Rapid online analysis of diesel-range Fischer-Tropsch products

via APCI mass spectrometry

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Highlights

- A fast MS-based method was developed for allowing to monitor dynamic PtL-processes.
- The online gas-phase analysis makes use of APCI(+) ionization to quantify *n*-alkane mixtures.
- Diesel-range analytes were characterized 8 times faster compared to a conventional GC analysis.

1. Introduction

The Fischer-Tropsch synthesis (FTS) is a catalytic reaction which converts syngas to hydrocarbons [1]. Within today's ambitions of transforming the energy supply and production processes to a sustainable economy, the process is considered as petrochemical alternative for manufacturing fuels and chemicals without fossil resources [2]. Together with carbon capture technologies and water electrolysis, FTS can be used as a long-term chemical energy storage in time periods of excessive energy production by renewable power plants (Power-to-liquid: PtL). Hence, FTS may contribute to energy grid stability [3]. In a PtL scenario, dynamic reactor operation is of great interest in order to handle a time-variant feed gas, caused by a fluctuating energy production [4, 5]. Moreover, dynamic operation might lead to process intensification with an increased space time yield of desired diesel-range products [6, 7].

To investigate a dynamic FTS process, a suitable analytical equipment is necessary which is able to monitor temporal changes. However, an online analysis of diesel-range products in a heated gas flow is usually performed by gas chromatography (GC) and takes 40 min or more. With such a rather long measuring time, only slow reactor changes can be monitored.

Mass spectrometry (MS) is an alternative measurement technique, which is able to perform fast scans of hydrocarbon samples. However, usually chain fragmentation occurs, which results in overlapping signals of different species and makes a quantification by MS often infeasible [8]. Moreover, the main product group of FTS are *n*-alkanes and they are considered to be reluctant for MS ionization [9].

Atmospheric Pressure Chemical Ionization, utilized in positive ionization mode (APCI(+)), is regarded as suitable MS ionization technique to measure saturated hydrocarbons [10]. However, the ionization mechanisms are not yet entirely understood and fragmentation typically cannot be prevented completely. Moreover, the method is usually applied for liquid samples and not used for online gas-phase analysis.

2. Methods

We developed an automated APCI(+)-MS analytical procedure for analyzing diesel-range *n*-alkanes in gas-phase flows. A Fischer-Tropsch set-up was modified in such way that liquid alkane standards can be injected via a syringe pump into an empty reactor which served as evaporation chamber. The gaseous outflow was transported in a heated pipe together with a Fischer-Tropsch syngas mixture ($CO/H_2/N_2$) to a mass spectrometer (ThermoFisher Q Exactive Plus) as well as to a gas chromatograph (Agilent 8860). The GC was used as state-of-the-art reference and was equipped with two flame ionization detectors (FID) for hydrocarbon detection. We ensured a reproducible sample injection into the MS by installing a two-position valve including a 500 µL sample loop upstream of the ionization chamber. Both the MS and the GC performed automated online sampling and monitor the species concentrations over time. Syringe pump injections of *n*-heptane and *n*-decane as exemplary alkane analytes were to systematically evaluate mass spectra, fragmentation pattern, peak shapes and concentration linearity. After species calibration, a several mixture characterizations were applied using a binary as well as a five-component alkane mixture with chain lengths up to *n*-eicosane (C_{20}).

3. Results and discussion

Mass spectra of *n*-heptane and *n*-decane determined $C_nH_{2n+1}^+$ and $C_nH_{2n-1}^+$ ions to be the most abundant ion groups. However, these ions were highly fragmented, i.e., signal allocation in alkane mixtures is difficult. On the contrary, oxygen-containing $C_nH_{2n+1}O^+$ ions did not undergo chain cleavage, which enabled an analyte-specific signal allocation. They are assumed to be formed by secondary reactions of primary hydrocarbon ions with surface-adsorbed water. They are denoted as $[M\text{-}3H]H_2O^+$. Unfortunately, these ions featured rather broad signal peaks, i.e., they required a prolonged measurement time. Still, mixture analysis was possible with a sampling frequency of 5 min.

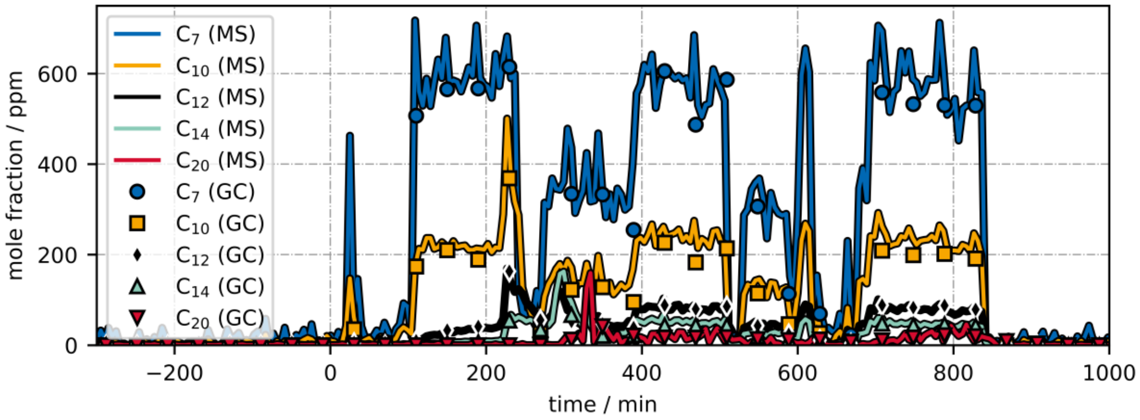

Figure 1. Concentration profiles of a $C_7/C_{10}/C_{12}/C_{14}/C_{20}$ *n*-alkane mixture diluted in a Fischer-Tropsch syngas feed gas, measured by gas chromatography (GC) and by mass spectrometry (MS).

Compared to the GC reference measurements, well-matched concentration profiles were achieved for one-, two-, and five-component alkane mixtures. Moreover, the increased sampling frequency allowed for capturing system dynamics that were not recognizable for the GC. Figure 1 shows an exemplary experiment using a $C_7/C_{10}/C_{12}/C_{14}/C_{20}$ *n*-alkane mixture as injection standard.

4. Conclusions

The results demonstrate that the developed APCI(+)-MS method is capable of analyzing diesel-range *n*-alkane species in the gas phase with sampling frequency eight times higher than the conventional GC instrument (5 min vs. 40 min). By using $[M\text{-}3H]H_2O^+$ ions for quantification, fragmentation pattern can be neglected, i.e., signals can be exclusively allocated to their corresponding alkane chain length. This allows for a straightforward species calibration. Matrix effects by other hydrocarbons, e.g., olefins, as well as by a changing CO, H_2 mole fraction are still under investigation. This will help to apply the method to a dynamic Fischer-Tropsch synthesis.

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Keywords

Fischer-Tropsch; dynamics; mass spectrometry; online monitoring