

Pyrolysis GC for thermal crackin

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Figure 1: Pyrolysis gas chromatograph

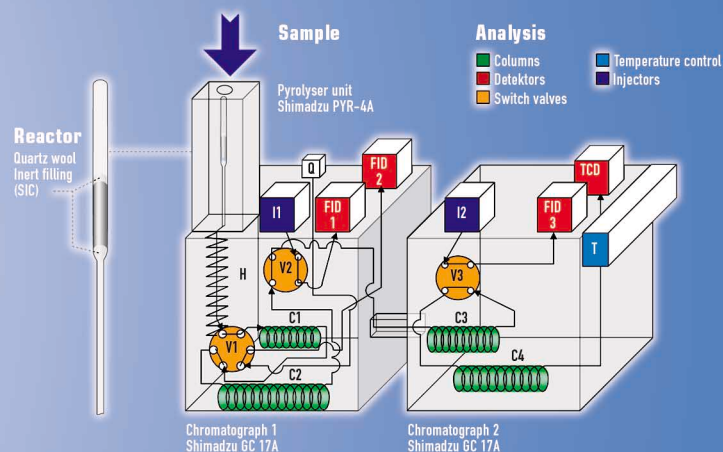


Figure 2: Diagram of the pulse reactor: R: reactor; K1-K4: capillary columns; V1-V3: change-over valves; I1-I2: injectors; FID1-FID3: flame ionization detectors; TCD: thermal conductivity detector; Q: carrier gas source; H: additional heating

Accurate characterisation of manufactured hydrocarbon steam cracking feedstocks is essential for optimal and economic ethylene production unit management. A special pyrolysis gas chromatograph has been developed and tested for feedstocks characterisation in the Research Centre for Complex Crude Oil Processing (consisting of Institute of Chemical Technology Prague and petrochemical holding Unipetrol a.s.).

Pyrolysis gas chromatography system

The apparatus for the laboratory study of hydrocarbon pyrolysis was compiled from a standard Pyr-4A Shimadzu pyrolysis unit and an on-line dual gas chromatography unit (2 x GC-17A Shimadzu, see Figure 1). The pulse quartz tube reactor was filled with carbide silica pellets to induce higher turbulent flow of the reaction mixture. A special syringe with a long needle is used for injecting gaseous and liquid feedstocks and also for melted samples which are solid at room temperature.

The gas chromatographic analysis of the reaction mixture is carried out in four capillary columns placed in a dual on-line chromatograph with four detectors and three change-over valves (Figure 2). The combination of two chromatograph units is necessary to attain different temperature programs in the assorted branches of the analytical path. The inlet of the reaction products into the V1 valve occurs through a short deactivated column, heat-

ed to 250 °C to ensure quick and uniform transfer of the sample into the chromatographic column C1. The chromatographic analysis traces all groups of pyrolysis products – pyrolysis gases, pyrolysis naphthas and pyrolysis oils (Figure 3). The evaluation of

pyrolysis product yields is based on the sequential analysis:

- first, the C₁₇ (and higher) hydrocarbons are retarded in the C1 column, other liquid and gaseous pyrolysis products continue to the next columns.

Product	Naphtha	AGO	HCVD	C ₉ fraction	Cyclopentane
Hydrogen	0.8	0.5	0.6	0.1	0.1
Methane	10.6	7.5	6.2	3.0	0.4
Ethane	2.5	1.4	1.5	0.5	0.2
Ethene	28.0	26.8	31.1	5.0	10.2
Propane	0.4	0.3	0.3	0.0	0.0
Propene	16.7	13.3	14.7	2.8	11.4
Ethyne	0.6	0.8	1.2	0.2	0.1
2-Methyl-propane	0.4	0.0	0.0	0.0	0.0
Propadiene	0.0	0.5	0.7	0.1	0.2
Butane	0.1	0.0	0.0	0.0	0.0
trans-But-2-ene	0.6	0.4	0.4	0.1	0.0
Bute-1-ene	2.3	1.9	3.1	0.1	0.2
2-Methyl-propene	2.5	1.4	1.5	0.2	0.2
cis-But-2-ene	0.5	0.3	0.4	0.1	0.0
Propyne	0.5	0.6	1.0	0.1	0.0
Buta-1,3-diene	7.0	6.4	8.4	0.0	0.4
^a Cyclopentadiene	2.6	2.5	3.6	15.1	3.8
Benzene	5.3	4.7	5.2	8.8	0.4
C ₅ -C ₆ residual fraction	8.1	1.8	2.7	2.3	71.5
Toluene	3.2	2.9	2.7	5.2	0.1
Ethylbenzene	2.8	0.3	0.4	0.4	0.0
p, m-Xylenes	0.4	0.7	0.5	2.1	0.0
Styrene	0.7	0.9	0.8	3.0	0.1
o-Xylene	0.7	0.4	0.3	1.2	0.0
Naphtalene	0.3	1.1	0.6	3.3	0.1
C ₇ -C ₁₂ fraction	0.2	6.3	4.1	36.8	0.4
Pyrolysis oil	2.3	16.5	8.2	9.7	0.2

^a: including isoprene.

Table 1: Pyrolysis product yields of basic feedstock types. Naphtha – primary naphtha (706 kg/m³), AGO – atmospheric gas oil (845 kg/m³), HCVD – hydrocracked vacuum distillate (855 kg/m³), C₉ fraction – recycled aromatic and naphthenic pyrolysis products, Cyclopentane – puris p.a. cyclopentane

g feedstocks evaluation

- hydrocarbons from the C1 column are analysed on the FID2 detector after the V1 valve switchover.
- hydrogen and methane from the C4 column are analysed on the TCD detector, and C₇-C₁₆ hydrocarbons from the C2 column are analysed on the FID1 detector after the V2 valve switchover. Alternatively, the TCD detector can be removed from the analytical path and the detection of all gaseous products (excluding hydrogen) can be performed using the FID3 detector.
- finally, C₂-C₆ hydrocarbons from the C3 column are analysed on the FID3 detector after the V3 valve switchover.

The experiments are conducted at a maximum temperature of 810 °C, Nitrogen carrier gas flow rate of 100 mL/min⁻¹ and a pressure of 300 kPa. The low-conversion experiments can also be carried out in the case of primary products selectivities study (range of maximum temperature 720 °C - 760 °C). The total time between analyses was reduced to 50 minutes by a thorough setting of all system parameters. The level of uncertainty of laboratory measurements is acceptable, e.g. ± 0.7 wt. % of absolute standard uncertainty for ethylene yield, ± 0.3 wt. % for propylene yield and maximum value of ± 0.7 wt. % for pyrolysis oil.

The illustrations of pyrolysis chromatography system utilisation in the sphere of rule-of-thumb and theoretical study of hydrocarbon ethylene cracking are detailed in Table 1.

Summary

The pyrolysis gas chromatograph with a pulse tube reactor and dual chromatographs has proved itself as an effective tool for evaluation of varied feedstocks in

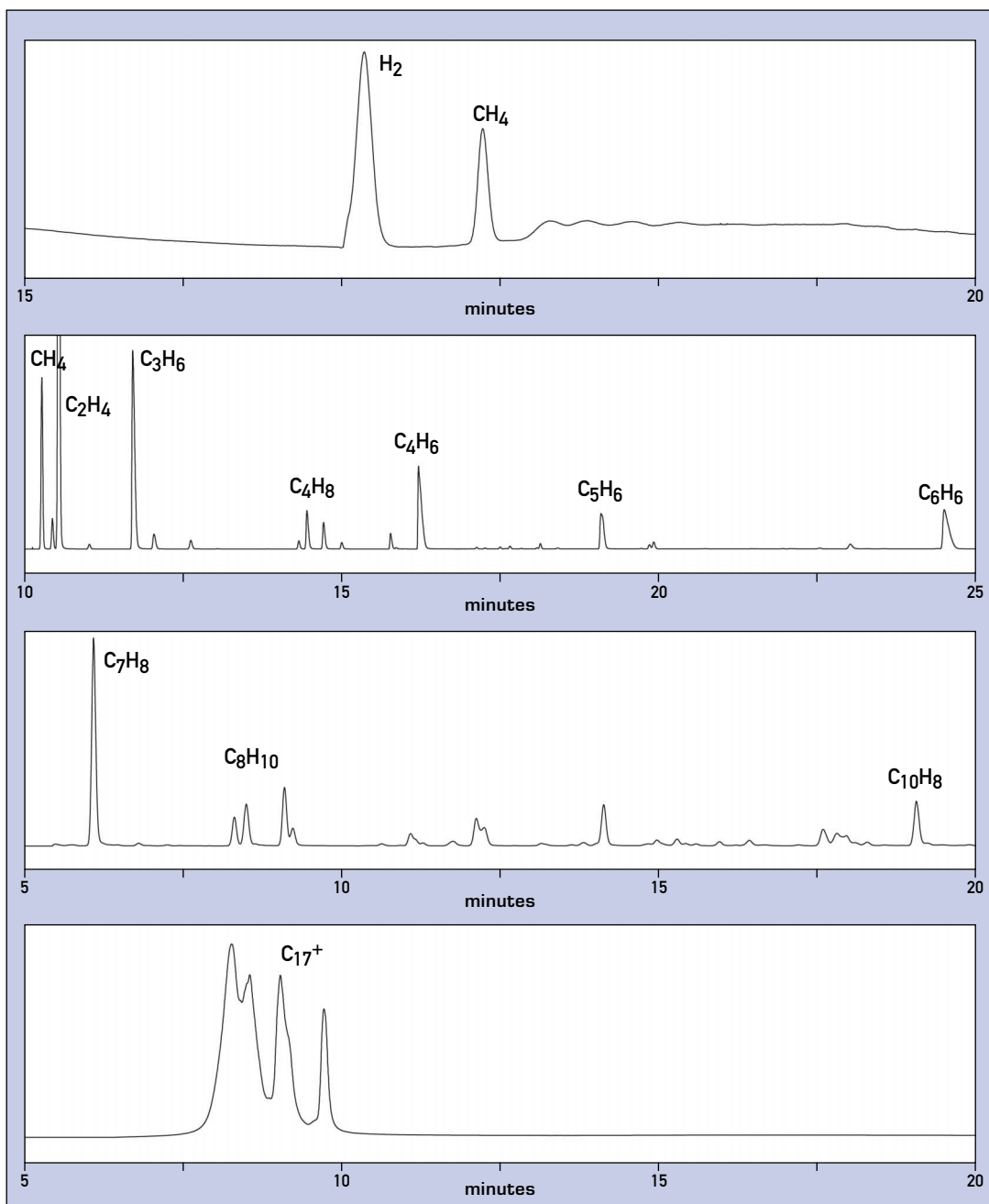


Figure 3: Example of chromatograms of pyrolysis products – hydrogen and methane, C₁-C₆ fraction, C₇-C₁₆ fraction and C₁₇⁺ fraction

ethylene cracking. The reliability of experimental measurements, lifetime and difficulty of laboratory tests are acceptable not only for practical operation, but also for the study of hydrocarbon fractions or individual hydrocarbons behaviour. No coke deposits in the reactor and chromato-

graphic system or other technical difficulties have been detected after a year of intensive full load operation.