Aqueous phase reforming of Fischer-Tropsch water fraction

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1. Introduction and Short Description:

The need of a sustainable and renewable production of fuels promoted the study of alternative processes to the conventional oil-based refinery. Among many technologies, Fischer-Tropsch (FT) reaction can convert CO and H_2 to transportation fuels. Despite its known performance, one of the economic bottlenecks is the production of large amounts of carbon-laden wastewater. As a consequence, it is necessary to treat the water fraction or recover the dissolved oxygenates, both for economic and environmental issues. Aqueous phase reforming is a catalytic process carried out at 230-270 °C and 30-60 bar with the aim of obtaining a gas mixture rich in hydrogen, according to the following reaction stoichiometry.

$$C_nH_{2y}O_n + nH_2O \leftrightarrow nCO_2 + (y+n)H_2$$

It has been greatly studied with model compounds (alcohols and polyalcohols), but very few studies have been referred to mixture, and it is even negligible the available literature for real industrial phase.

2. Methodology, Results and Discussion

In the present work, methanol, ethanol, 1-propanol, 2-propanol, butanol and acetic acid were tested as representative compounds for FT water; an actual liquid phase coming from a low temperature FT process has been tested at different reaction temperatures (230-270 °C) and time (0-4 hours) with a developmental 5% Pt/C catalyst.

Together with the gas phase, a thorough characterization of the liquid phase was performed to determine key intermediates/by-products present at the end of the reaction.

The catalytic tests have been performed in a Parr bench top reactor, equipped with a temperature controller. The screening of the model compounds was performed at equal carbon concentration (0.9 wt.%). At the end of the reaction, the gas phase was collected in a sampling syringe and the analysis performed by an SRA μGC. The liquid phase was characterized by HPLC Shimadzu system, equipped with a Rezex ROA organic acid column. The quantification of the compounds was performed via external calibration.

In Figure 1 the HPLC chromatogram of the FT water is reported; the main compounds present are C1-C4 alcohols and the corresponding carboxylic acids.

Among the obtained results, it is highlighted in Figure 2 the influence of reaction time on the FT water APR studied at 270 °C, that was found to be the temperature with the highest hydrogen yield. It was observed that ethanol and propanol were readily converted during the heating time, while methanol was less reactive. Moreover, acetic acid did not convert at all, in agreement with previous results.

In the gas phase it is highlighted the constant increase of hydrogen and carbon dioxide, while the amount of alkanes was almost constant, after that 270 °C was reached (i.e. 0 hour in the graph). This is directly linked to the complete conversion of ethanol and propanol that lead to methane and ethane respectively. Indeed, from the APR of the representative compounds it is possible to ascribe the produced gases to the single alcohols present in the FT water.

3. Conclusion and Outlook

Water-soluble oxygenates in the aqueous effluent of Fischer-Tropsch are not easily recoverable, as they can form complex azeotropes, and are often in low concentration. While the wastewater treatment is the most used option, we proposed to investigate the catalytic route of aqueous phase reforming to produce hydrogen as valuable by-product, solving at the same time environmental and economic concerns.

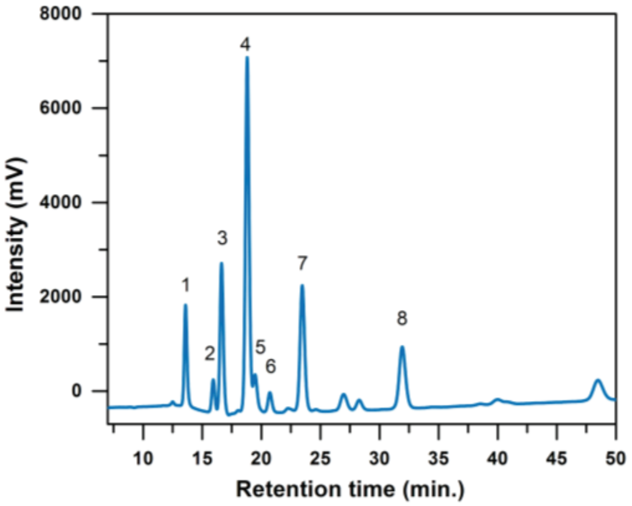

Fig. 1: HPLC chromatogram of FT water (1: acetic acid, 2: propionic acid, 3: methanol, 4: ethanol, 5: butanoic acid, 6:2-propanol, 7:1-propanol, 8: butanol)

Acknowledgement

This work was supported by the European Union´s Horizon 2020 research and innovation programme under grant agreement number 764675.

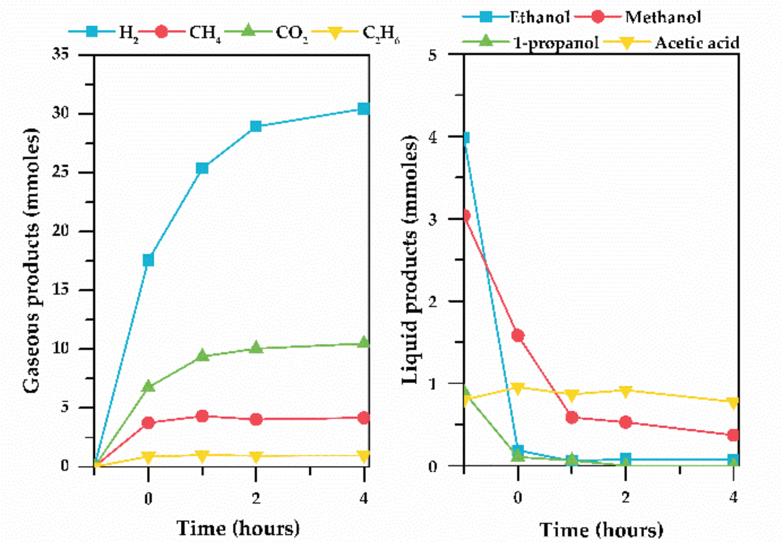

Fig. 2: Influence of reaction time on the aqueous phase reforming of FT water. Reaction conditions: 270 °C, 0.375 g Pt/C, 75 mL FT solution.