UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Steam Cracking:
from Feedstock Analysis to Plant Optimization

Stoomkraken:
van voedingsanalyse tot fabrieksoptimalisatie

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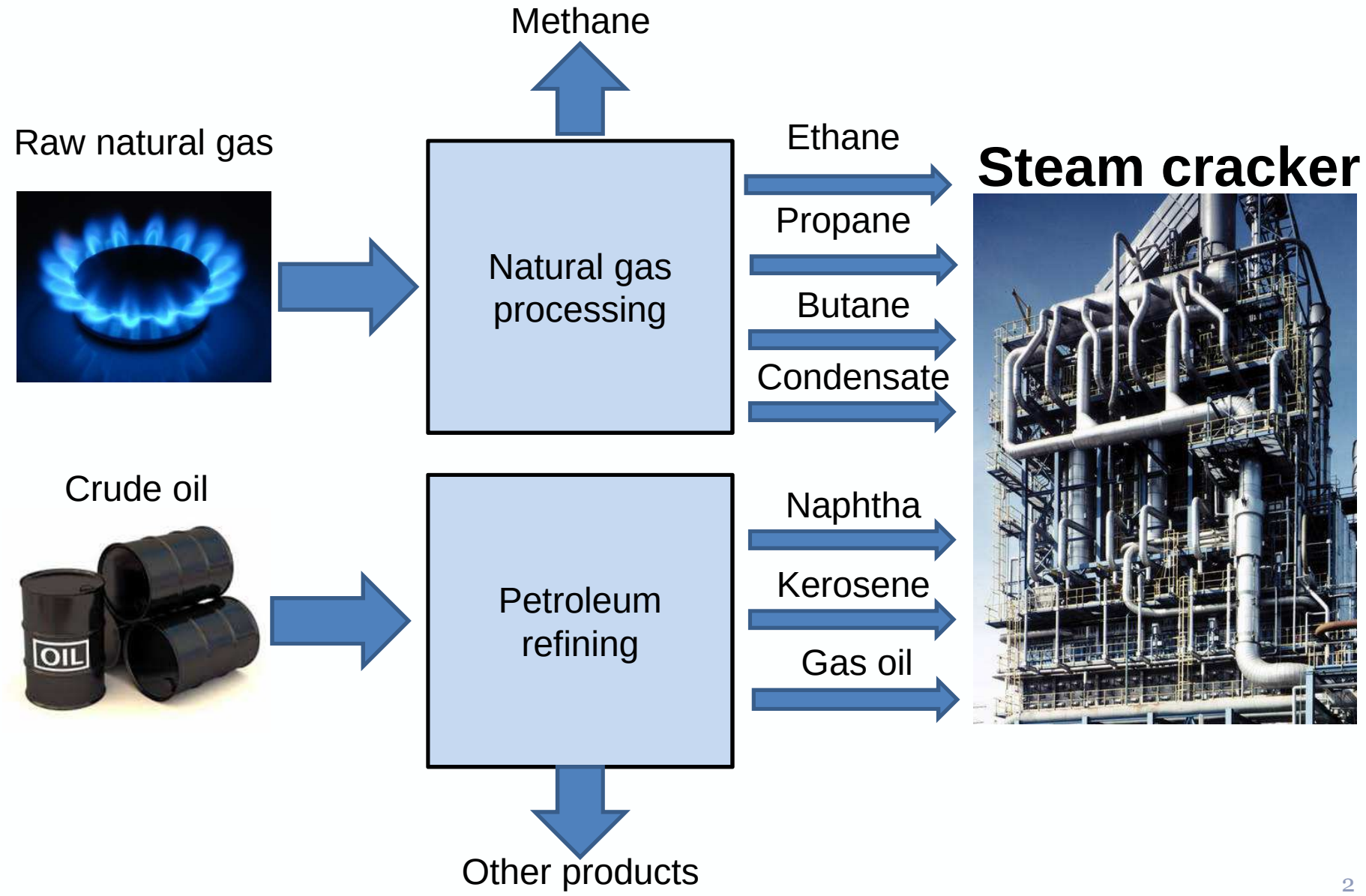
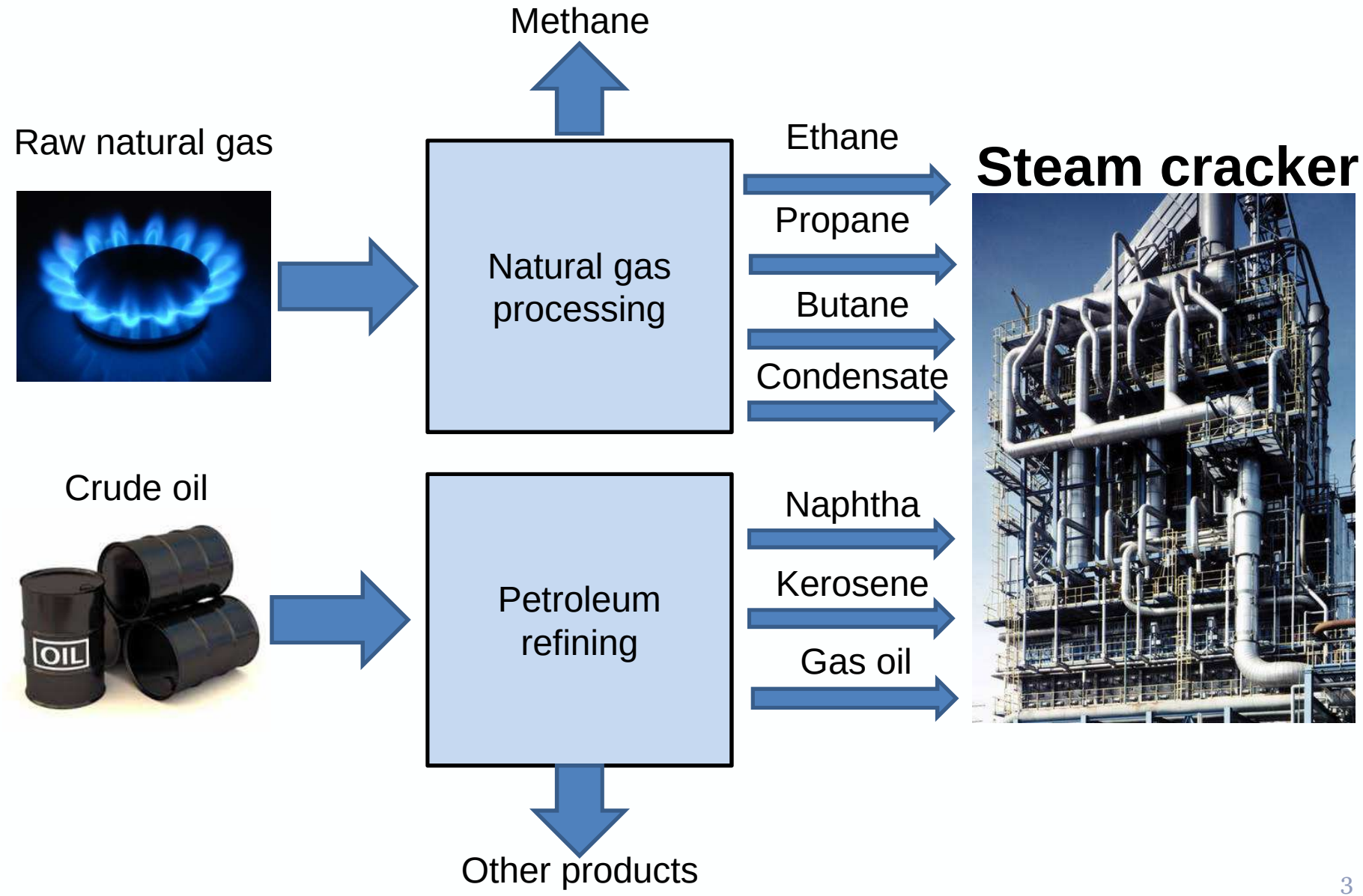
The heart of a petrochemical plant



The heart of a petrochemical plant



The heart of a petrochemical plant

Steam cracker

Ethylene

Propylene

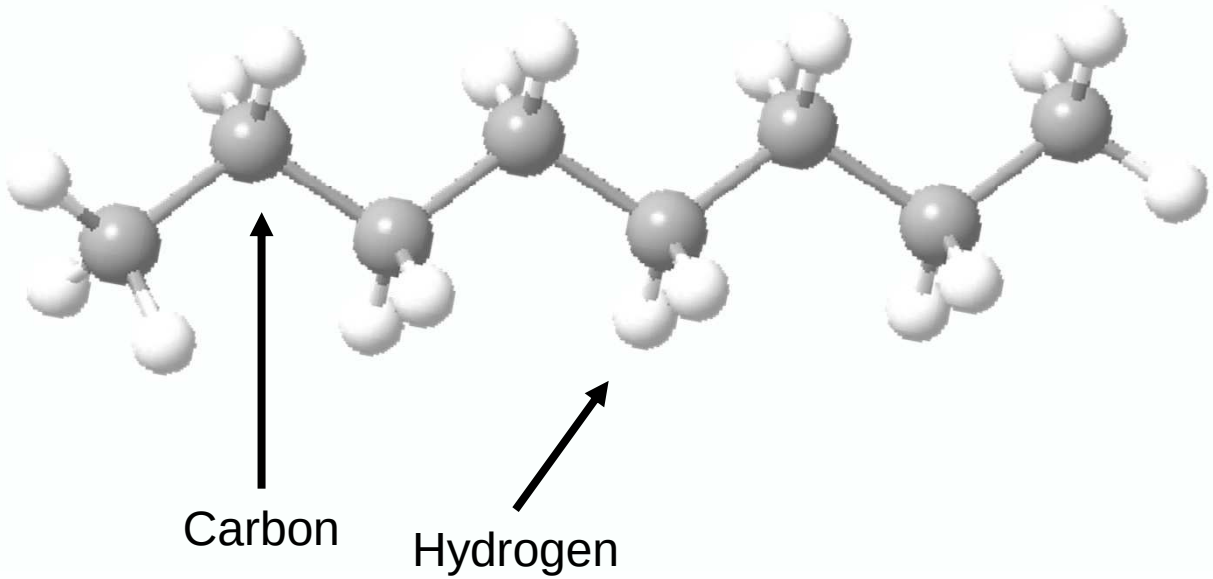
Butadiene

Benzene

Polyolefin plants,…

Crash course hydrocarbon chemistry

Hydrocarbons is a chain of carbon atoms linked to hydrogen

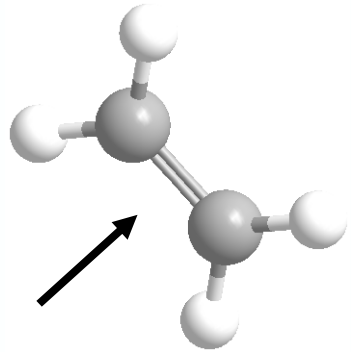


Carbon number = Number of carbons in the chain
Elemental composition = Relative amount of H, C, … on a 100% scale (weight based or mole base)
Branched hydrocarbons = Carbons with branches instead of a straight chain

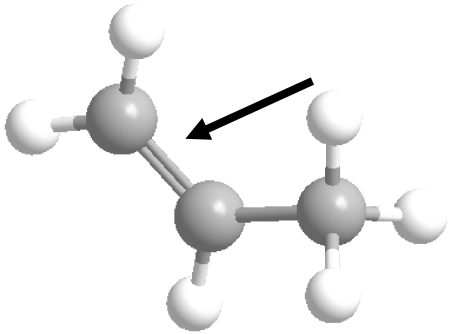
Cracking = Breaking of those chains to form smaller unsaturated hydrocarbons
New bonds can off course also be formed during the process

Crash course hydrocarbon chemistry

Unsaturated hydrocarbons have a double bond between two carbon atoms



Ethylene

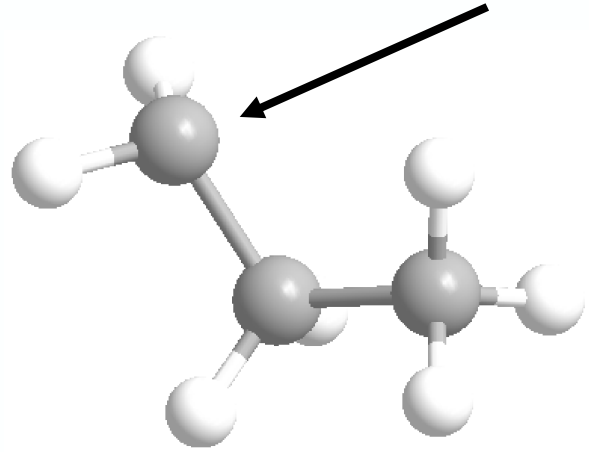


Propylene

It is this double bond that provides the reactivity needed for the downstream processes and makes these molecules special

Crash course hydrocarbon chemistry

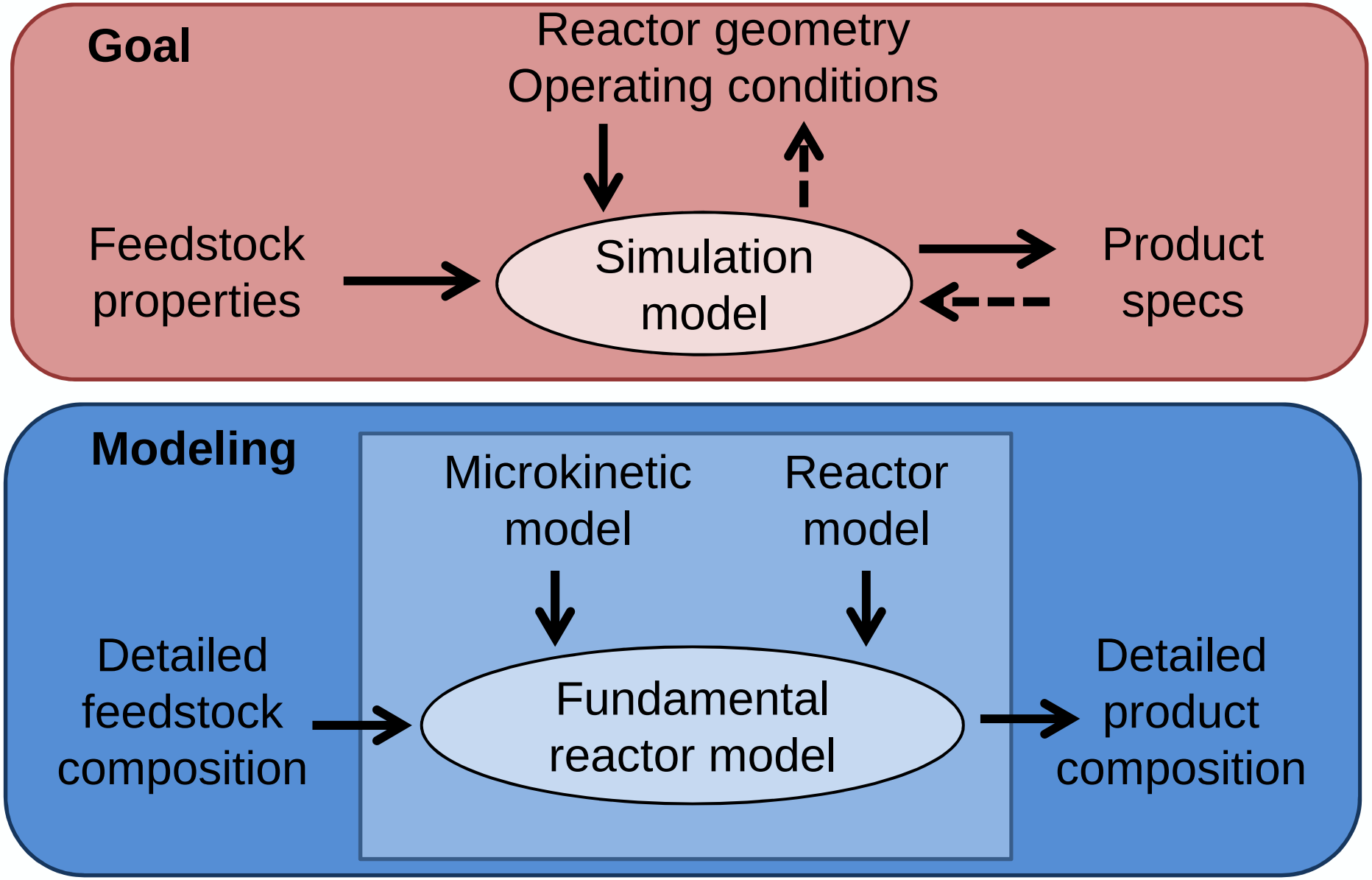
Radical are species that have a missing bond



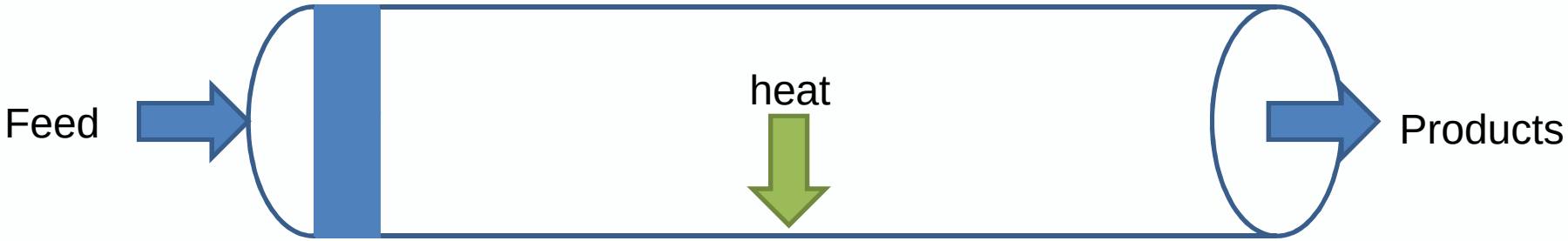
This missing bond makes them very reactive and unstable

These are important intermediate species for steam cracking

Developing of a model for steam cracking



Plug flow reactor model



Molecules and radicals move as a plug through the reactor and each individual plug does not influences other plugs

Energy (heat) can go in or out of the reactor

Mass balances ($N_{species}$)

$$\frac{dF_j}{dz} = \left(\sum_{k=1}^{n_r} v_{kj} r_k\right)\Omega$$

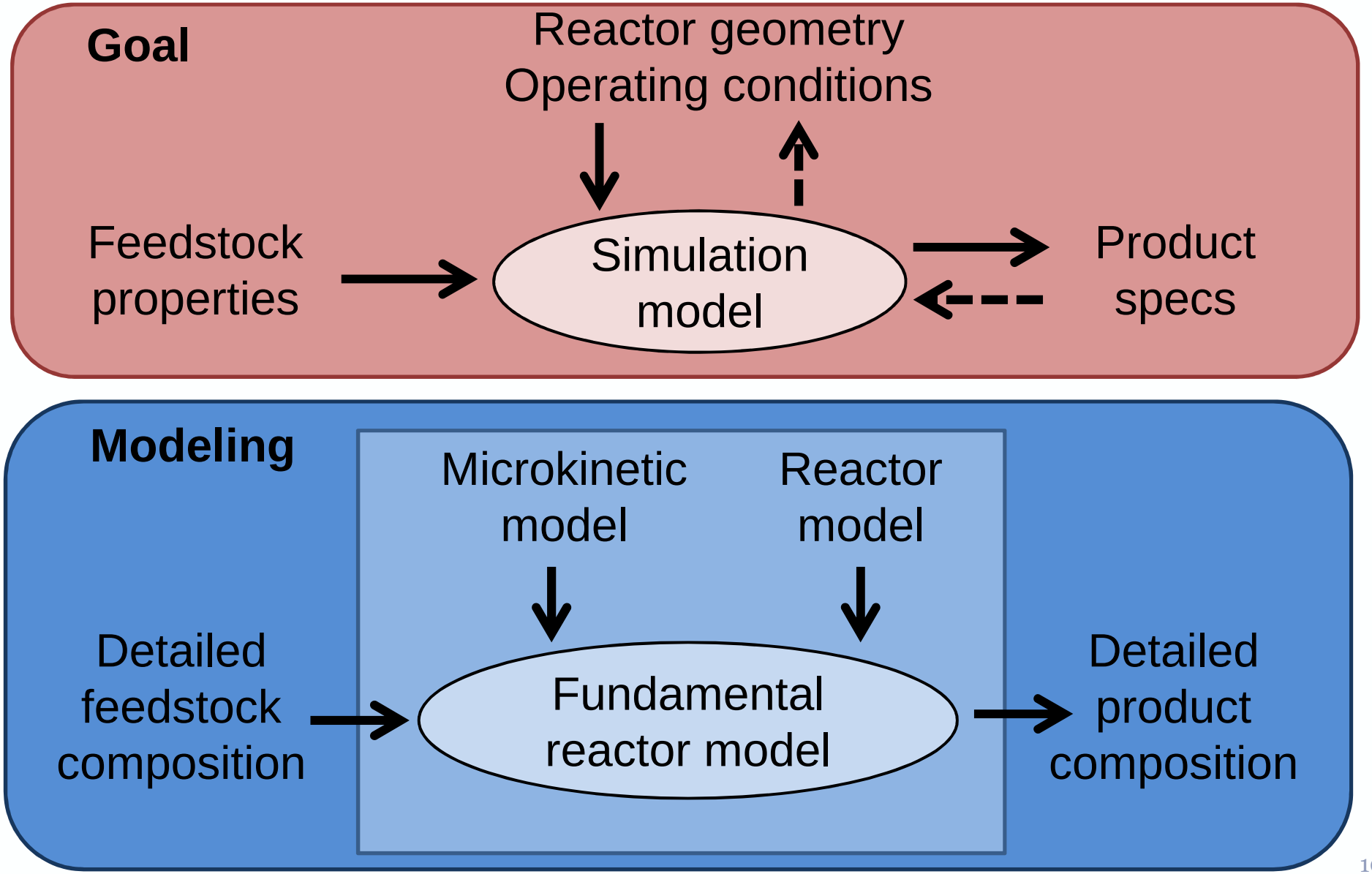
Energy balance (1)

$$\sum_{j=1}^{n_s} F_j c_{p,j} \frac{dT_g}{dz} = \omega q + \Omega \sum_{k=1}^{n_r} r_k . (-\Delta H_k)$$

Momentum balance (1)

$$\frac{dp_{t,g}}{dz} = -\left(\frac{2f}{d_i - 2d_c} + \frac{\zeta}{\pi r_b}\right)\rho_g v_g^2 - \rho_g v_g \frac{dv_g}{dz}$$

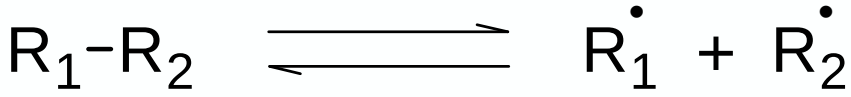
Developing of a model for steam cracking



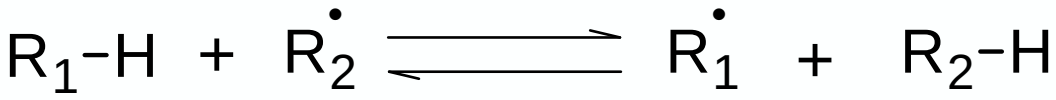
Main reaction families

Reaction Families:

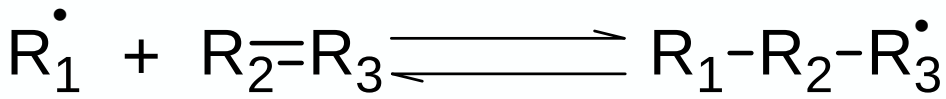
Bond dissociation and radical recombination



Hydrogen abstraction (inter- and intramolecular)



Radical addition and β-scission (inter- and intramolecular)



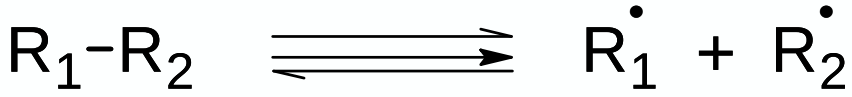
Need to limit the reaction size

μ radical hypothesis

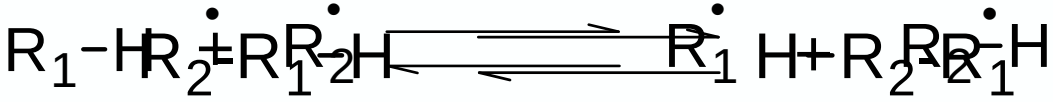
μ hypothesis =

Monomolecular reactions dominate for long chain radicals (#C>5)

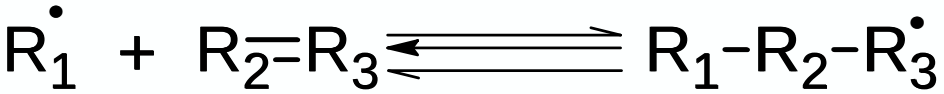
Bond dissociation and radical recombination

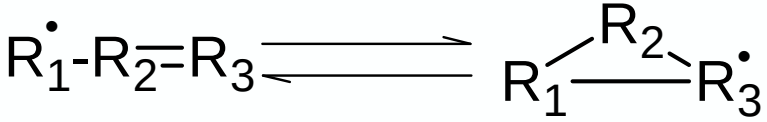


Hydrogen abstraction (inter- and intramolecular)

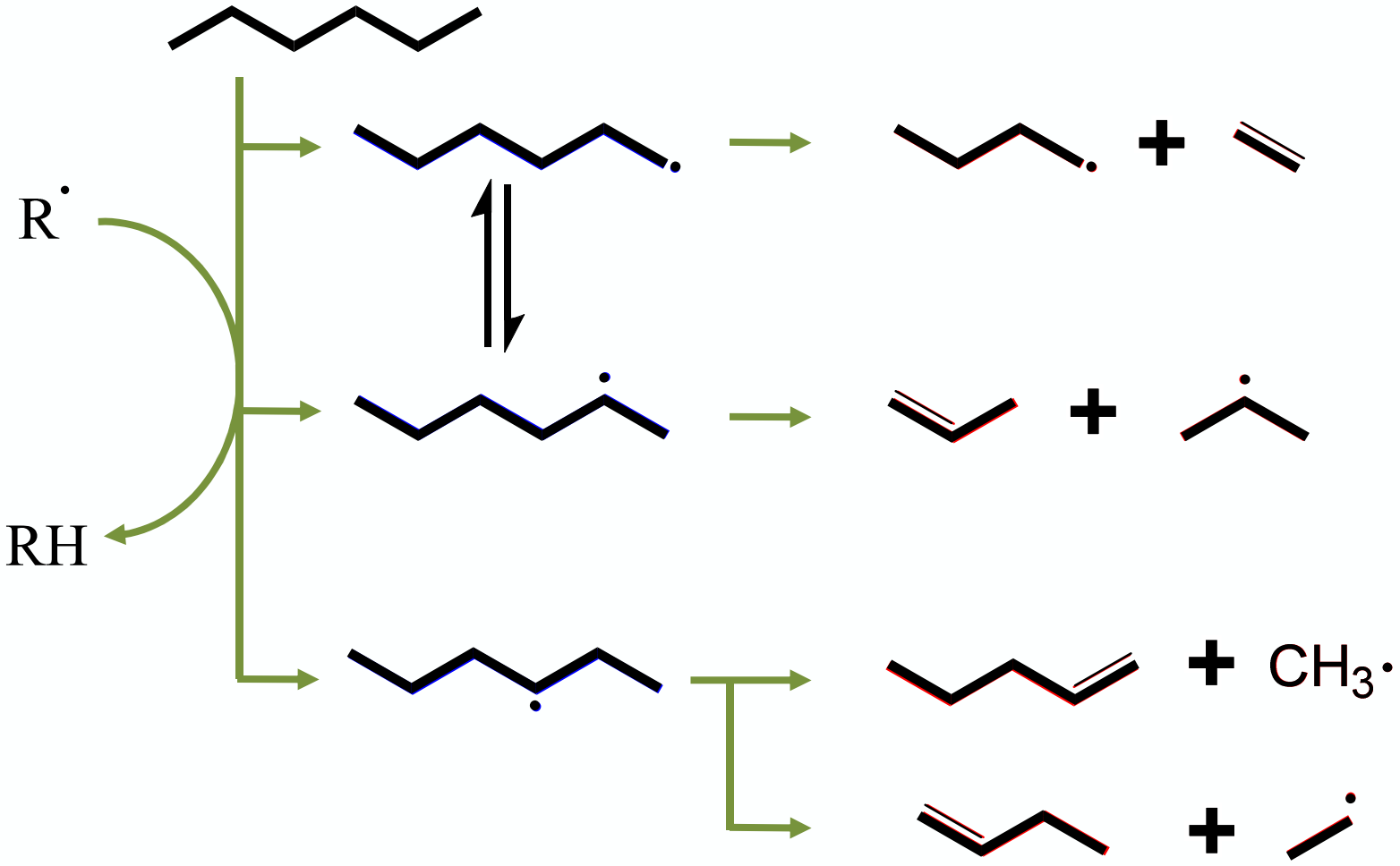


Radical addition and β-scission (inter- and intramolecular)





Decomposition scheme: hexane



β molecules

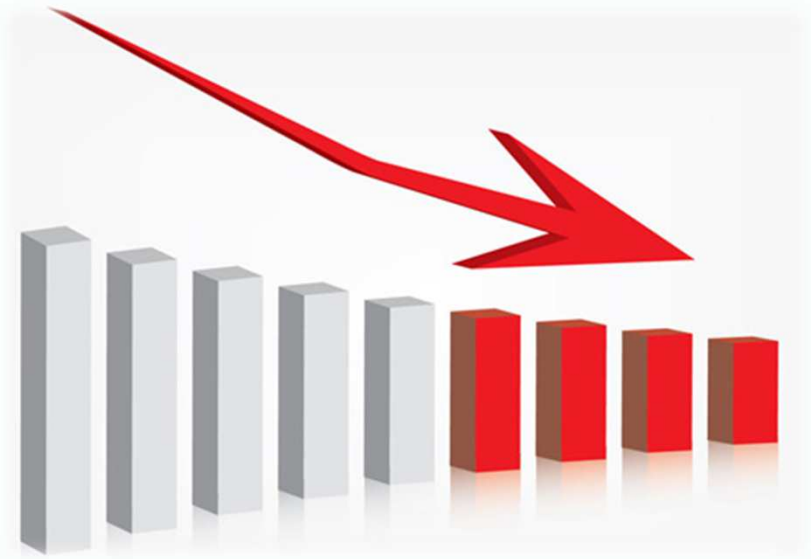
QSSA species

Decomposition scheme: hexane (2)

Applying QSSA reduces this reaction scheme to:

$$n\,C_6H_{14} + R^{\bullet} \rightarrow \sum_{j=1}^{n_{ol}} \frac{k^{pseudo}(O_j)}{\left(\sum_{i=1}^{3} k_i\right)} O_j + \sum_{l=1}^{n_{rad}} \frac{k^{pseudo}(\beta)}{\left(\sum_{i=1}^{3} k_i\right)} \beta + RH$$

- Drastic reduction of the number of species to need to be considered in the final ODE's
- Drastic reduction of the number of reactions

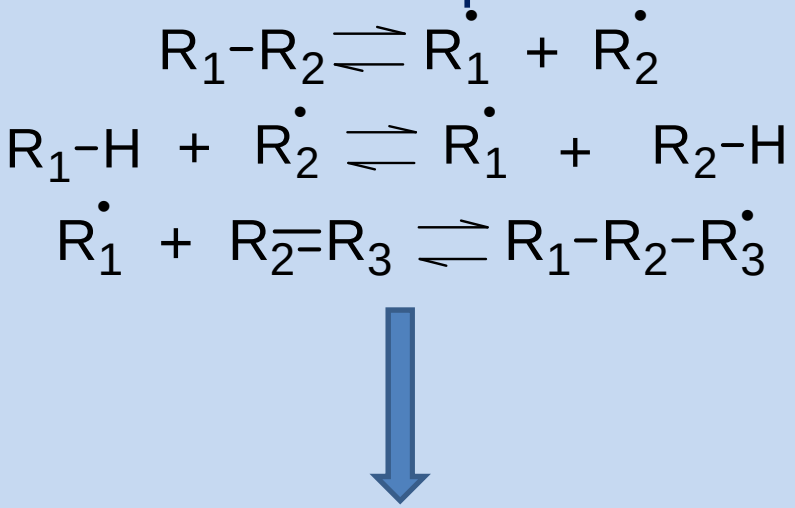


Microkinetic network

CRACKSIM

β network

Bi- and monomolecular reactions for β radicals



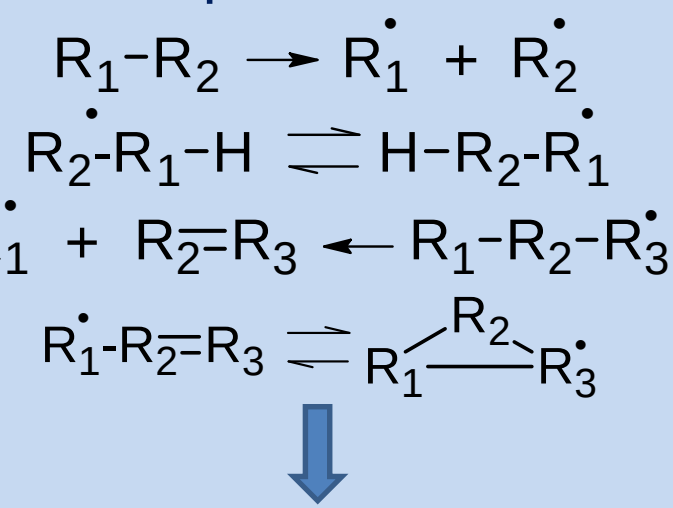
1324 reversible reactions

51 molecules

43 radicals

μ network

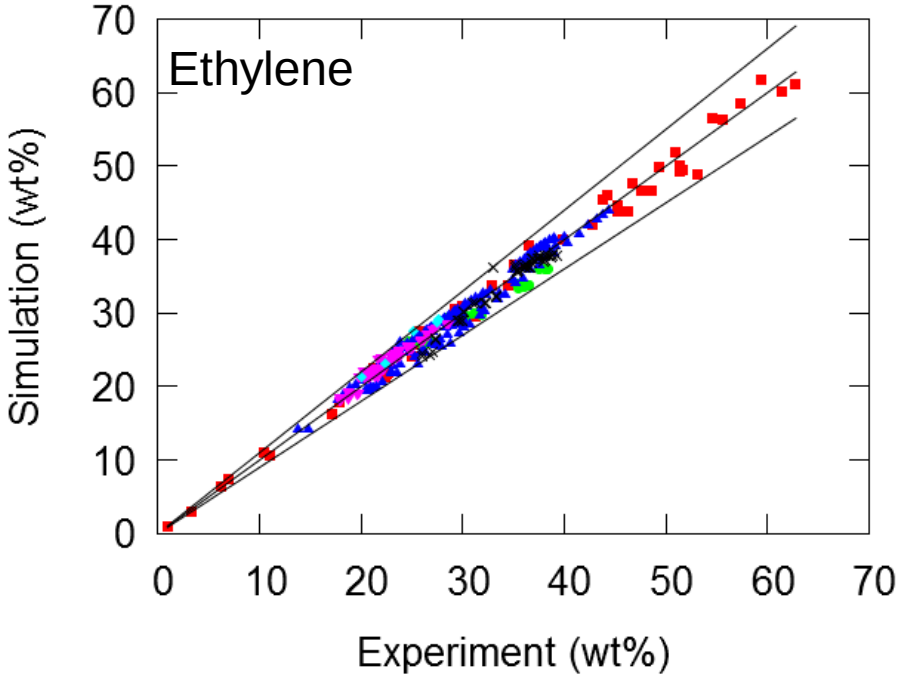
Monomolecular reactions for μ radicals

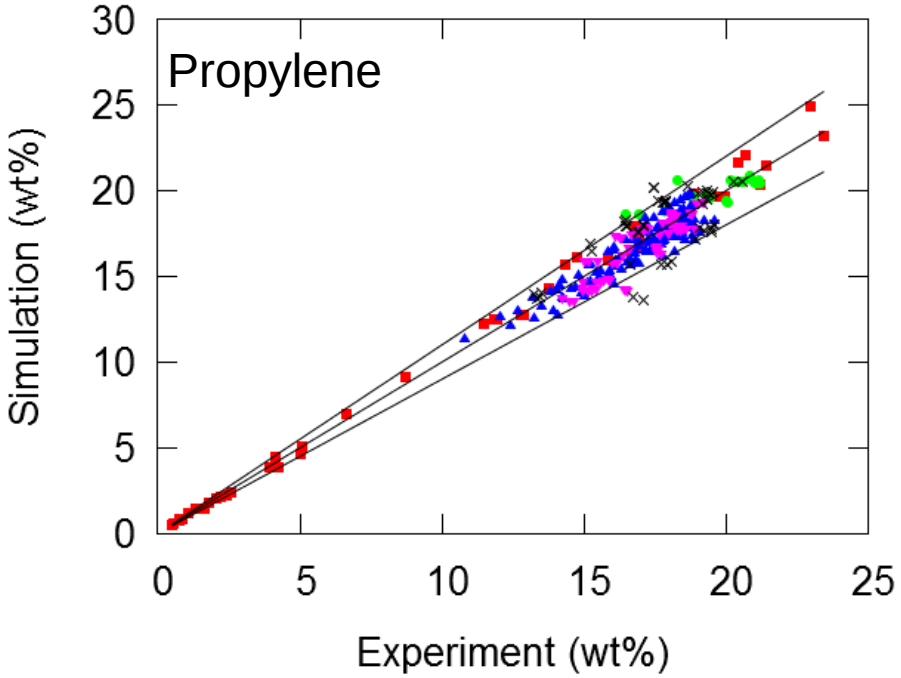


13584 schemes

676 molecules

Validation radiant coil

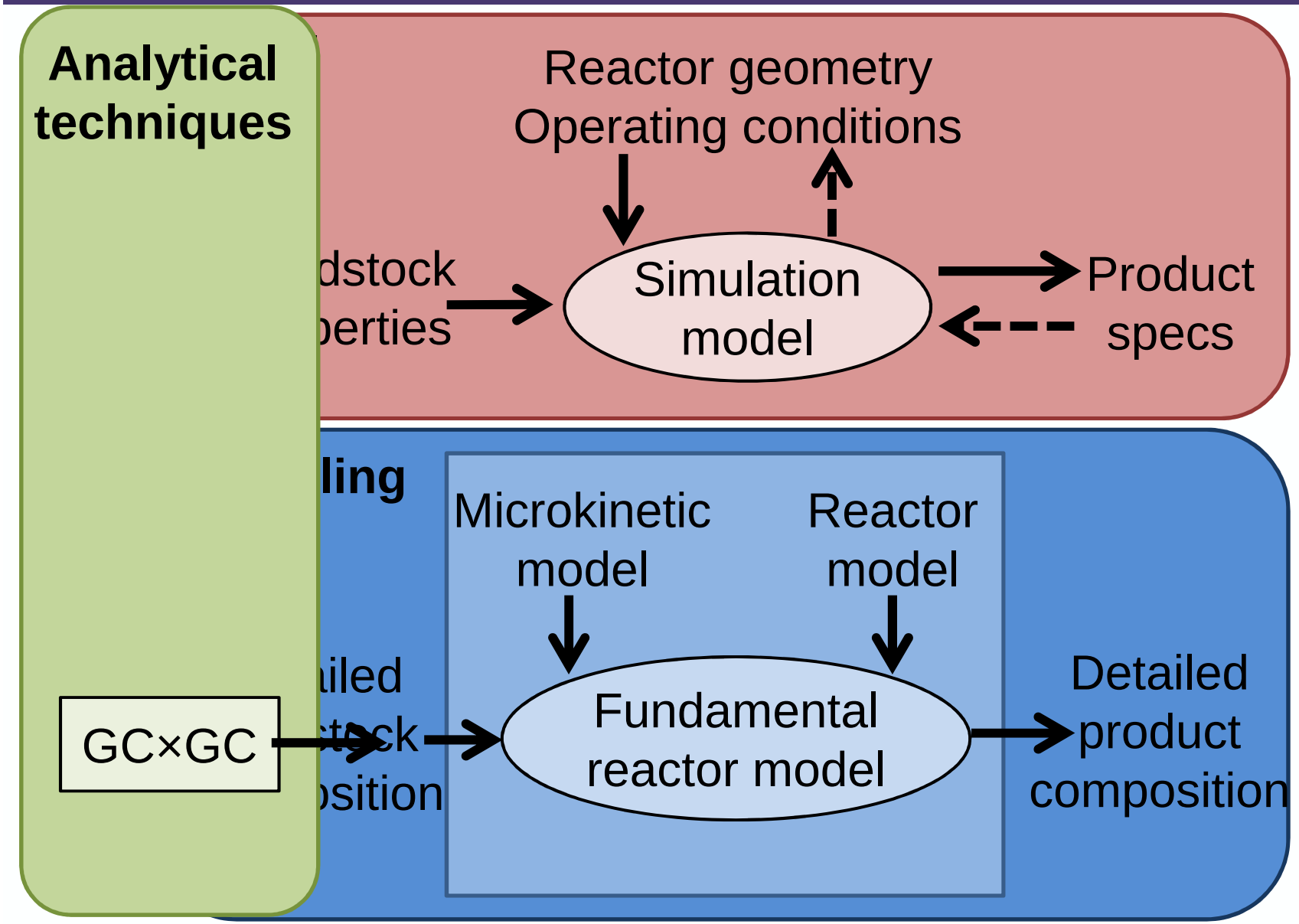




Feedstocks:

- Ethane and/or Propane
- Butane
- Naphtha
- Gas condensate
- Gasoil
- Other

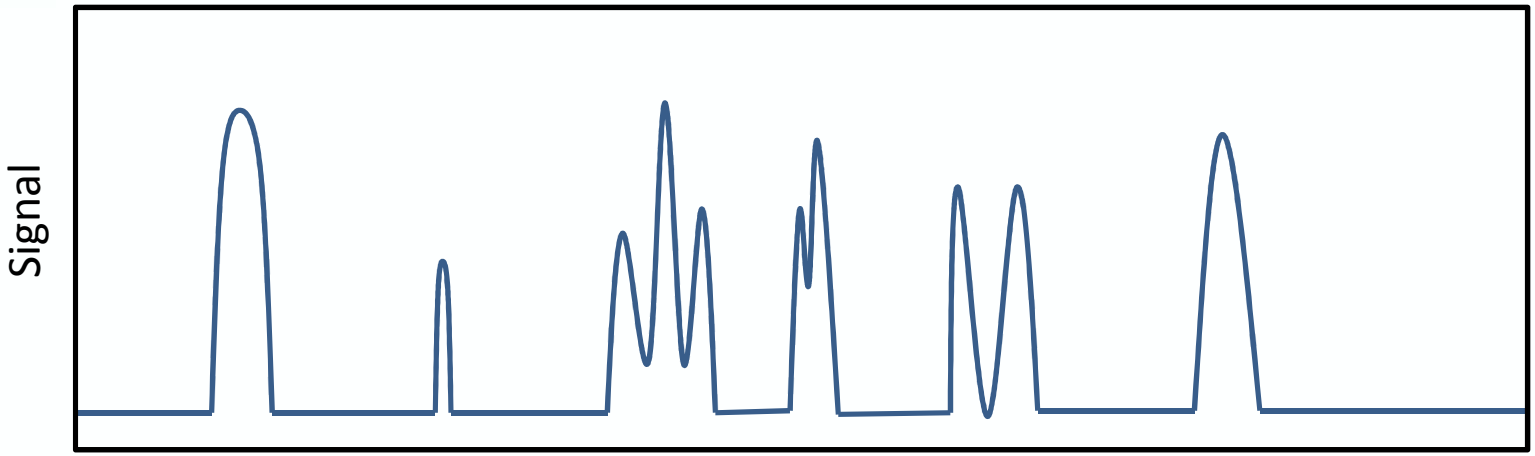
Fundamental modeling approach



1-dimensional chromatography

Injector

Detector

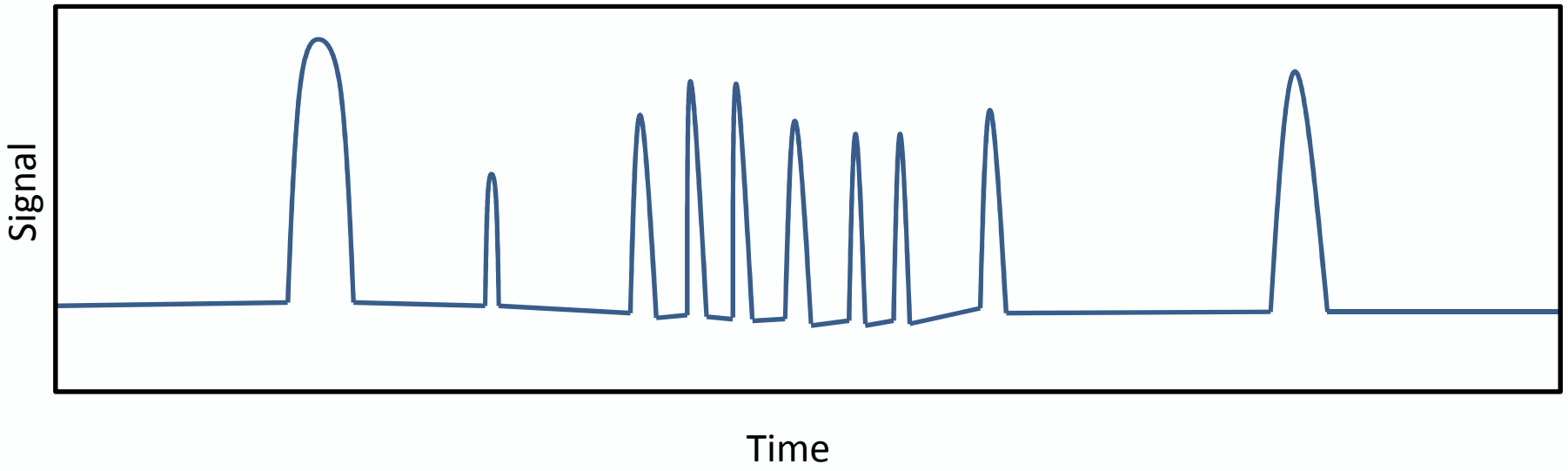


GC × GC

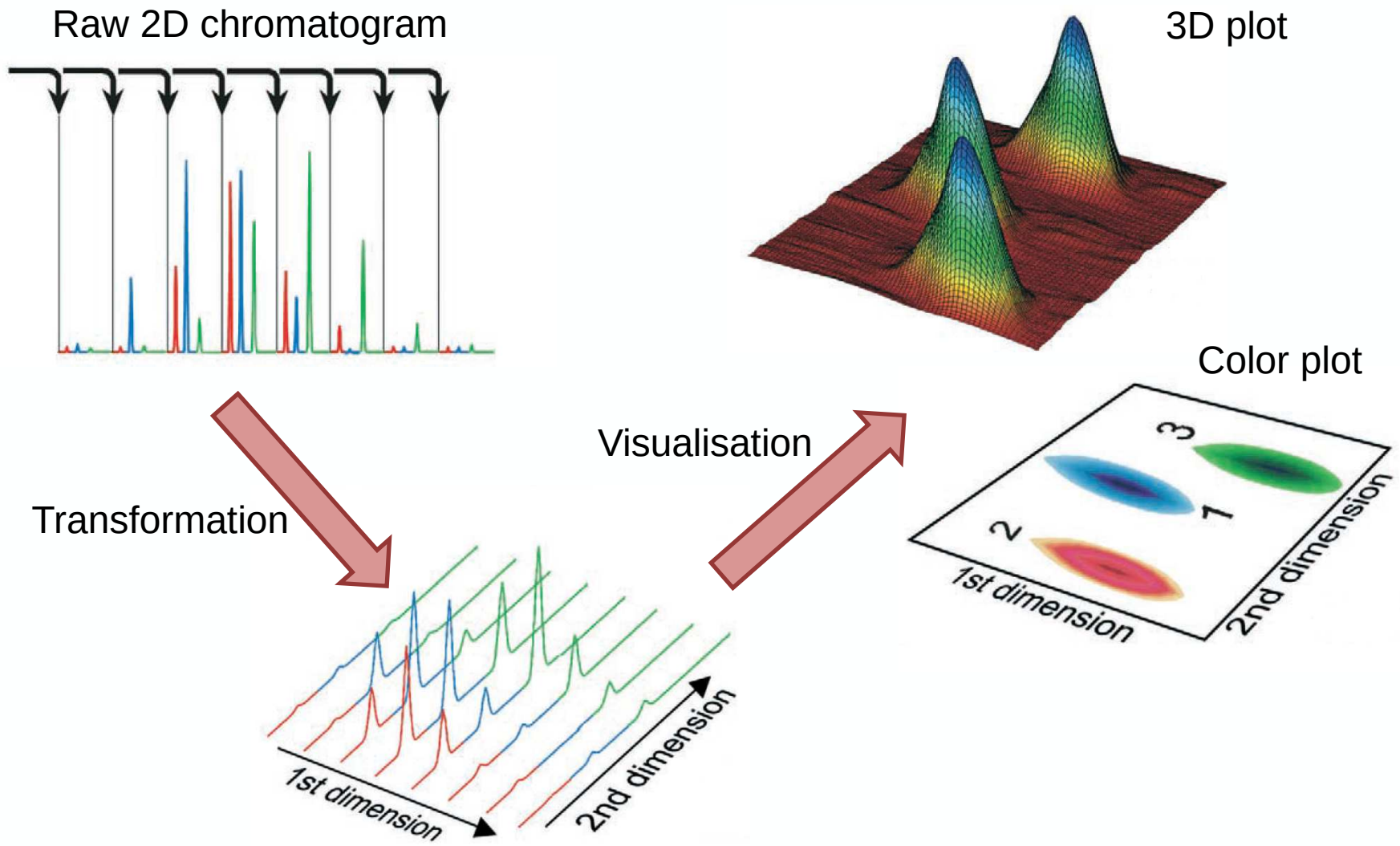
Injector

Modulator

Detector

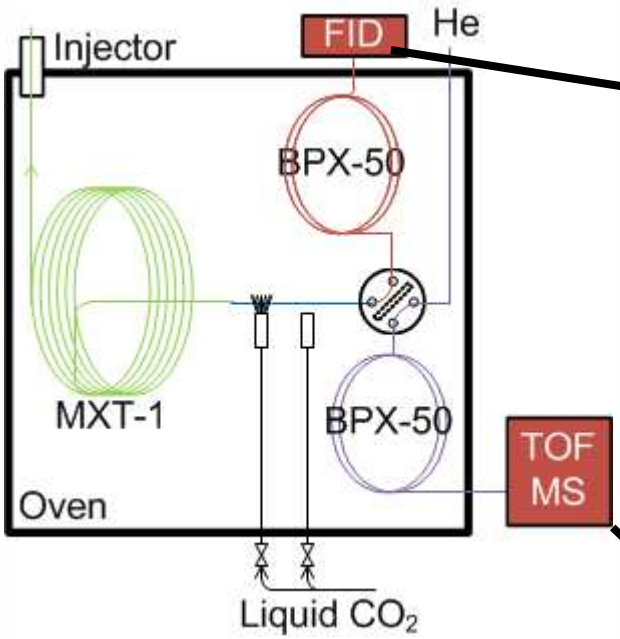


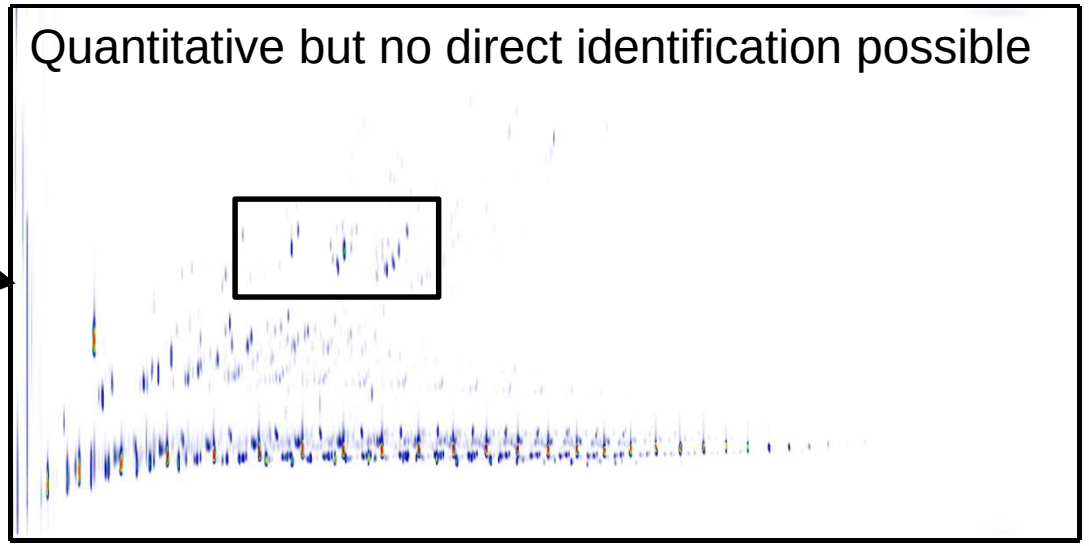
1D to 2D chromatogram

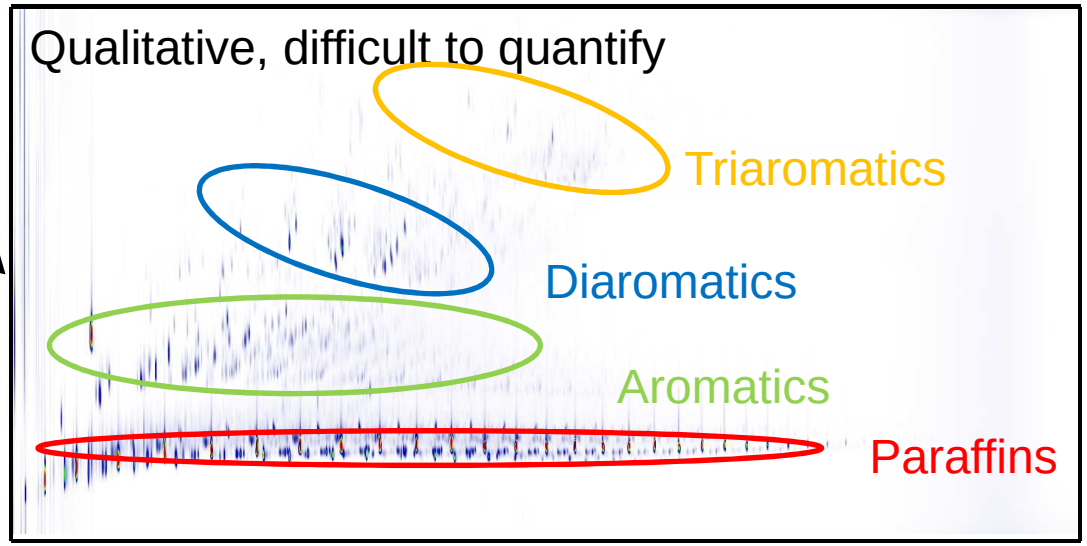


Dallüge et al., *J. Chrom. A* 2003

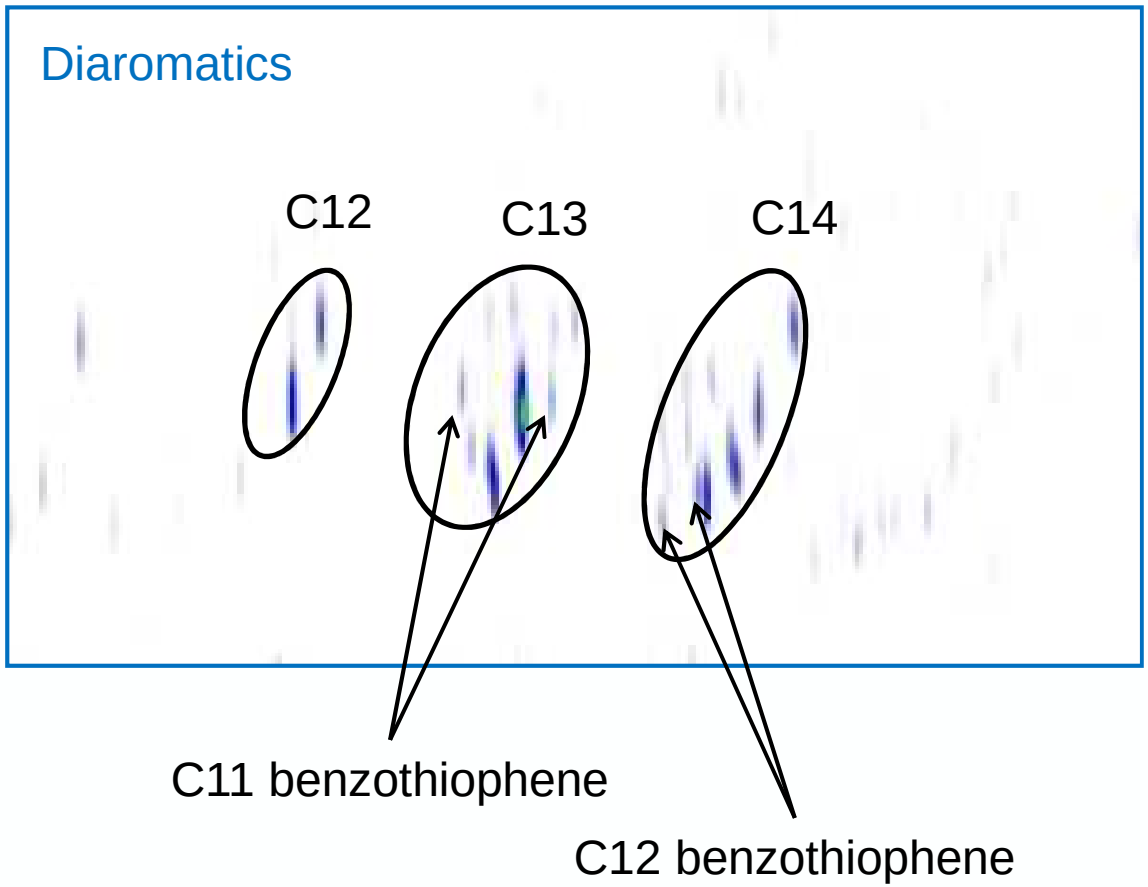
GC × GC – FID/TOF-MS





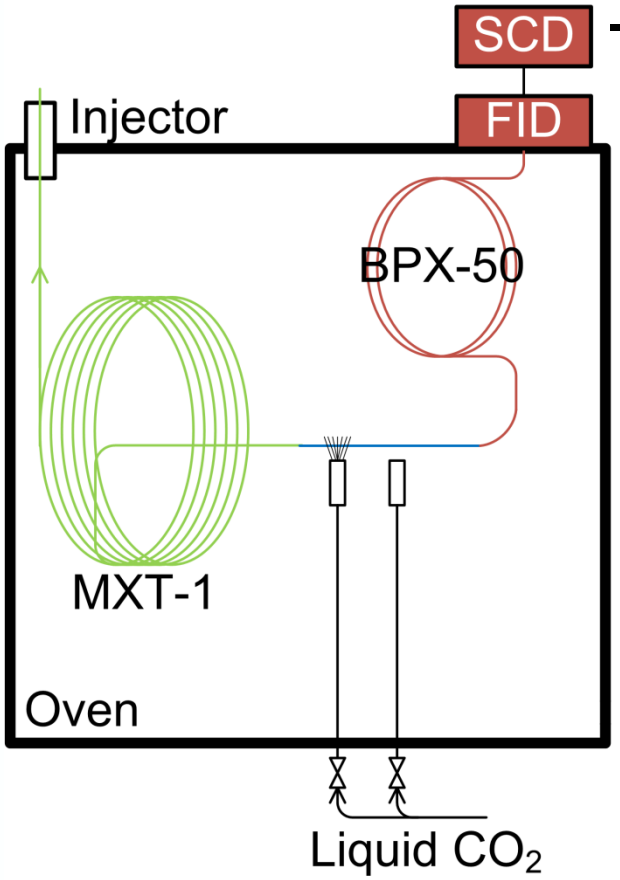


SCD

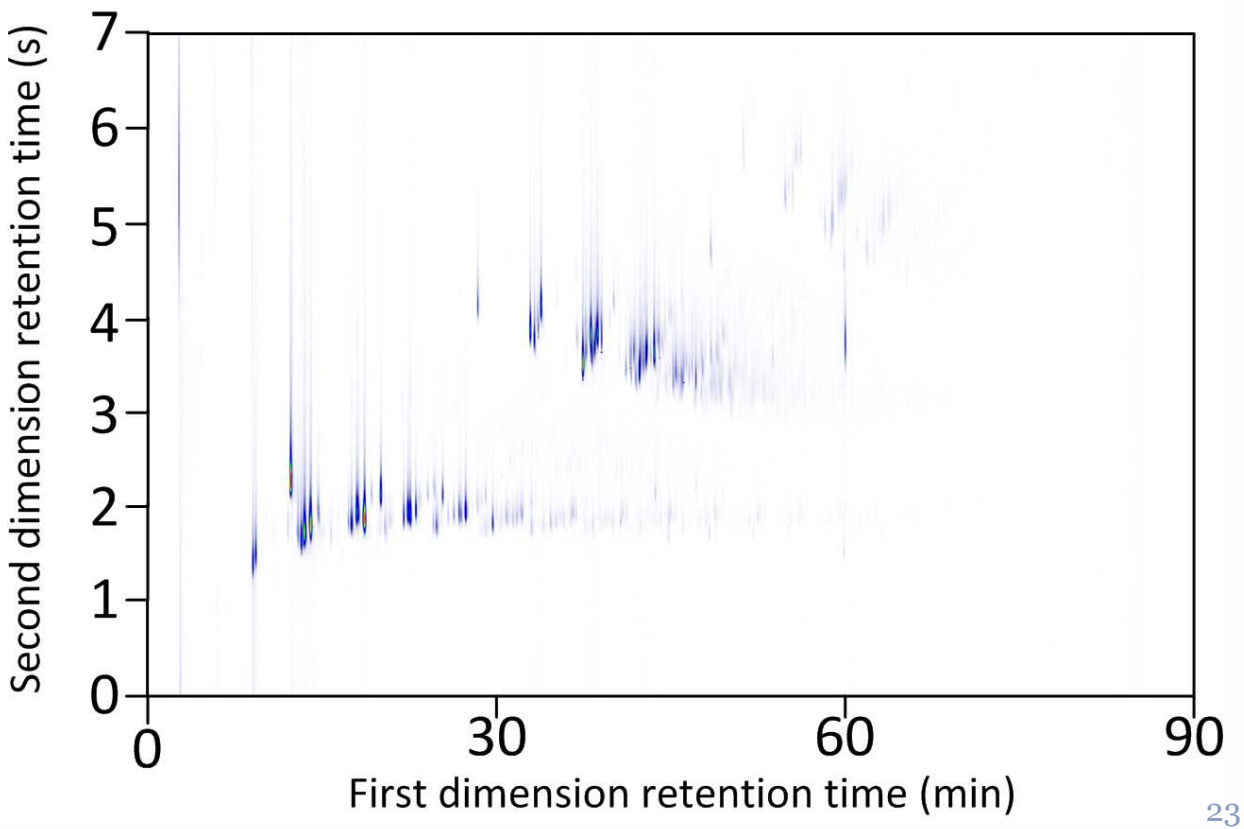


- Roof tile structure helps identification
- Overlap of sulfur containing hydrocarbons with pure hydrocarbons
- Not all sulfur containing hydrocarbons can be found with TOF-MS due to high differences in concentration

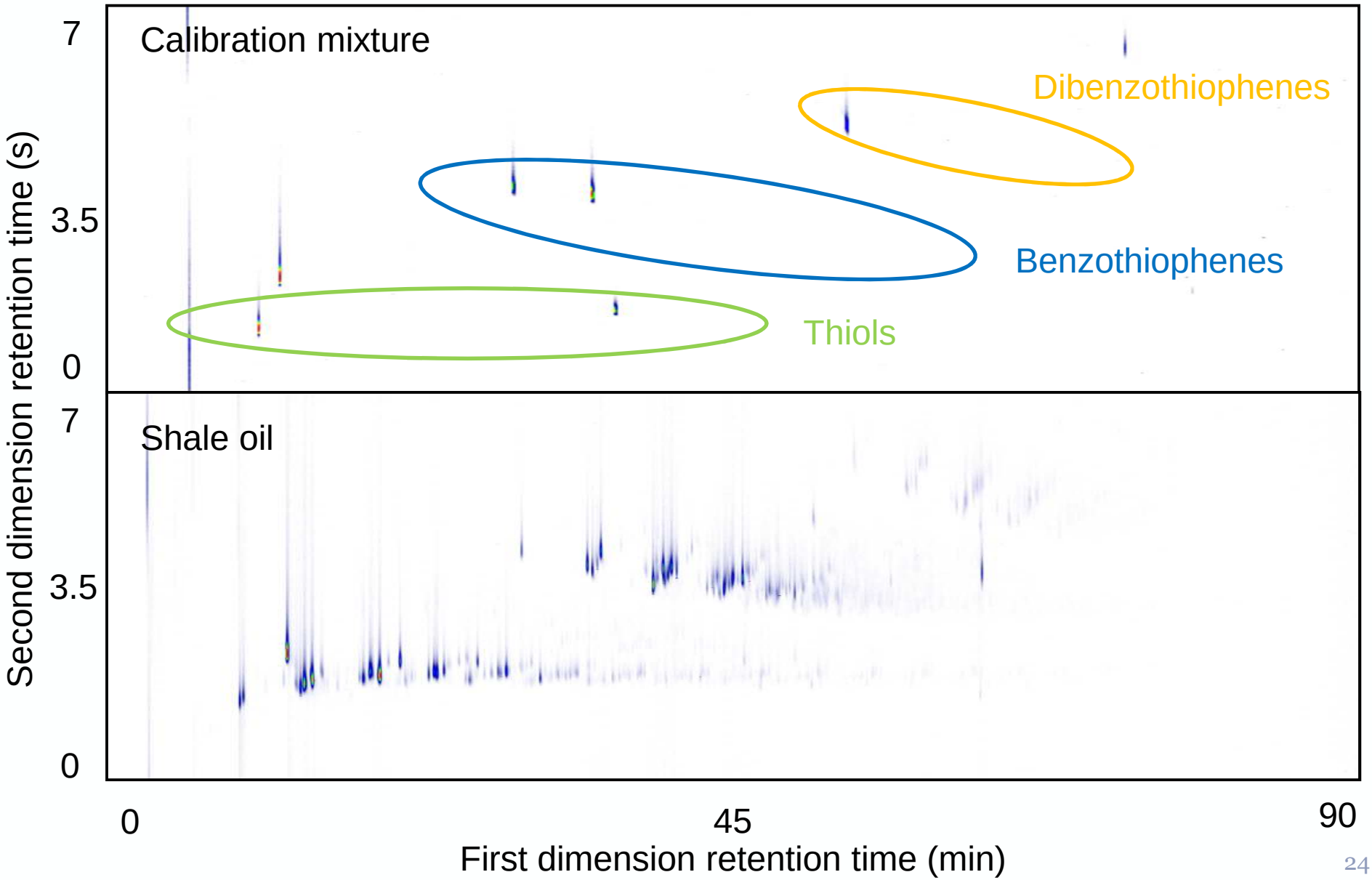
GC × GC – SCD



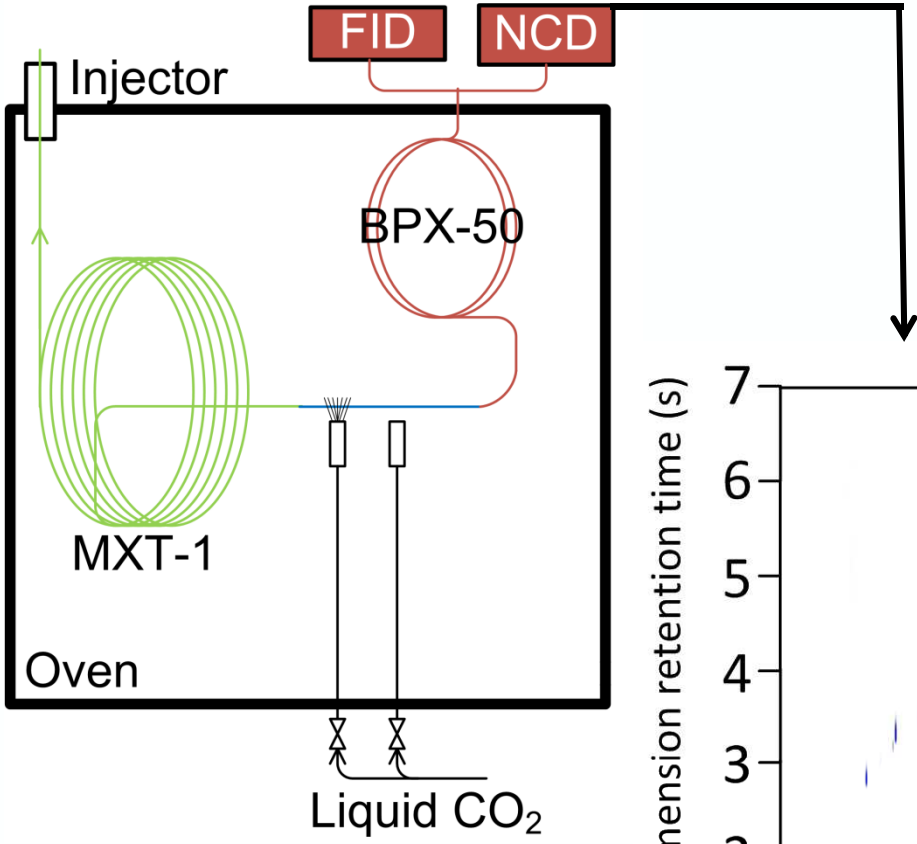
Again no direct identification is possible



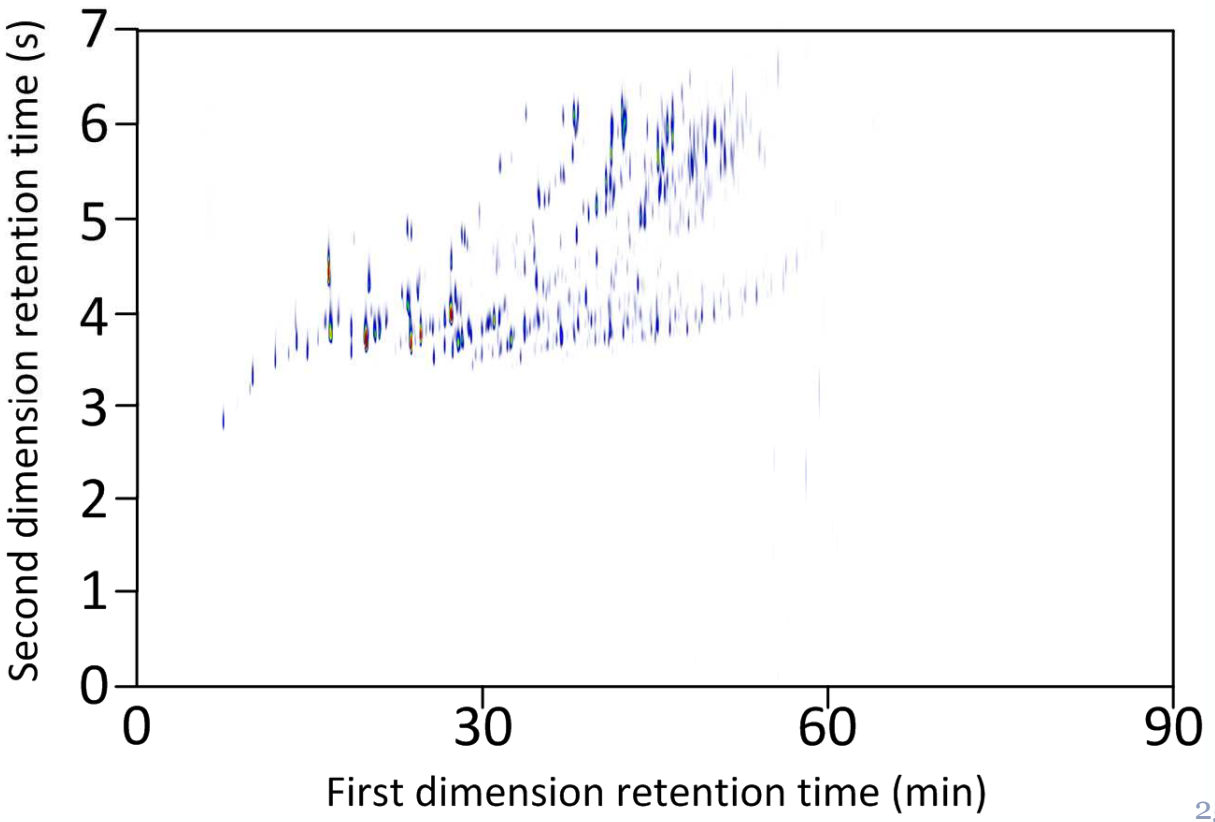
GC × GC – SCD (2)


Calibration mixture
Dibenzothiophenes
Benzothiophenes
Thiols
Shale oil
Second dimension retention time (s)
7
3.5
0
7
3.5
0
0
45
90
First dimension retention time (min)

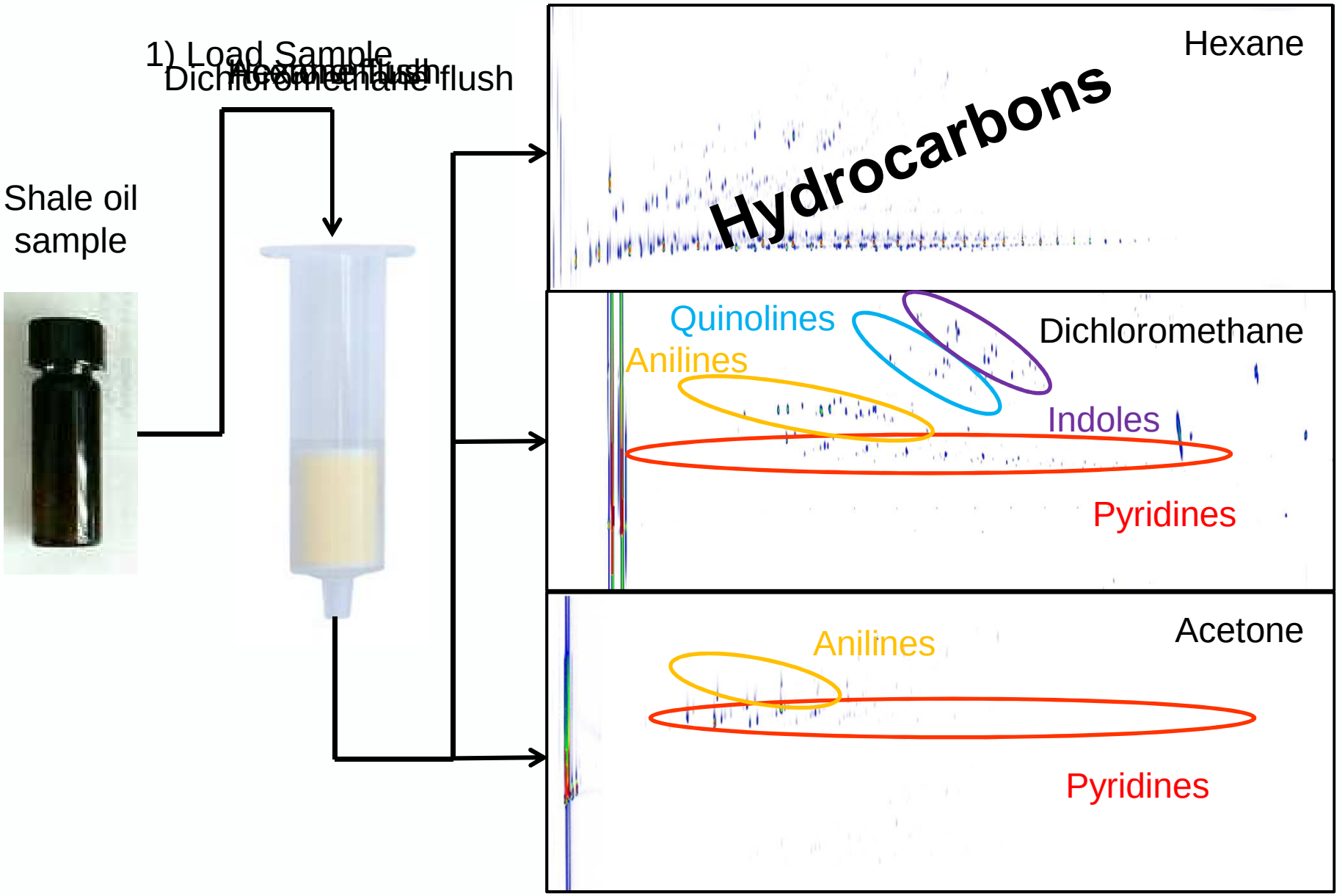
GC × GC – NCD



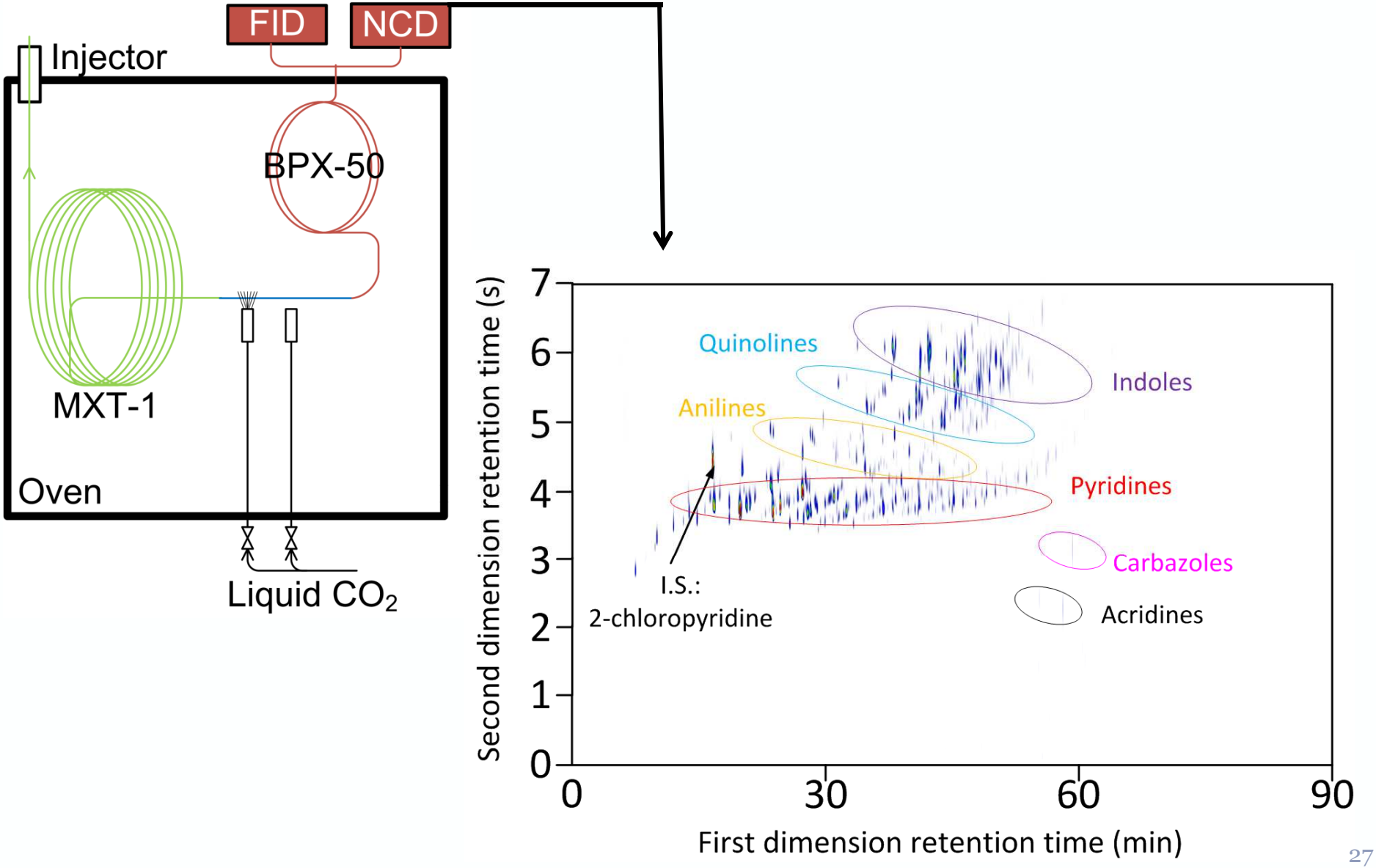
Again no direct identification is possible



SPE -GC ×GC - TOFMS



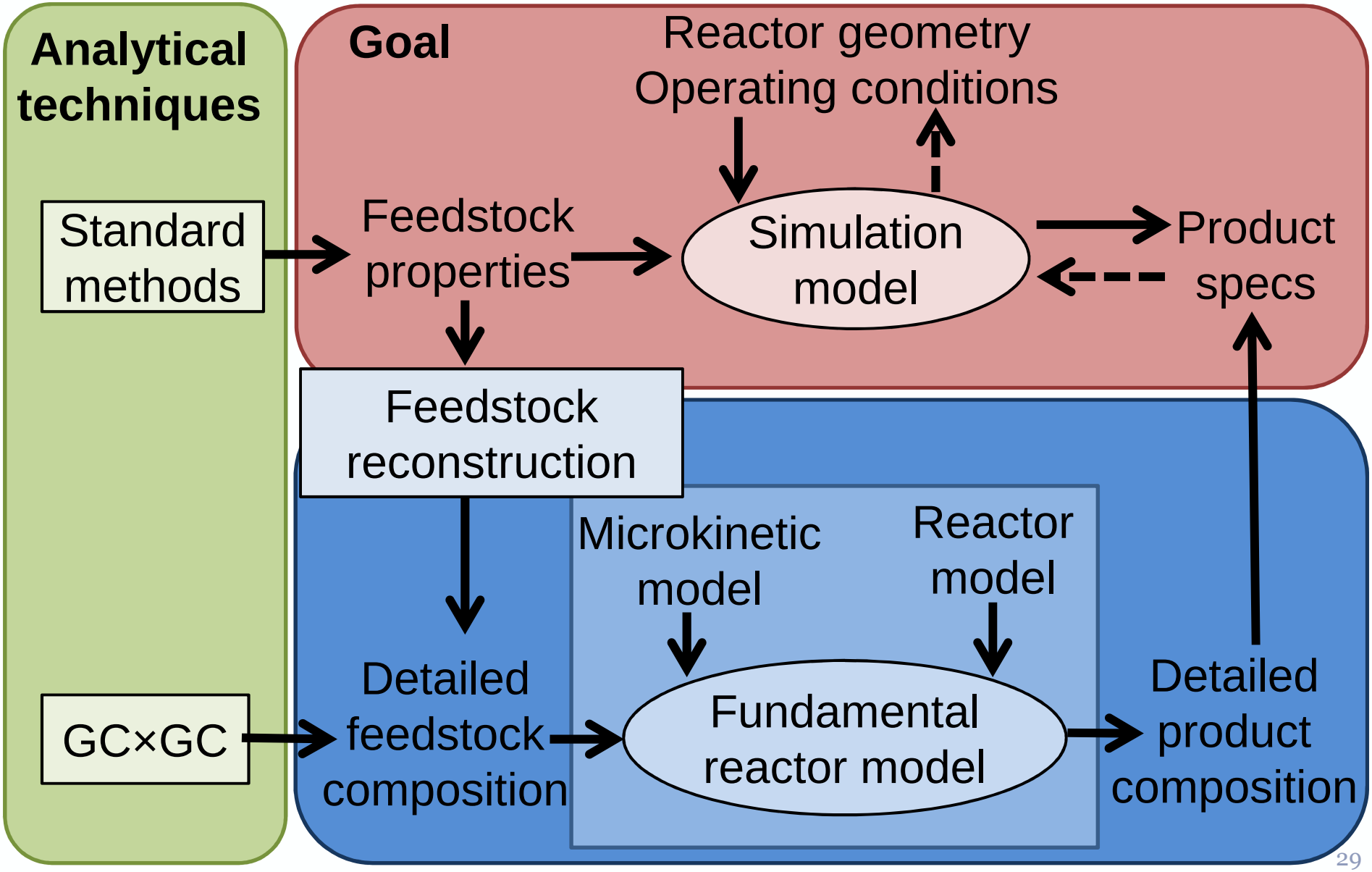
GC × GC – NCD


FID
NCD
Injector
BPX-50
MXT-1
Oven
Liquid CO_2
Second dimension retention time (s)
First dimension retention time (min)
0
1
2
3
4
5
6
7
0
30
60
90
Quinolines
Indoles
Anilines
Pyridines
Carbazoles
Acridines
I.S.:
2-chloropyridine

GC × GC – FID/SCD/NCD

#C	P	I	MN	DN	MA	NA	DA	NDA	TA	Pd	An	Q	In	Ac	Ca	T	BT	NBT	DBT	Ph	Total
5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.25
6	1.62	2.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.00	0.00	4.21
7	2.26	1.48	0.00	0.00	0.11	0.00	0.00	0.00	0.00	0.11	0.02	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.07	4.19
8	2.20	1.98	0.00	0.00	0.70	0.00	0.00	0.00	0.00	0.26	0.05	0.00	0.01	0.00	0.00	0.10	0.02	0.00	0.00	0.11	5.41
9	2.36	2.24	0.57	0.00	1.68	0.00	0.00	0.00	0.00	0.47	0.07	0.01	0.06	0.00	0.00	0.07	0.14	0.00	0.00	0.12	7.79
10	2.33	1.53	0.86	0.00	1.78	0.39	0.05	0.00	0.00	0.15	0.11	0.08	0.17	0.00	0.00	0.04	0.33	0.00	0.00	0.05	7.87
11	2.33	1.18	1.09	0.00	1.36	0.33	0.40	0.01	0.00	0.18	0.11	0.17	0.28	0.00	0.00	0.03	0.33	0.00	0.00	0.00	7.77
12	2.36	0.98	1.21	0.01	0.95	0.26	1.01	0.16	0.00	0.12	0.08	0.19	0.30	0.00	0.00	0.03	0.20	0.01	0.01	0.00	7.84
13	2.31	1.41	1.14	0.13	0.88	0.42	1.08	0.20	0.00	0.18	0.03	0.12	0.16	0.00	0.02	0.02	0.06	0.00	0.03	0.00	8.19
14	2.28	1.09	1.06	0.14	0.62	0.34	0.76	0.40	0.03	0.17	0.00	0.03	0.14	0.01	0.02	0.00	0.03	0.00	0.08	0.00	7.20
15	2.24	1.06	0.91	0.26	0.81	0.26	0.41	0.33	0.17	0.13	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.04	0.00	6.65
16	2.22	0.71	0.78	0.18	0.50	0.16	0.24	0.16	0.40	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.43
17	2.09	0.85	0.88	0.10	0.49	0.11	0.14	0.10	0.14	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.94
18	2.00	0.81	0.92	0.09	0.30	0.09	0.03	0.07	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.33
19	1.65	0.73	0.58	0.09	0.26	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.40
20	1.55	0.48	0.76	0.06	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.03
21	1.37	0.38	0.58	0.07	0.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.59
22	1.36	0.37	0.43	0.05	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.30
23	1.13	0.32	0.28	0.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.81
24	0.90	0.25	0.20	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.38
25	0.78	0.07	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
26	0.60	0.08	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.77
27	0.46	0.06	0.08	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.60
28	0.31	0.05	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40
29	0.21	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
30	0.13	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18
31	0.05	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.09
32	0.03	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07
33	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
Total	39.08	20.50	12.71	1.21	11.00	2.43	4.14	1.42	0.74	1.98	0.46	0.59	1.10	0.04	0.04	0.93	1.10	0.01	0.16	0.34	100.00

Fundamental modeling approach



Feedstock reconstruction

Feedstock properties

- Average molecular weight
- Elemental composition
- Specific density
- Global PINA analysis
- Boiling point data (e.g. D2887 simdist)
- Aromatic Sulfur

± 20 properties

Shannon entropy maximization

Feedstock reconstruction

Molecular library

Detailed composition

- ~~Specific identity~~
- Mole or mass fractions

More than 100 unknown mole fractions

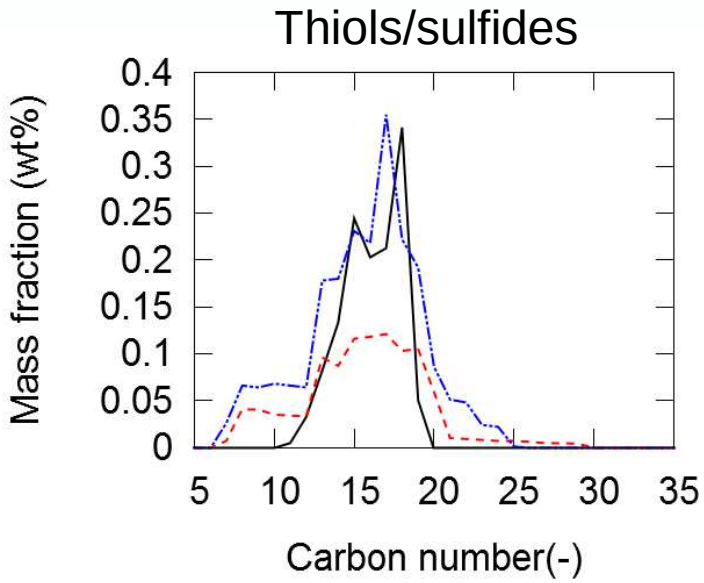
$$\text{MAX} \quad S(y_i) = -\sum_{i=1}^{N_M} y_i \ln(y_i) \qquad \text{with} \quad \sum_{i=1}^{N_M} y_i = 1$$

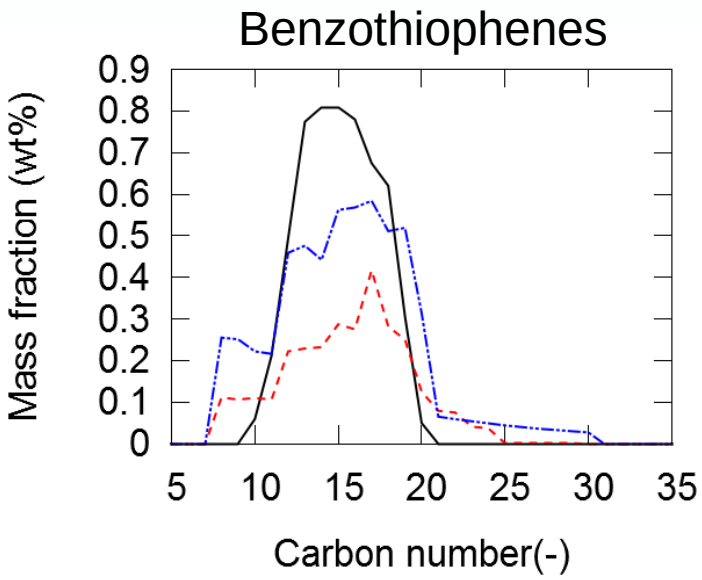
Constraints from mixing rules (example):

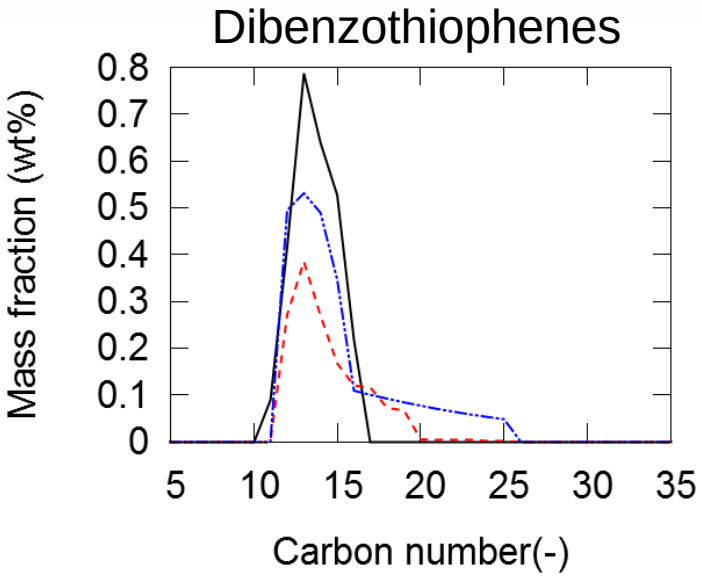
$$\frac{1}{\mathrm{d}_{\exp}} = \sum_{i=1}^{N_M} \frac{y_i \mathrm{Mw}_i}{\mathrm{d}_i \sum y_i \mathrm{Mw}_i}$$

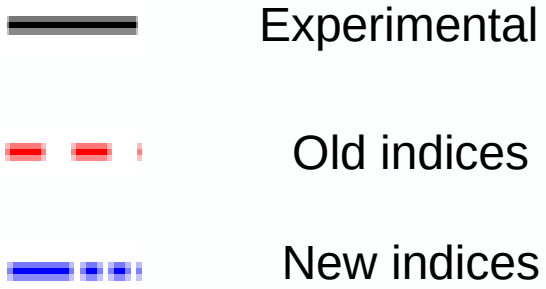
$$\mathrm{Mw}_{\exp} = \sum_{i=1}^{N_M} y_i \mathrm{Mw}_i$$

Results: Sulfur containing hydrocarbons

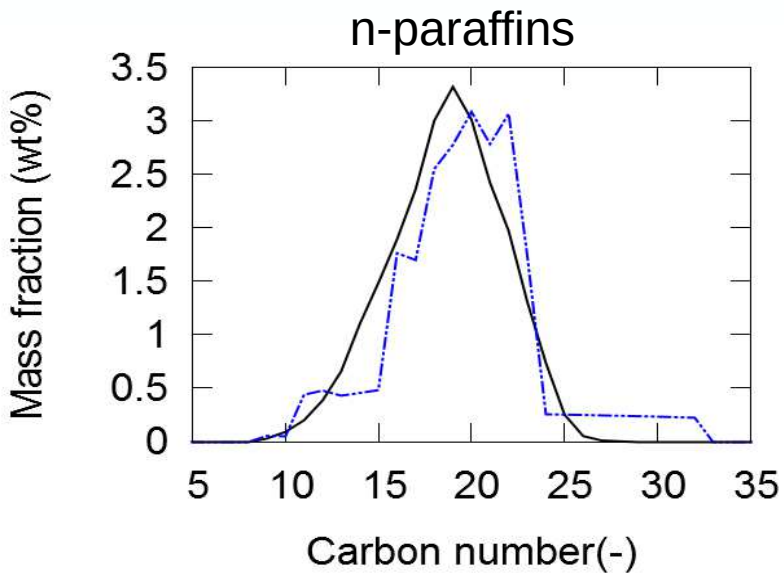


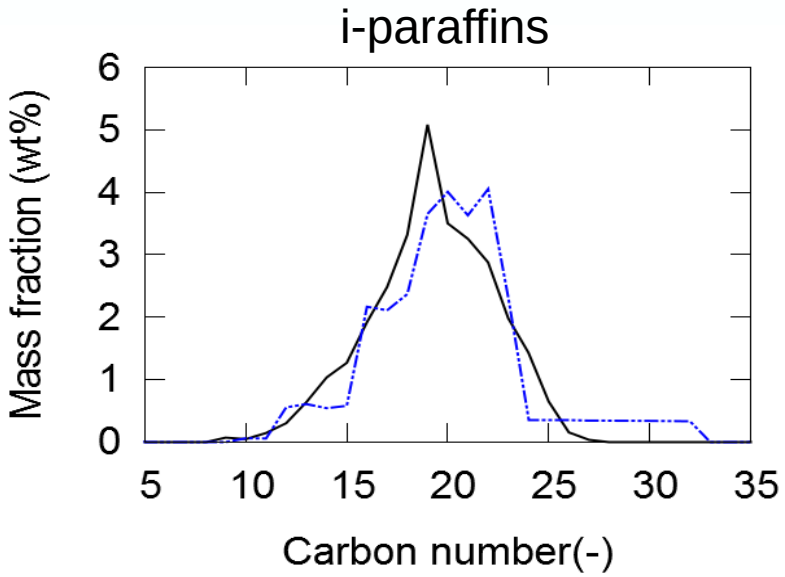


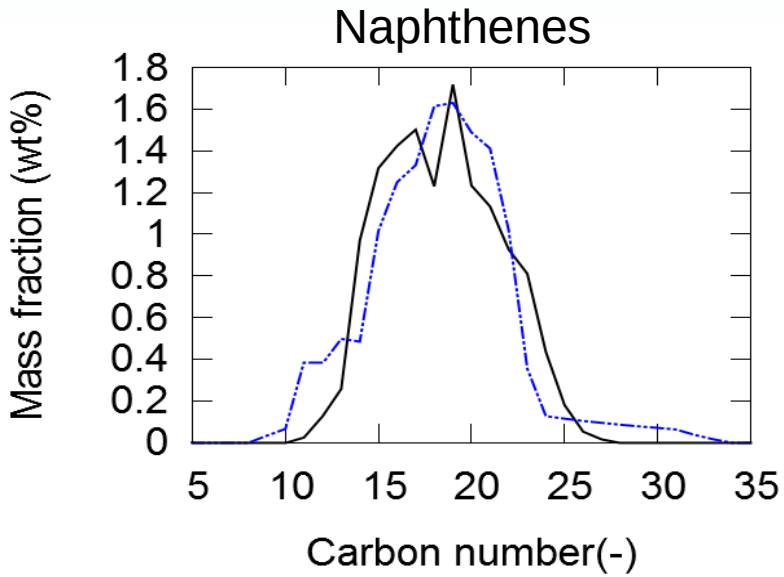


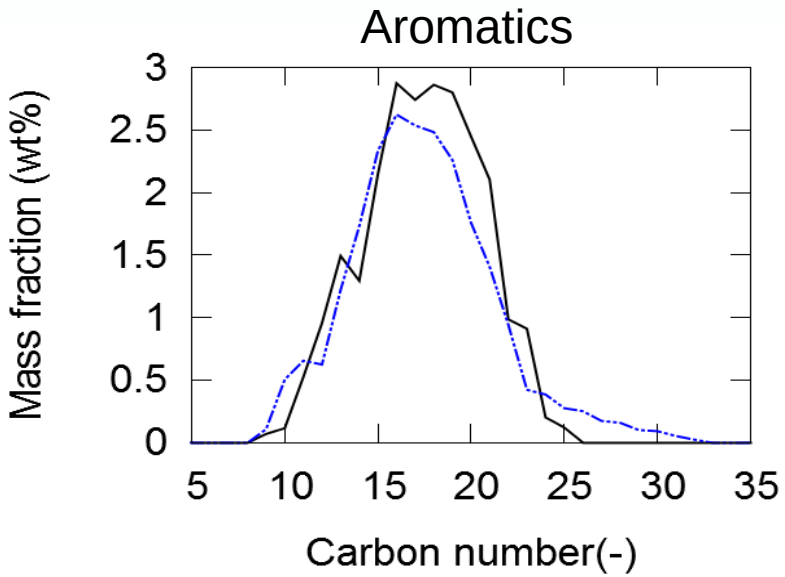


Results: Hydrocarbons

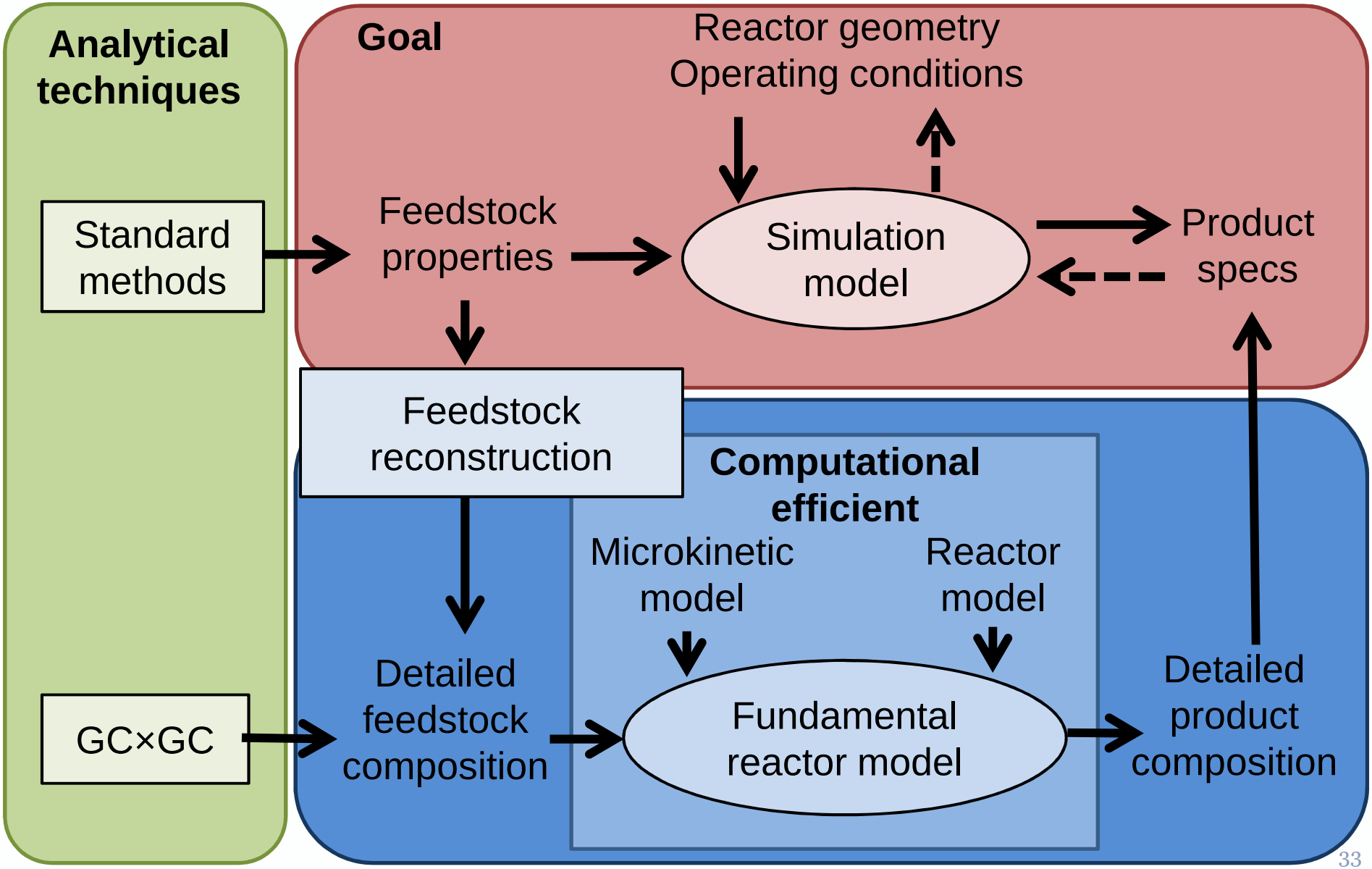








Fundamental modeling approach



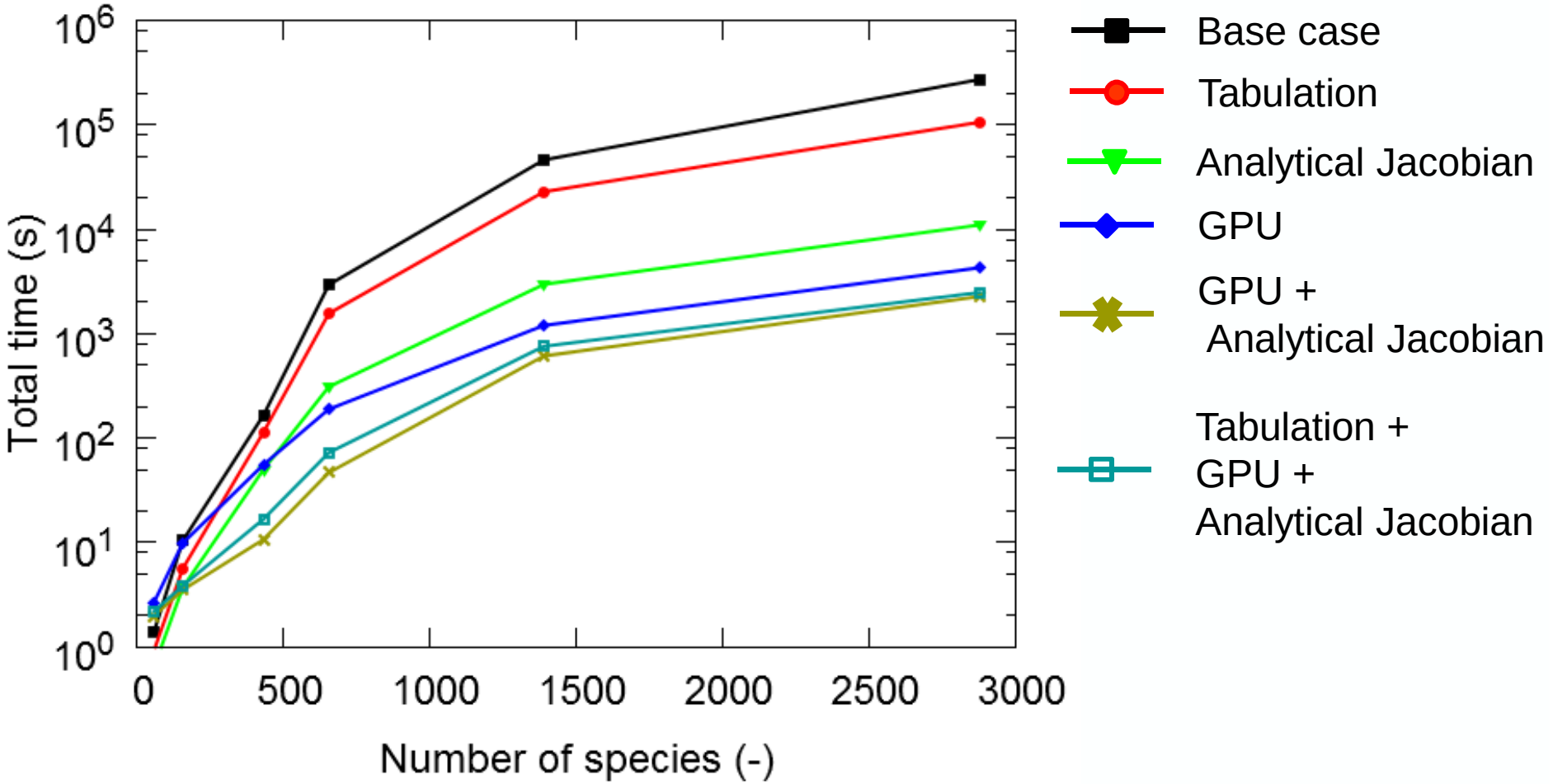
Decreasing simulation time

- Chemical techniques
  = simplify kinetic mechanism by network reduction

- **Mathematical techniques**
  - **Using a different solving technique (e.g. analytical Jacobian)**
  - **Alternative calculation of functions that are difficult to evaluate**

- **Computational techniques**
  - **Using a graphical card to perform certain calculations**

Total simulation time



Conclusions

- Development of a fundamental simulation tool requires the use of different state-of-the-art techniques such as:
  - Single-event microkinetic models to account for all the reactions occurring between species
  - GC × GC or feedstock reconstruction to obtain a detailed feedstock composition
- The models are however valid over a broad range of process conditions and for different feedstocks

Conclusions (2)

- The simulation time of such fundamental reactor models can drastically be reduced by:
  - Tabulation
  - Calculating an Analytical Jacobian instead of a finite-difference Jacobian
  - Using the graphical processing unit to handle part of the calculations

Questions