lubricants, bitumens, etc.) and chemical feedstocks have more limited composition ranges to meet performance specifications.

Individual petroleum streams

- Are described by process history and boiling point / carbon number range. These parameters give an indication of the chemical composition, which is complex and variable.

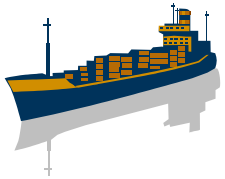

C2-100+

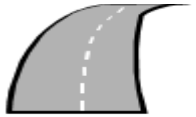

C4-11


C8-15

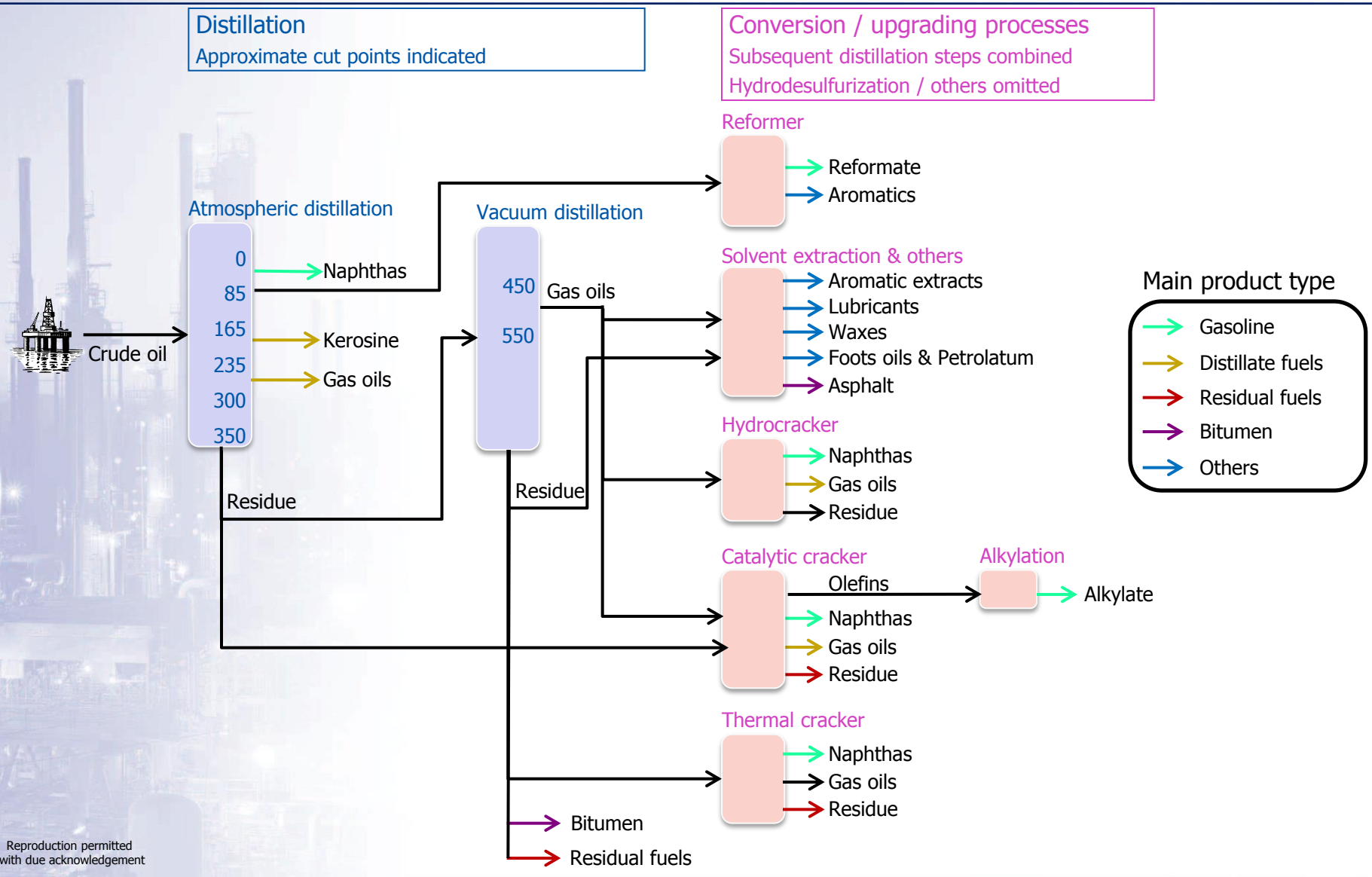

C10-25


C15-65


C20-100+


C35-100+

Fractionation and Chemical Processing (simplified)



Fractionation

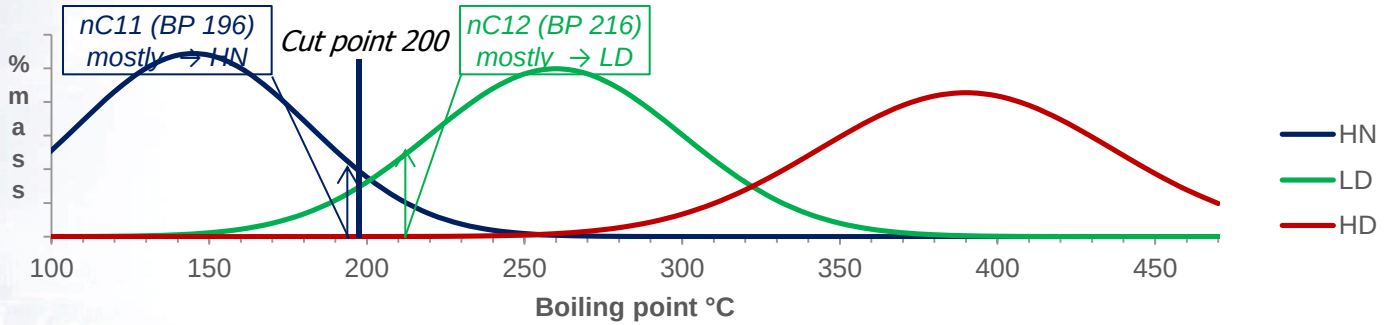
Fractionated distillation splits a feed stream into product streams with components preferentially distilling according to their boiling points.

Due to imperfect separation each product stream includes compounds with true boiling points outside the intended boiling point range.

Cut point °C	
200	→ Heavy naphtha HN
320	→ Light distillate LD
450	→ Heavy distillate HD

Example

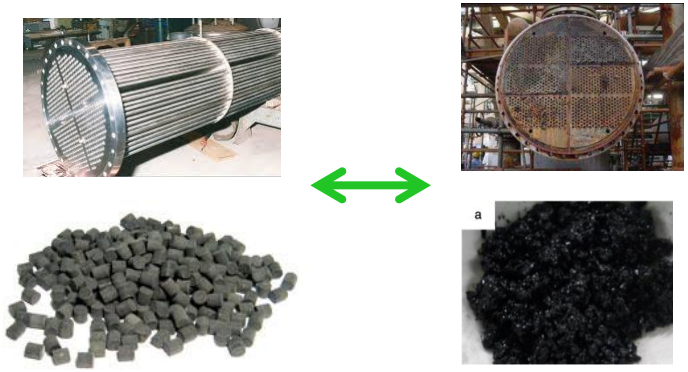
The fractionation scheme for the fictional unit illustrated above could result in product constituent distributions as below, indicated by boiling point ranges



Variability

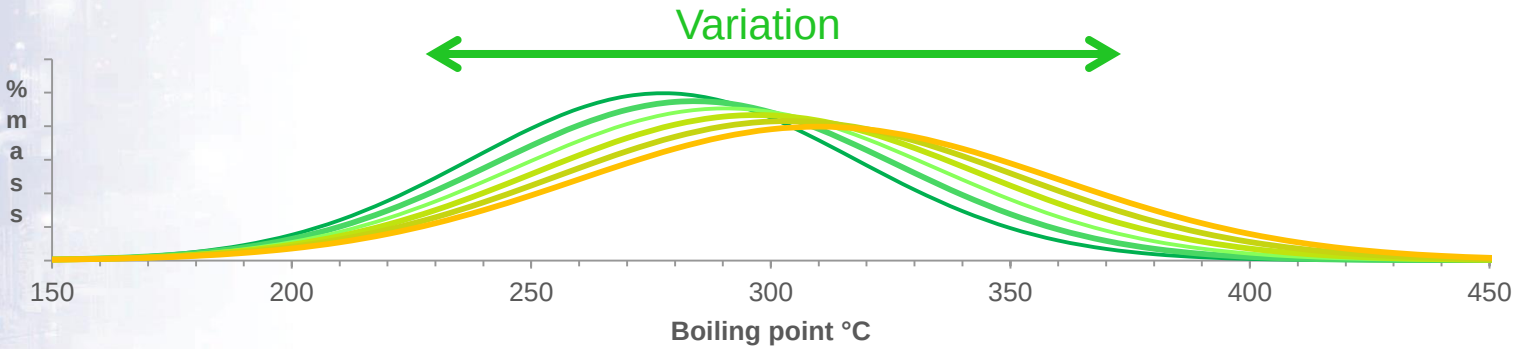
Stream composition varies continuously over time due to several factors

- Feedstock composition
- Processing severity
- Separation temperatures, sharpness
- Catalyst / equipment performance



Example

Illustration below based on previous example



Complexity

PS are UVCBs.

- The number of individual chemical compounds increases rapidly with carbon number.

The predominant compounds are described by carbon number / boiling point ranges and hydrocarbon types.

- Carbon number / boiling point ranges are influenced by fractionation.
- Hydrocarbon types (n-/i-alkanes, aromatics, olefins etc) are influenced by chemical processing.

To correctly and practically consider the hazards, testing is conducted on the *whole substances*, not individual constituents or groups of constituents.

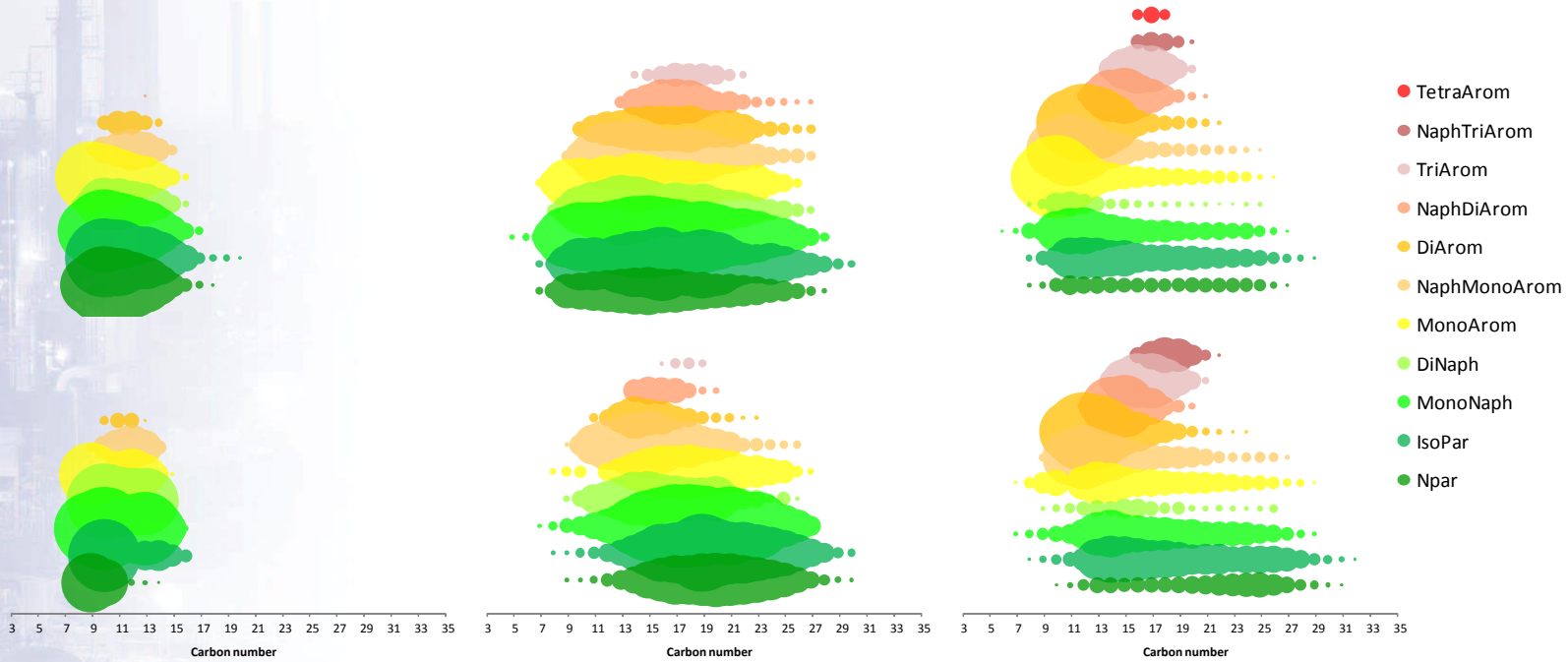
C number	Boiling point °C (n-alkanes)	Number of isomers (linear/branched alkanes only!)	
3	-42		1
4	-1		2
5	36		3
6	69	Gasoline & naphthas	5
7	98		9
8	126		18
10	174		75
15	269	Gas oils	4 347
20	343		366 231
25	402	Heavy products	36 777 419
30	450		4 108 221 447
35	490		493 054 243 760
40	525		62 353 826 654 563

Duties and Challenge for Registrants

Duties on registrants: assign endpoint values & hazard classification to each substance, avoid underestimating hazards & minimize testing.

Challenge: large number of substances with similar compositions that are variable and overlap.

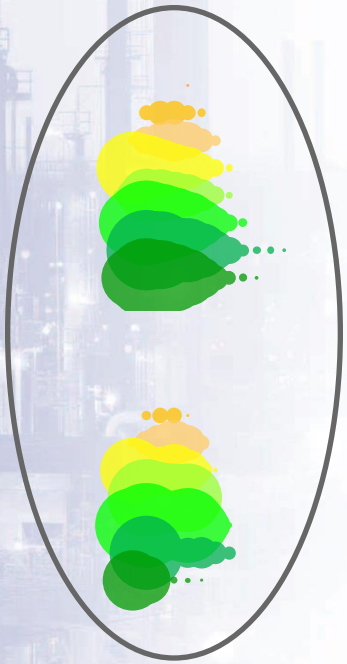
6 example compositions by carbon number / hydrocarbon class



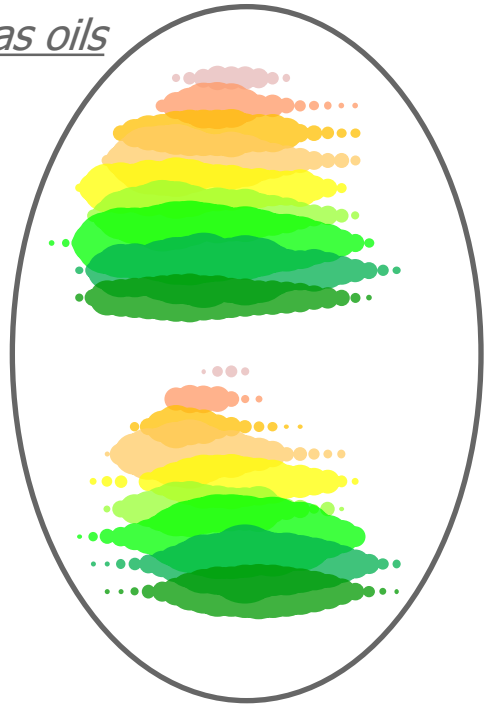
Concawe Category Approach

1. Group substances of similar composition based on process history & carbon number / boiling point range.
2. Per endpoint, identify value or hazard driver(s).
3. Fill in data gaps by read-across from worst case to ensure proper risk mgmt.

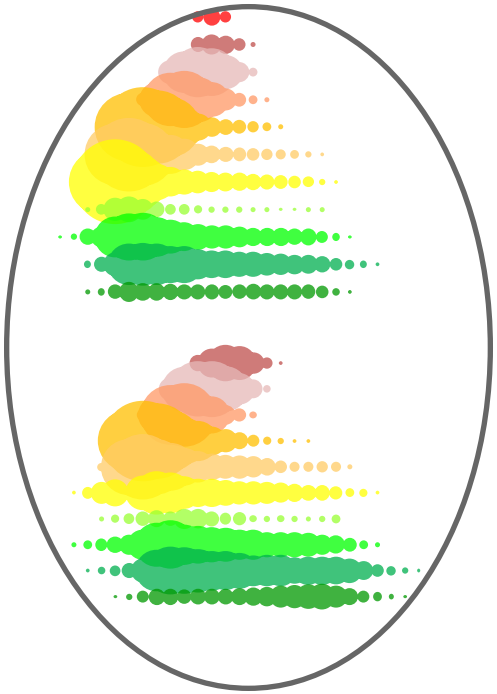
Kerosines



Vacuum/hydrocracked gas oils



Cracked gas oils



Substance ID assignment – Use of EC numbers

The need for substance ID is driven by chemical control regulations (TSCA, REACH, CLP etc), not commercial specification.

Variability and the continuum of products is accommodated by EC inventory entries (EC numbers) which describe the carbon number / boiling point ranges using 'predominantly' & 'approximately'; this leads to a finite and manageable number of substances.

EC #	Substance	Description
265-060-4	Distillates (petroleum), light catalytic cracked	A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers **predominantly** in the range of C9 through C25 and boiling in the range of **approximately 150°C to 400°C**. It contains a **relatively large proportion of bicyclic** aromatic hydrocarbons.
265-062-5	Distillates (petroleum), intermediate catalytic cracked	A complex combination of hydrocarbons produced by the distillation of products from a catalytic cracking process. It consists of hydrocarbons having carbon numbers **predominantly** in the range of C11 through C30 and boiling in the range of **approximately 205°C to 450°C**. It contains a **relatively large proportion of tricyclic** aromatic hydrocarbons.

Existing EC inventory entries are preferred rather than inventing multiple new substance ID's.

Principle accepted under REACH/CLP:

- Phase-in status
- Harmonized classifications
- Annex XIV (authorization) / XVII (restriction) lists

} could be bypassed if multiple new substance IDs created

Concawe SID Guidance and Sameness Controls

Concawe goal is to ensure that members of joint submissions are entitled to register together.

Concawe inventory is based on EINECS *

- Includes intermediate streams and finished fuels.
- Substance as produced from crude oil or natural gas condensates.

Substance identity / composition in registrant dossiers

- Concawe guidance is consistent with ECHA Guidance on identification and naming, specifically for petroleum substances (section 4.3.2.2).
- In IUCLID Section 1.2 report classification markers, hydrocarbon classes, and individual constituents present at > 10% w/w

Controls on licence purchase

- 2010: Registrant responsible for identification of substance. Dossier is licensed for substance described by EC/CAS number.
- 2013 through 2015: Request for analytical data to verify boiling point / carbon number ranges and hydrocarbon classes.
- Corrected obvious mismatches based on composition. Some subs assigned to different EC#s, others excluded from category.

* Exceptions for MK1 diesel and naphtha polymerizates

Classification Variations ("Notes")

Some classifications can vary depending on certain component concentrations and/or physico-chemical properties, as described by regulatory "**Notes**", included in CLP Annex VI.

The thresholds in the Notes relate to minor constituents (e.g. benzene) that do not drive substance identity.

Index No	International Chemical Identification	EC No	CAS No	Classification		Labelling			Specific Conc. Limits, M-factors	Notes
				Hazard Class and Category Code(s)	Hazard statement Code(s)	Pictogram, Signal Word Code(s)	Hazard statement Code(s)	Suppl. Hazard statement Code(s)		
649-310-00-3	Aromatic hydrocarbons, C_8, catalytic reforming-derived; Low boiling point cat-reformed naphtha	295-279-0	91995-18-5	Carc. 1B Muta. 1B Asp. Tox. 1	H350 H340 H304	GHS08 Dgr	H350 H340 H304			▶M2 — P

Note P: "*The classification as Carc/Muta need not apply if it can be shown the substance contains <0.1 % benzene*"

The relevant substances still have single identities and joint registrations.

Use of classification to determine (or as part of) identity would be problematic.

Composition: Analytical Methods & Challenges

There is no universal set of methods for all the petroleum substances.

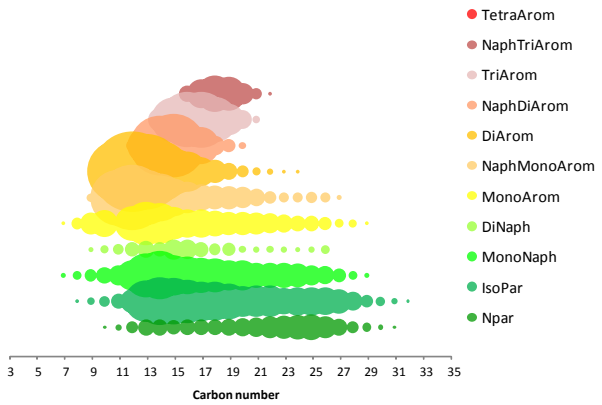
Complexity makes "full" analysis /identification of all constituents impossible.

The heavier the product the less detail is possible – for higher C numbers it is only feasible to specify hydrocarbon classes (groups of constituents).

"Standardized" techniques give data sufficient for commercial purposes. (hydrocarbon class totals; boiling range; PIONA to ~C11)

"Advanced" techniques give more detail but with limitations.

GC x GC gives hydrocarbon classes by carbon number up to ~C30.
PAH analysis detects certain defined PAH constituents.



Composition: Analytical Methods & Challenges (II)

A realistic view on compositional characterization of petroleum UVCB's is needed due to the large number of constituents.

2014-5 Work plan

- Concawe will analyse samples of each registered substance with both standardized and advanced techniques, including identification of constituents expected to drive hazards.
- Concawe recommends registrants to continue analysing their substances with standardized techniques.
- If standardized results are within the Concawe-reported ranges and the manufacturing process applies, it can reasonably be assumed that detailed composition is within the range covered by the Concawe category.

Describing Manufacturing Processes

Each company/refinery/plant has slight differences in manufacturing processes. The challenge is how to be sufficiently specific in manufacturing process description without defining each company's product or batch as a different substance.

Concawe approach is to follow the established EINECS level of detail.

✓	✓	✓	✘
Feedstock type	Crude oil or natural gas condensates	Multi-stage processes	Specific crude oil field
Chemical processing	Basic reaction type (cracking, reforming, hydrotreatment)	Type of reactions (hydro- catalytic- thermal- cracking, alkylation)	Reactor pressure, temperature, catalyst details
Physical separation	Distillation / solvent extraction	Atmospheric pressure vs. Vacuum; approx. cut points	Precise pressures & cut points

Increasing detail → Excessive detail

Blended Fuels

Some substances on EINECS (e.g. gasoline, diesel, fuel oil) are produced by blending multiple streams in an integrated manufacturing process; they are considered as substances, not mixtures.

- Composition is constrained by specifications not process
  - Explicitly: benzene, aromatics, olefins
  - Implicitly: boiling/evaporation limits, density, octane / cetane ratings
- Identities only cover petroleum components, not biofuels etc.
- Describing such substances as mixtures would be unworkable in complex supply chains
  - SDS would have to list all **possible** blend components (up to 70, but hazard and risk management information is identical for all)
- Hazards not understated:

Product	Components	Hazard approach
Gasoline	Naphthas, butane	As naphthas (CMR)
Diesel	Treated/hydrocracked gasoils, kerosine	As hydrocracked gasoils (Carc 2)
Fuel oil	Any (mostly "HFO components")	CGO/HFO (CMR)
Asphalt	Vacuum residue, propane asphalt	Non hazardous

Summary

- Petroleum substances are variable and complex and arise from many refinery processes
- Concawe category approach to avoid underestimating hazard
- SID based on EC descriptions (C number range/ Boiling point range / Process)
- Concawe guidance consistent with REACH SID guidance
- Ongoing programme to gather more analytical data
- Identify substances that are obvious outliers from category based on C number / B.pt range / hydrocarbon classes