

Improving the Selectivity to Liquefied Petroleum Gas by Combining Fischer-Tropsch Synthesis with Zeolite Cracking

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Abstract

The Fischer-Tropsch synthesis (FTS) plays a major role in the large-scale production of hydrocarbons (HCs) from syngas ($\text{CO} + \text{H}_2$) in the so-called gas-to-liquid process. By the use of renewable hydrogen by water electrolysis and CO_2 , such a process can help to reduce anthropogenic greenhouse gas emissions and thus mitigate the effects of climate change. In Wunsiedel, a small city in Upper Franconia (Bavaria), one of the largest water electrolyzers in Europe was put into operation in Sept. 2022. In addition to direct use, the produced hydrogen can be converted to HCs, especially liquefied petroleum gas (LPG) which is needed as fuel in households or small businesses in this rural areas.

The kinetics of the FTS results in a statistical distribution of hydrocarbons, known as Anderson-Schulz-Flory distribution, which limits the use of the reaction, since it is impossible to selectively produce one hydrocarbon or a hydrocarbon cut with a narrow carbon number distribution. For instance, the selectivity towards LPG ($\text{C}_3 + \text{C}_4$ fraction) is therefore limited to a theoretical maximum of $\approx 32 \text{ wt}_\text{C}\%$. To overcome the limitations of FTS and increase the selectivity to LPG, downstream processing of the primary longer-chain FT compounds by means of cracking on an acidic zeolite is an option.

In this project, the optimal process parameters for the production of LPG by a FTS/hydrocracking tandem process were determined. Furthermore, the influence of the gas composition of FTS on the downstream hydrocracking reaction was investigated, i.e. non-reacted carbon monoxide as well as the FT by-product water are present during hydrocracking.

The tested operation configurations and process parameters delivered the best results for a separated two stage operation of FTS and hydrocracking, since both catalysts can operate under optimal conditions. The FT reaction parameters ought to be selected in a way that the lowest possible selectivity to C_1 and C_2 compounds prevails, as these compounds cannot be further converted to LPG at the zeolite. Hydrocracking should be performed at a bifunctional platinum doped H-ZSM-5 zeolite at a maximum of $350 \text{ }^\circ\text{C}$, since a further temperature increase leads to the formation of undesired short chain HCs (C_1+C_2).

The product gas of FTS was deliberately simulated by using different mixtures of n-hexadecane (model substance for C_{5+} -HCs typically formed by FTS), H_2 , CO and H_2O in order to study the effect of each compound separately, independent of the upstream FTS. The results showed that it is useful to modify the two stage process of FTS and subsequent hydrocracking by the installation of a product separation downstream of FTS, since CO and water from FT reaction negatively influences the cracking reaction to LPG components.