HIGHBIO - INTERREG NORD
2008 - 2011

Högförädlade bioenergiprodukter via förgasning
Korkeasti jalostettuja bioenergiatuotteita kaasutuksen kautta
Refining of Novel Products by Biomass Gasification

EUROPEAN UNION
European Regional Development Fund

Recent advances in FT-research at Chydenius

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KARLEBY UNIVERSITETSCENTER
CHYDENIUS

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Content

1. Recent advances in Fisher-Tropsch

2. Tar collection
   Some experiences of tar collection

Future experiments (from last seminar in Ylivieska)

- FTS on real syngas in the near future
- New equipment for gas analysis (CO, H_2, N_2 and C1-C5) after reactor in order to measure conversion rate is needed
- Analysis of tar-content in real syngas will be performed

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Advances in FTS

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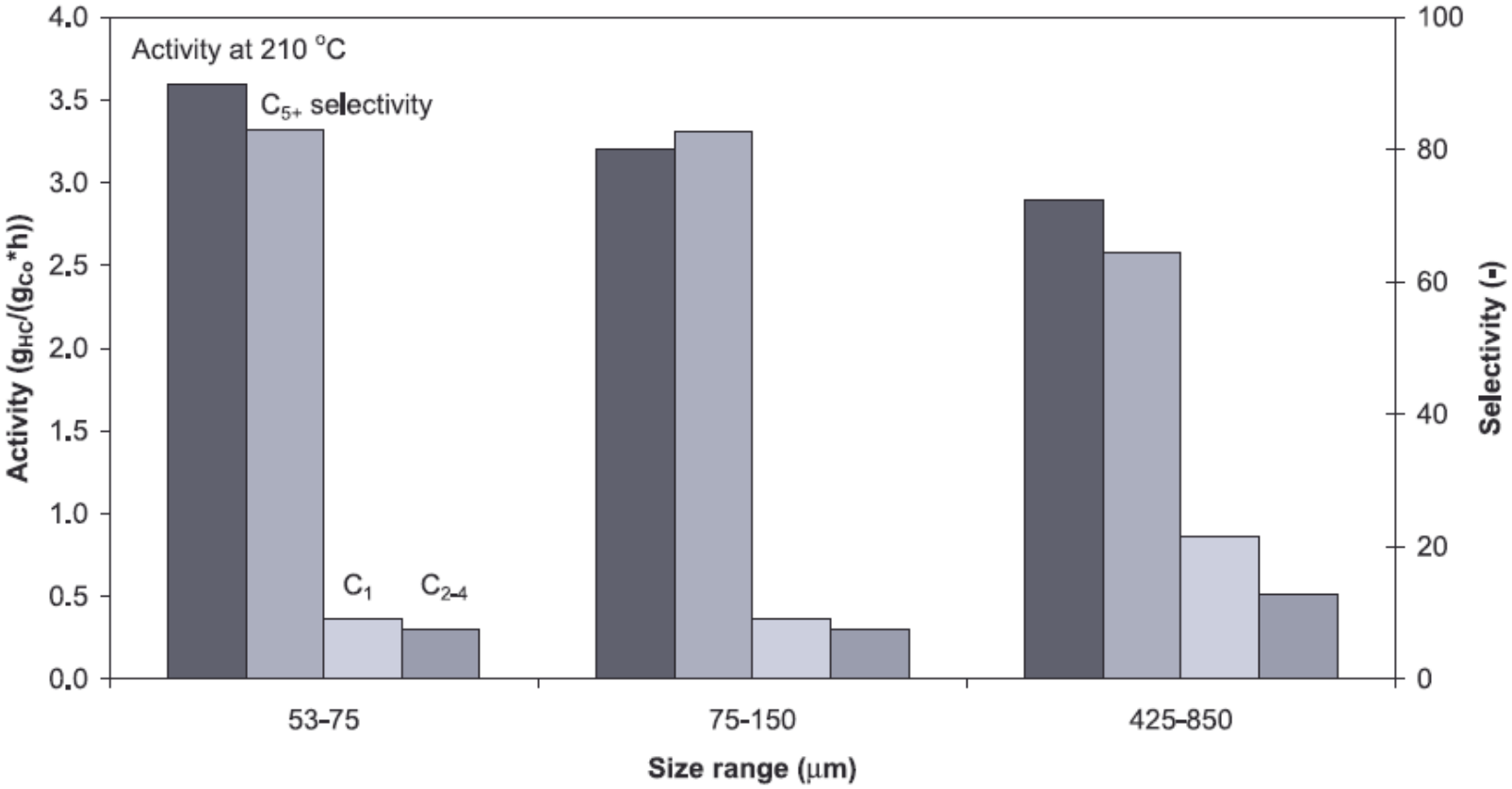
Catalysts used in our research

- Metals
  - Co Ru
  - Fe Ru
- Carriers
  - Al_2O_3 pelleted
  - Al_2O_3 100-150 µm, 240 m^2/g
  - Al_2O_3 –SiO_2 60-40 50-100 µm 500 m^2/g
- Precursors
  - $Co(NO_3)_2 * 6H_2O$
  - $Fe(NO_3)_2$
  - $Ru(NO)(NO_3)_3$
  - $Co(Ac)_2$

Particle size of the carrier affects catalytical activity and selectivity



Deugd et al., Trends in Fischer-Tropsch reactor tegnology-opportunities for structured reactors, *Topics in Catalysis*, vol.26, 2003, p.29-39

Modifications on the catalyst preparation (1)

Dry impregnation :

- Carrier is dried
- Precursor is dissolved in a small volume of water
  Volume = pore volume + 10%
- Dry carrier is impregnated, the whole volume is used

- Dry impregnation gives a higher metal content compared to incipient wettnes technique?
- Some problems with small particle carriers Al_2O_3-SiO_2

Modifications on the catalyst preparation (2)

- Calcination:
  We have used a lower calcination temperature than previous, performed in a stream of air
- Previous: High temperature in ambient atmosphere
- Precursors are modified to MeO on the surface of the carrier

- Reduction, performed in reactor
  We are using a lower reduction temperature than previous.
  H_2 flow 25 ml/min
  Metallic catalyst

Results

- More metal is introduced into the carrier?
  - Most likely but not confirmed yet
- Higher activity
  - More hydrocarbons are formed
  - Catalyst has to be more diluted
  - More heat is produced
  - With Al_2O_3-SiO_2: more compounds containing double bonds are formed

Reactions

1. $CO_{(ad)} \rightarrow C_{(ad)} + O_{(ad)}$
2. $H_{2\ (ad)} \rightarrow 2\ H_{(ad)}$

} Adsorbtion and bond cleavage

3. $C_{(ad)} + 2\ H_{(ad)} \rightarrow -CH_2-_{(ad)} \rightarrow (-CH_2-)_n$
4. $O_{(ad)} + 2\ H_{(ad)} \rightarrow H_2O_{(ad)} \rightarrow H_2O$

} Synthesis reactions

$\Delta H_r = -165\ kJ/mol \rightarrow$ exothermic

```
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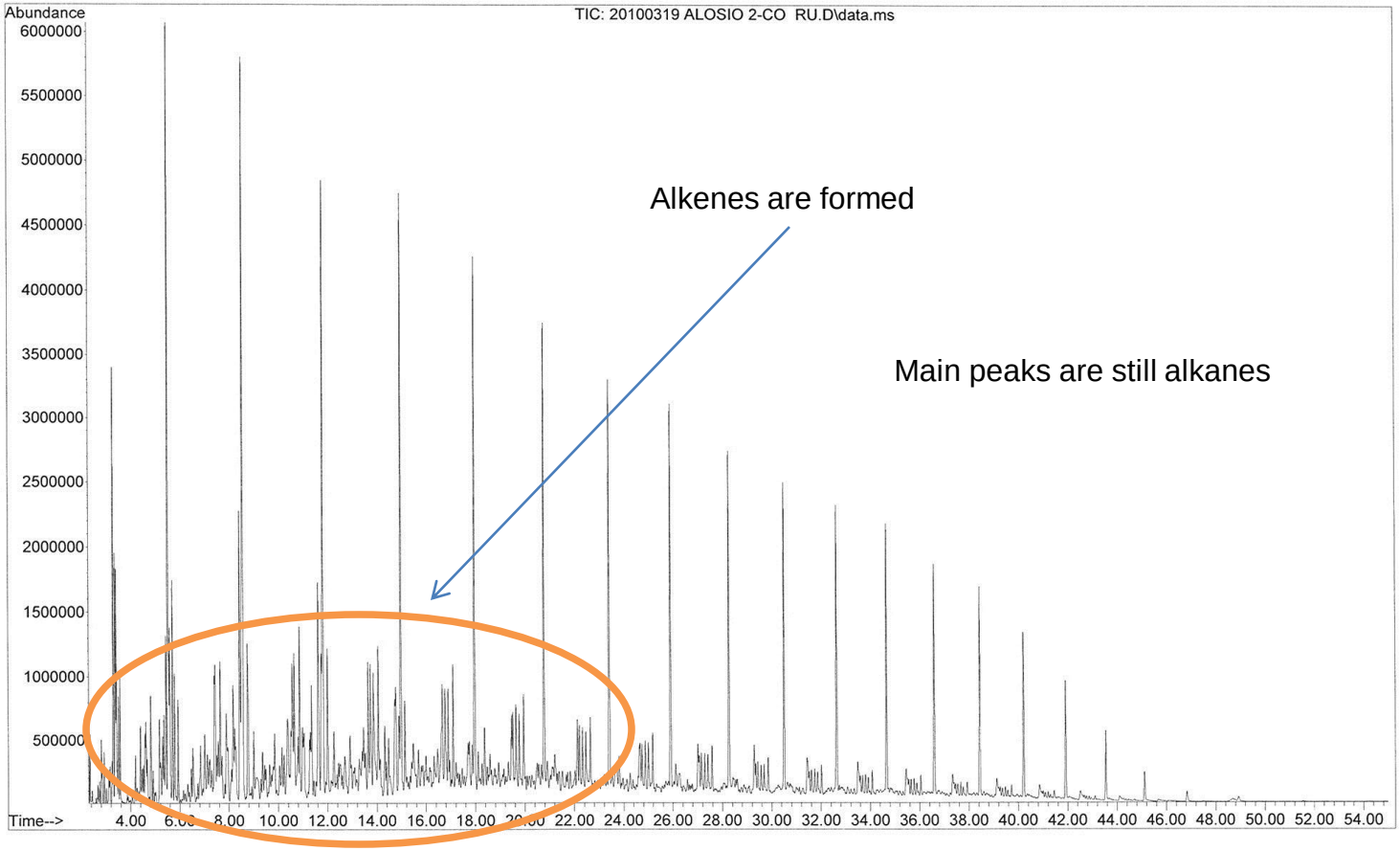

Tests with ”near real syngas”

- A gas with known composition was used as feed for the FT-synthesis
- This composition is close to real syngas, the H_2/CO is 1

Gas	Mol %
H_2	20
CO	20
CO_2	10
CH_4	1,5
N_2	Make up gas (48,5%)

Tests with ”near real syngas”

- This ”syngas” was tested with two different catalysts
  - CoRu on Al_2O_3 and CoRu on Al_2O_3-SiO_2
  - With the syngas we were able to have a slightly higher pressure than in previous runs
  - In both cases catalysts were active and produced hydrocarbons for 3 days
  - Beside liquid hydrocarbons a big amount of solid and semi-solid waxes was formed with CoRu on Al_2O_3

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Tar measurements from gasifiers

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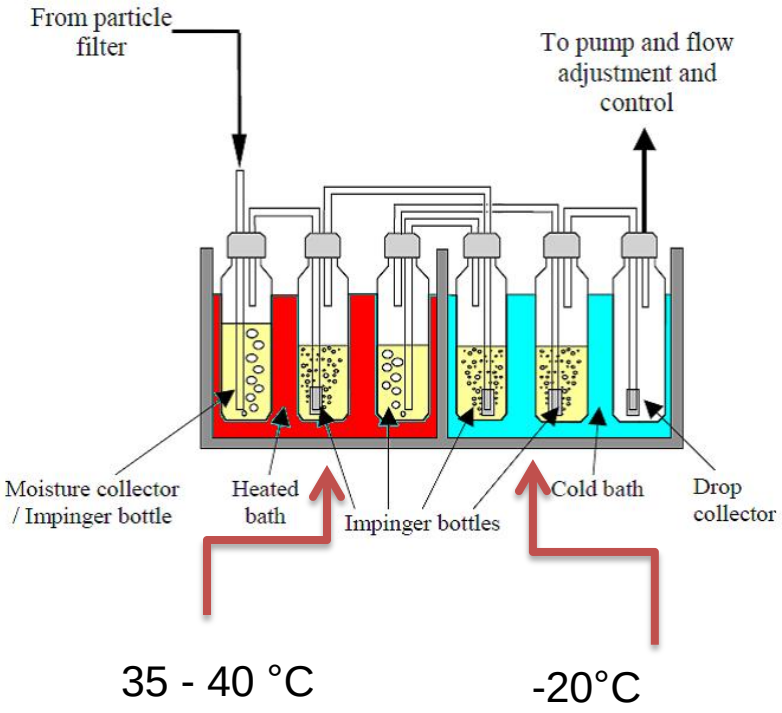
Tar measurement

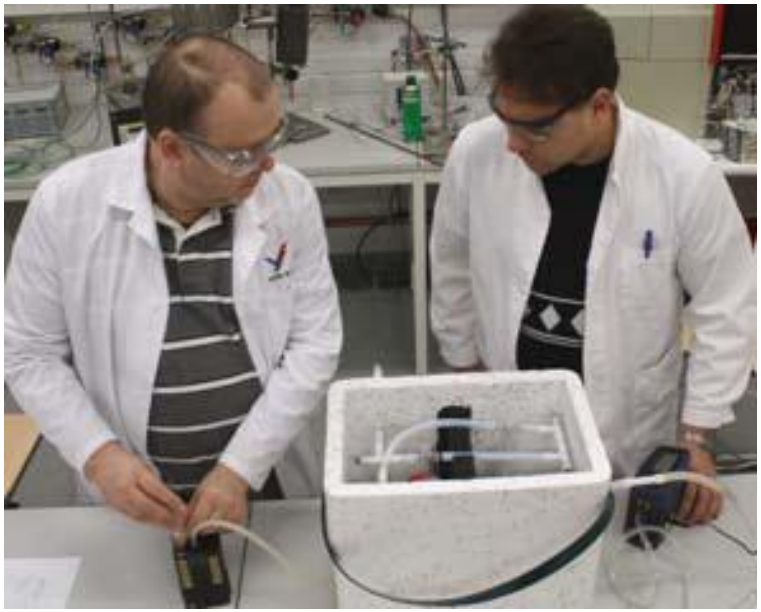
- In order to collect tar compounds a sampling system system has been built

- Some preliminary tests have been made on real gas from the Sievi gasifier

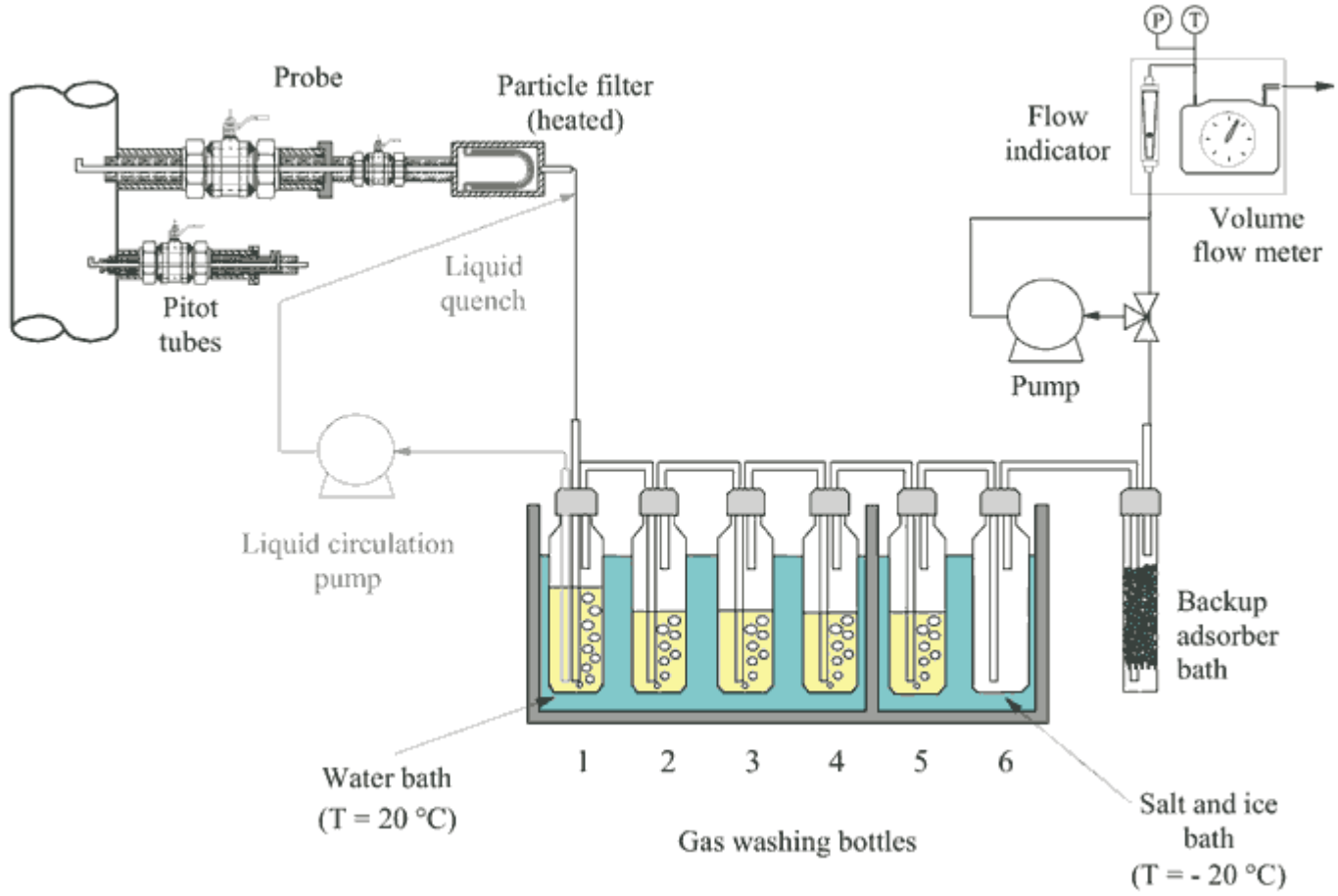
Tar sampling system

- consists of
  - sampling probe (heated)
  - filter for particulates
  - moisture collector, (heated)
  - absorption bottles filled with iso-propanol
  - equipment to measure gasflow, sampling time, gas pressure and temperature


From particle filter
To pump and flow adjustment and control
Moisture collector / Impinger bottle
Heated bath
Impinger bottles
Cold bath
Drop collector
35 - 40 °C
-20°C



The newer version of the protocol



Results

- The sampling equipment is under optimisation
  - We know that (heavy?) tars condensate in the sampling line
  - Results are by no means quantitative
- Results are preliminary
  - We have found the compounds one can expect to see in producer gas
  - So far nothing can be said about concentrations

GC-MS chromatogram, tars

```
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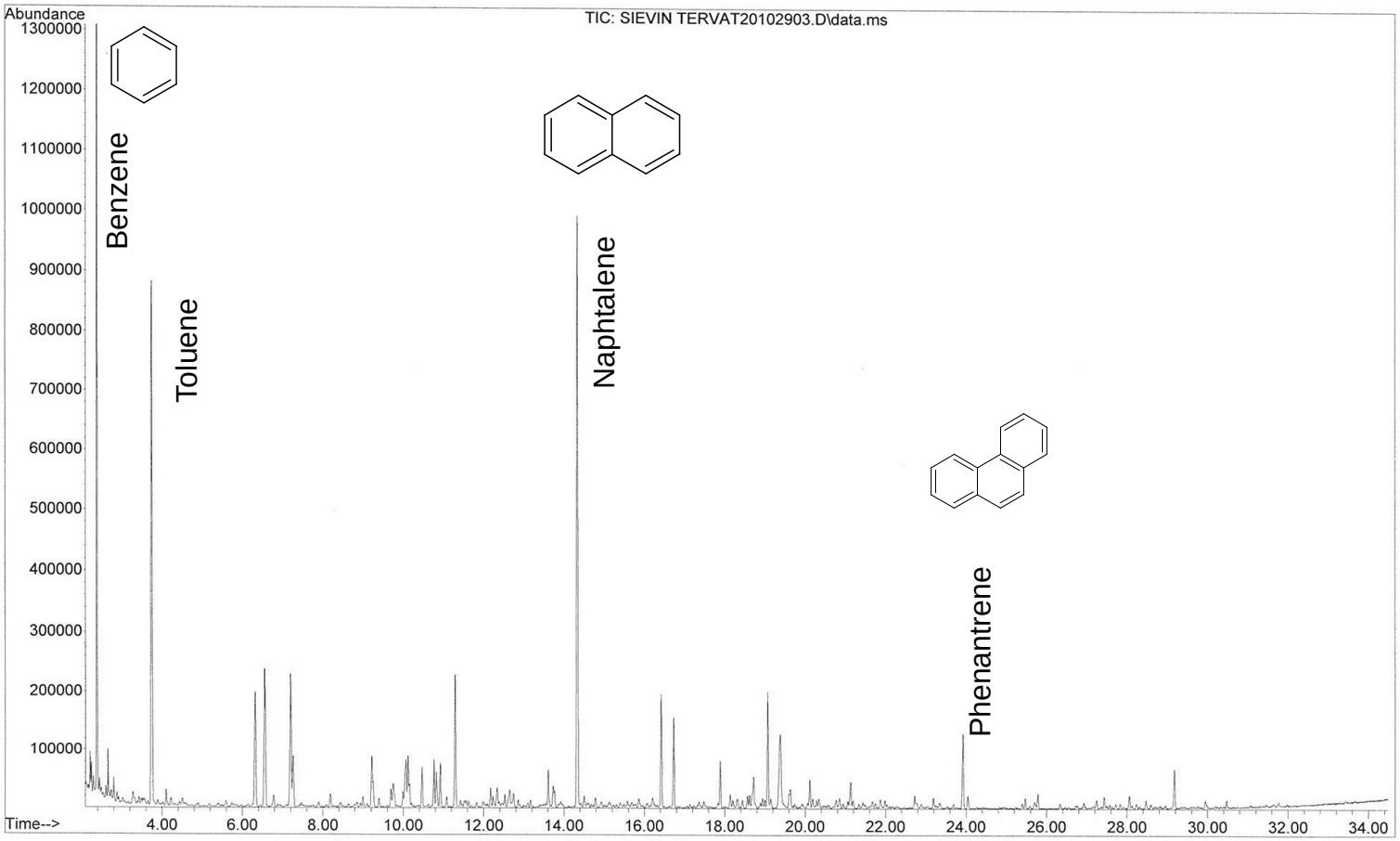

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Thank You!

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