On-line detection of heteroatomic compounds in steam cracking effluents

Marko R. Djokic, Kevin M. Van Geem and Guy B. Marin

Laboratory for Chemical Technology (LCT), Ghent University, Belgium
Technologipark 914, 9052 Ghent, Belgium
https://www.lct.ugent.be

Steam cracking: from conventional to unconventional

- **Steam cracking** is the leading technology applied for production of ethylene and propylene
- Typically requires a liquid or a gas feed such as ethane, LPG or naphtha
- Increasing oil prices are driving the industry towards heavier petroleum feeds (gas oils, waxes and vacuum gas oils)
- Heavy feeds contain high amounts of sulfur- and nitrogen-compounds
- These heteroatomics exert a significant influence on the steam cracking process
- Trace analysis of the heteroatomics is important but challenging

Research at the LCT: from molecule to industrial level

- Process level, m
- Molecular level, nm

LCT’s steam cracking setups

- Detailed Feedback Characterisation
- Process Conditions
- Detailed Product Characterisation

Automated mechanism generation

- GENESYS® - GENERation of reacting SYStems
- GENESYS supports automated implementation of new elements such as heteroatoms

3D reactor technology

- Velocity profile in 3D coils
- 3D reactors lead to a better performance of steam crackers

Conclusions

- An extremely flexible pilot plant for steam cracking
- Dedicated GC x GC combining FID with SCD as well as FID with NCD for analysis of heteroatomics
- Successfully applied for on-line analysis of sulfur- and nitrogen-compounds in steam cracking effluents

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Methodology and Results

Pilot plant setup for steam cracking

- On-line analysis of the pilot plant:
  - High-temperature on-line sampling (300 °C)
  - Dedicated analysis section: 2 GC×GCs + 2 RGAs
  - FID used to measure hydrocarbon matrix
  - SCD and NCD to selectively measure S- and N-compounds
  - RGA used to measure low molecular species (C₄)
  - Internal standards based quantification
  - Total mass balance closed with max 5 % of rel. st. dev.

On-line detection of sulfur-compounds¹

- Vacuum gas oil (VGO) containing 780 ppm-w in the form of benzothiophenes and dibenzothiophenes is cracked
- 75% of the sulfur in the feed is converted to hydrogen sulfide (H₂S) and 13% to alkyl homologues of thiophene
- 12% of the sulfur in the feed still remains in the form of dibenzothiophenes
- The sulfur balance was closed within 5%¹

On-line detection of nitrogen-compounds²

- On-line analysis method developed by cracking pyridine-heptane mixture under mild conditions (COT = 800 °C) to obtain mainly qualitative data
- Qualitative analysis done using the GC×GC-TOF-MS (Fig. a), while GC×GC-FID (Fig. b) is used for HC matrix quantification

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E-mail: marko.djokic@ugent.be
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