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GC × GC: A novel technique for investigating selectivity in the Fischer–Tropsch synthesis

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ABSTRACT

A study has been conducted to illustrate the benefit of the GC × GC-technique over the classically used 1D-GC technique to analyse the selectivity of iron catalysed low temperature Fischer–Tropsch synthesis. The selectivity of the products obtained from the iron catalysed Fischer–Tropsch synthesis at 225 °C; H_2/CO feed ratio = 1.5 and total pressure = 27 bars was evaluated. The selectivity results obtained from these methods were compared with special focus on the minor compounds such as oxygenates. The superiority of the GC × GC-technique above the 1D-GC technique were proven when minor product compounds such as the linear acids, secondary alcohols, ketones and aldehydes, and branched paraffins, olefins, alcohols, acids could be quantified using the GC × GC-technique but not using the 1D-GC system. It is further shown that the GC × GC-technique displayed a higher level of accuracy than 1D-GC system when detecting compounds in complex mixtures.

1. Introduction

Fischer–Tropsch synthesis is the catalytic conversion of hydrogen and carbon monoxide into a complex, but regular array of hydrocarbons and oxygenates of different chain lengths and different functionality [1]. A number of models [2–6] have been proposed to describe the full product spectrum (ranging from C_1 to C_{100+}). However, the complexity of the product and shortcomings of certain analytical techniques (or equipment) limits the description of the full product spectrum, which is typically extrapolated to high carbon numbers [1–9]. In most cases the selectivity information focused on the major compounds present in the products such as linear paraffins and olefins whereas limited information is available on the selectivity of minor compounds such as oxygen containing product compounds (carboxylic acids, aldehydes, ketones) [10–12], branched hydrocarbons [5,10,13], and even aromatic compounds [14]. The formation of minor products in the Fischer–Tropsch synthesis is of great interest, since it will give insight in the governing elementary reaction steps occurring on the surface [1,5,13,15].

Gas chromatography (GC) is the most common method used to separate the product compounds of the Fischer–Tropsch synthesis. It can be performed in a relatively short time (ranging from 10 to 80 min depending on the required product separation) and in general delivers good separation. However, problems may be encountered, when interest shifts to the detection and quantification of minor compounds, such as branched hydrocarbons, oxygenates and aromatic compounds. Specific pre-analysis steps are required to obtain insight in the formation of these product compounds. For example, the analysis of branched product compounds typically require a pre-hydrogenation of the Fischer–Tropsch product [5,13], thereby losing valuable information on the olefin content and the position of the double bond in this product group. Furthermore, the analysis of oxygen containing product compounds is difficult, if these compounds are not separated according to their functional groups prior to GC-analysis. In most cases these compounds co-elute with some of the major compounds making accurate determination of the amounts formed challenging.

A recent development in GC-technology is the introduction of the so-called comprehensive two-dimensional gas chromatography (GC × GC) [16,17]. The GC × GC-technique utilizes two GC-separations based on two fundamentally different separation mechanisms applied to the whole sample and it is well suited to analyse complex mixtures, e.g. fuel mixtures, with good separation for the minor compounds [17,18].

In this contribution, the benefits of the comprehensive two-dimensional gas chromatographic technique (GC × GC) over the classical one dimensional gas chromatography (1D-GC) for the analysis of product compounds formed in the Fischer–Tropsch synthesis are highlighted. Particular emphasis will be given to the challenging determination of the selectivity of oxygen containing compounds in the Fischer–Tropsch synthesis.

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2. Experimental

2.1. Fischer–Tropsch synthesis

The Fischer–Tropsch synthesis reaction was performed over a precipitated iron catalyst [19,20]. The catalyst (10 g) was suspended in ca. 350 g H1 wax and activated with synthesis gas (H_2/CO = 1.5) for 16 h at 255 °C and 14.5 bars prior to the Fischer–Tropsch synthesis. After activation, the reaction conditions were changed to 245 °C and 27 bars (SV = 9500 ml(STP)/g_{cat}/h) keeping the H_2/CO feed ratio at 1.5. After 100 h on stream, the synthesis temperature was adjusted to 225 °C and the space velocity to 4800 ml(STP)/g_{cat}/h keeping all other parameters constant. The products collected after 150 h on stream are used for this discussion.

The experiments were performed in a slurry reactor set-up (schematically shown in Fig. 1). The reactor acts as a Continues Stirred Tank Reactor (CSTR) and has a liquid volume of 670 ml (78 mm ID). The reactor was connected to a feed supply system that comprised of hydrogen (H_2: 99.999%) and carbon monoxide (CO: 99.97%). Argon (Ar: 99.999%) was also co-fed to the reactor system at approximately 10 mol% of the total feed stream serving as an internal standard for the accurate quantification of the components in the gas analysis. The H_2, CO and Ar were fed separately to the reactor (CSTR) using Brooks mass flow controllers. The outlet gas passed through a hot trap (at 200 °C) and cold trap (at ambient temperature) where wax and liquid product condensed out of the stream, respectively. The hot and cold traps were drained manually every 24 h. Part of the hot outlet gas stream (hot tail gas) feeding to the cold trap was transferred directly from the reactor through a system of heated (200 °C) valves and filters to chromatographic system comprising of a traditional capillary GC and a two-dimensional GC × GC system (GC/GC × GC). A nitrogen purge line was introduced to minimize contamination of the sampling system with heavy products. The incondensable cold outlet gas passed through a back pressure regulator and then went either to a vent system or to an on-line gas chromatography sampling system.

2.2. Product analysis

The inorganic compounds and methane in the effluent of the cold trap were analysed using an Agilent 6890N chromatograph equipped with a thermal conductivity detector (TCD). The hydrocarbons (ranging from C_1 to C_{10}) present in this stream were analysed using an Agilent 6890 GC equipped with a flame ionization detector (FID) and a Varian WCOT silica column.

The GC/GC × GC system contains two heated sample loops (see Fig. 2). The contents of each sample loop were injected through a guard column designed to protect the analytical system from heavy product compounds. The content of the first sample loop was injected into a thick phase non-polar column (CP Sil-5) to separate C_1–C_4, since these compounds were not separated on the GC × GC column setup (conditions given in Table 1). The content of the second sample loop was injected onto the first column of the GC × GC column setup. The GCxGC system consisted of two columns, a 1.5

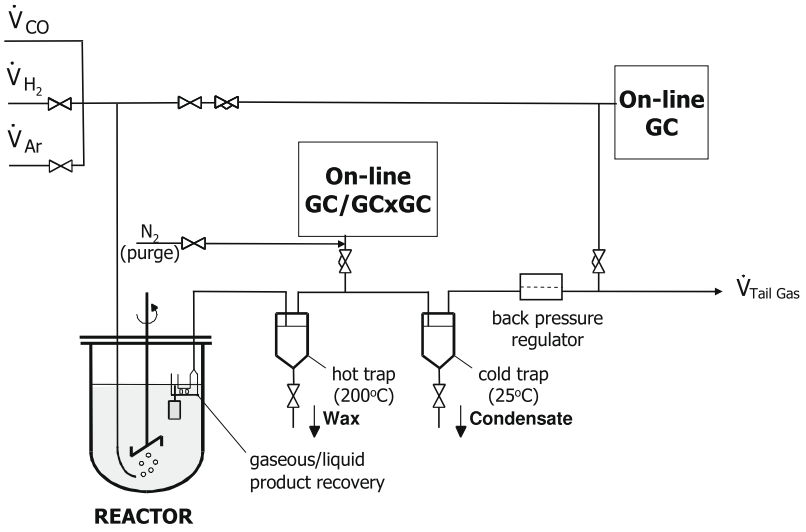

Fig. 1. Schematic diagram of the experimental set-up.

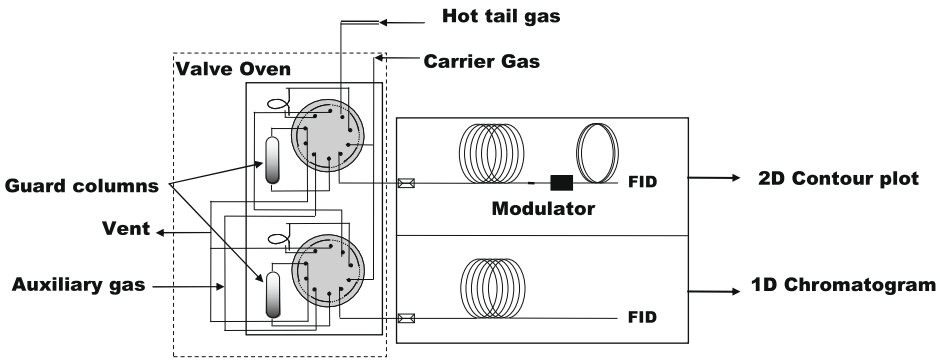

Fig. 2. Schematic diagram of on-line GC/GC × GC system.