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Master's thesis and Internship : Modelling and Integration of a Hydrocracking Unit for Fischer-Tropsch Syncrude in a Power-to-Kerosene Process

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Modelling and Integration of a Hydrocracking Unit for Fischer–Tropsch Syncrude in a Power-to-Kerosene Process

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Abstract

Aviation is among the hardest sectors to decarbonise: long-haul flight depends on high-energy-density liquid fuels for which direct electrification offers no realistic substitute. The Power-to-Liquids route, in which captured CO_2 is combined with electrolytic hydrogen to synthesise drop-in jet fuel, represents a relevant pathway for reducing aviation's dependence on fossil kerosene. In the low-temperature Fischer-Tropsch route over a cobalt-based catalyst, syngas is converted into a broad hydrocarbon distribution that is, however, weighted towards the heavy C_{17+} paraffinic wax fraction rather than the C_8-C_{16} kerosene cut targeted by the process. Converting this heavy fraction into kerosene-range products therefore requires a dedicated upgrading step, and hydrocracking over a bifunctional catalyst is the technology retained for this purpose. The present work develops a hydrocracking reactor model and integrates it downstream of the Fischer-Tropsch (FT) unit of the Power-to-Kerosene process under development at the University of Liège (ULiège) within the Neutral-Kero-Lime project, completing the upstream chain previously modelled by A. Rouxhet and A. Morales [1, 2].

Three modelling approaches were evaluated successively. A stoichiometric model and a thermodynamic-equilibrium model were both shown to be structurally unable to reproduce the experimental hydrocracking behaviour, confirming that the reaction is kinetically rather than thermodynamically controlled. The Langmuir-Hinshelwood-Hougen-Watson kinetic model of Pellegrini et al. (2007) [3] was consequently retained, because it resolves the product stream at the component level, a resolution required to track the C_8-C_{16} cut without committing to a fixed lump definition, under the simplifying assumption of a single vapour phase combined with midpoint cracking. Two pieces of information omitted from the original publication had to be recovered in Python before the model could be applied: the inlet distribution, identified through hypothesis testing as corresponding to the distribution later reported by Pellegrini et al. (2008) [4], and the final optimised kinetic parameters, reconstructed by regularised parameter estimation against the published model curves.

The validated model was then applied to the ULiège FT hydrocarbon stream after olefin-hydrogenation pre-treatment, with the objective of identifying the temperature, pressure, weight hourly space velocity (WHSV) and hydrogen-to-wax ratio that maximise the C_8-C_{16} mass fraction at the reactor outlet. Within the Pellegrini calibration domain, the procedure converges at $T = 369.3\,^{\circ}\mathrm{C}$, $P = 60$ bar, WHSV $= 3.00\ \mathrm{kg_{n\text{-}C,in}\,kg_{cat}^{-1}\,h^{-1}}$ and H_2/wax $= 0.150$ kg/kg, yielding 52.0 wt-% of C_8-C_{16} at the outlet for a C_{17+} mass conversion of 55.9 %. At the pilot-scale throughput of the ULiège installation, applying standard plug-flow design criteria to this operating point yields a preliminary trickle-bed reactor geometry of approximately 26 mm internal diameter and 132 mm bed height, holding close to 38 g of bifunctional Pt/SiO_2-Al_2O_3 catalyst. Three of the four coordinates lie on the upper bound of the calibration window, indicating that the model response would continue to climb beyond the calibrated range. Dimensional sensitivity analyses around this point expose two limitations of the model: the H_2/wax ratio acts on the model exclusively through the hydrogen partial pressure, so the genuine two-phase character of the system is not captured; and the midpoint cracking stoichiometry underestimates the iso-paraffin yield relative to the experimental data. A comparison of the recommended conditions across feed selection (full C_1-C_{70+} stream versus C_{17+} fraction only), exploration domain (author calibration versus extended literature range) and optimality criterion (strict versus relaxed economic ranking) further isolates the contribution of each modelling choice. One caveat conditions the reading: the kinetic parameters, calibrated on the Pellegrini C_4-C_{70} feedstock and not refitted to the ULiège stream (for which no experimental data exist), make the reported yields and conditions order-of-magnitude indications and a transferable methodology, not definitive design values, though a check on the calibration feed itself suggests the trends carry over between feeds.

Several perspectives follow naturally. At the reactor scale, replacing the single-phase partial-pressure assumption with a proper vapour-liquid description and the midpoint cracking with a breakage-probability stoichiometry would address the two structural limitations identified by the sensitivity analyses. At the process scale, integrating the model into the full Power-to-Kerosene flowsheet in Aspen Plus would enable a techno-economic assessment of the recommended operating point.

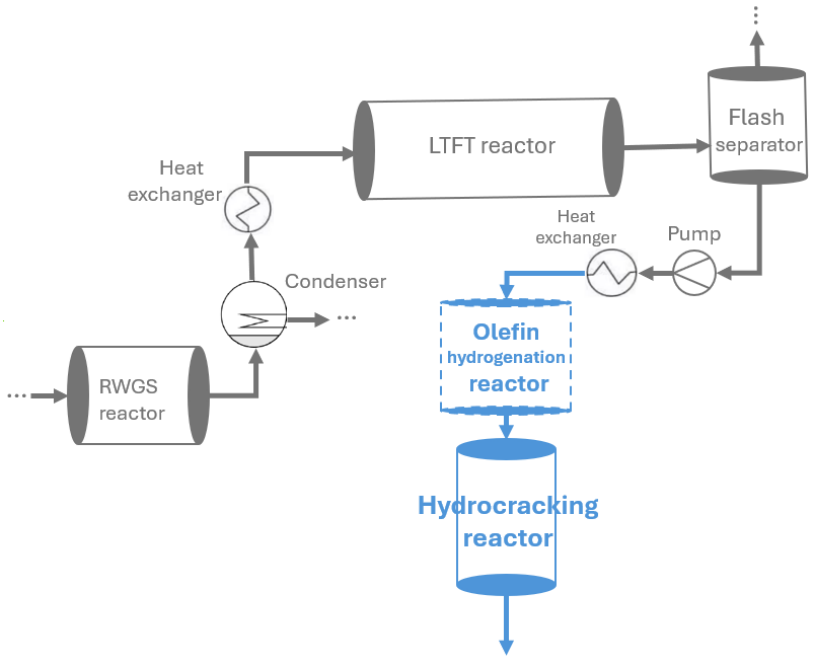


Figure 1: Simplified block flow diagram of the relevant section of the ULiège process and the hydrocracking unit modelled in this work.

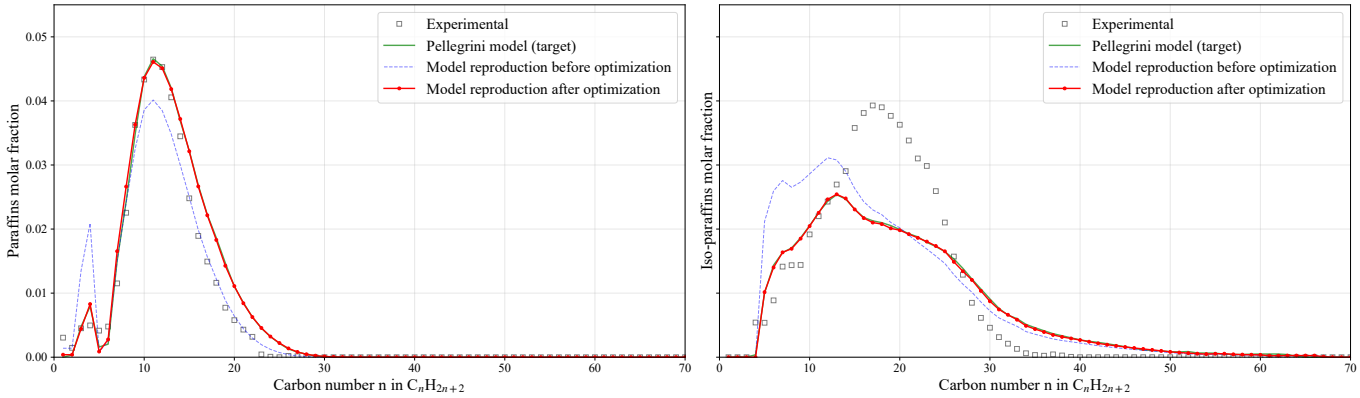
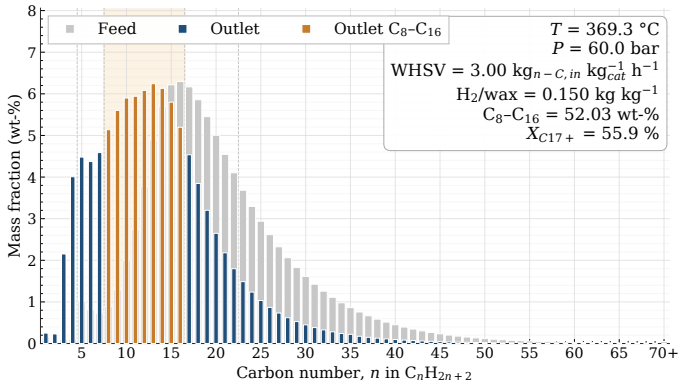
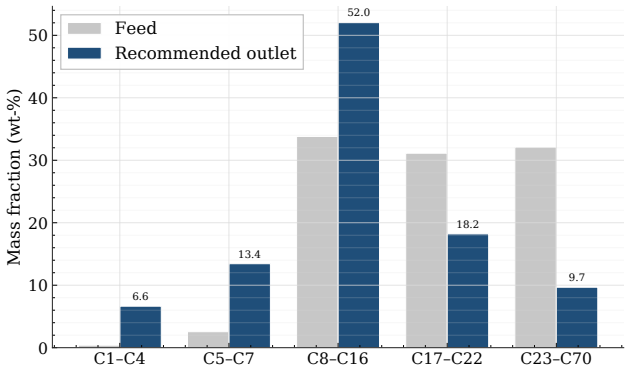


Figure 2: Outlet molar fraction distributions of n-paraffins (left) and iso-paraffins (right) simulated before and after parameter optimisation against the model curves of Pellegrini et al. (2007) [3], under conditions (T = 367 °C, P = 53.75 bar, H_2/wax = 0.1275 kg/kg, WHSV = 2.5 $kg_{n\text{-}C,in}\ kg_{cat}^{-1}\ h^{-1}$).

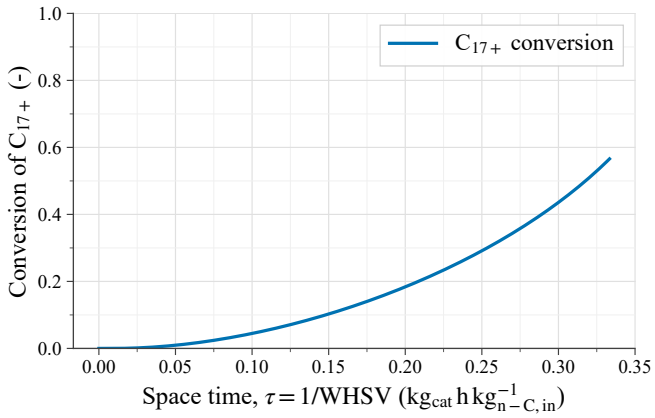


(a) Inlet and outlet carbon-number distribution on a mass basis.

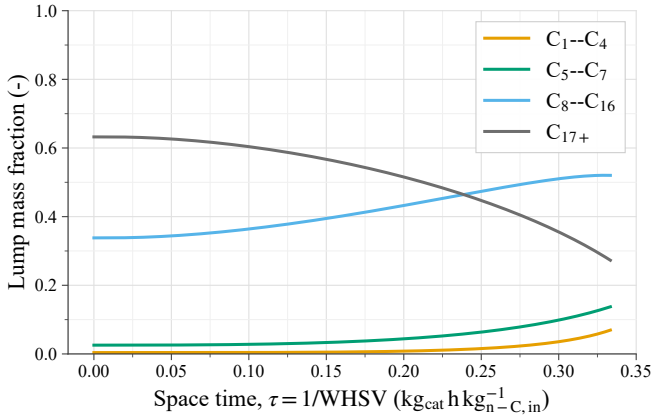


(b) Lump breakdown of the inlet and outlet streams.

Figure 3: Inlet and outlet carbon-number distributions at the optimal operating point (T = 369.3 °C, P = 60 bar, WHSV = 3.00 $kg_{n\text{-}C,in}\ kg_{cat}^{-1}\ h^{-1}$, H_2/wax = 0.150).



(a) C_{17+} mass conversion along the reactor.



(b) Lump mass fractions along the reactor.

Figure 4: Reactor profiles as a function of the space time $\tau = 1/\mathrm{WHSV}$ at the recommended operating point.

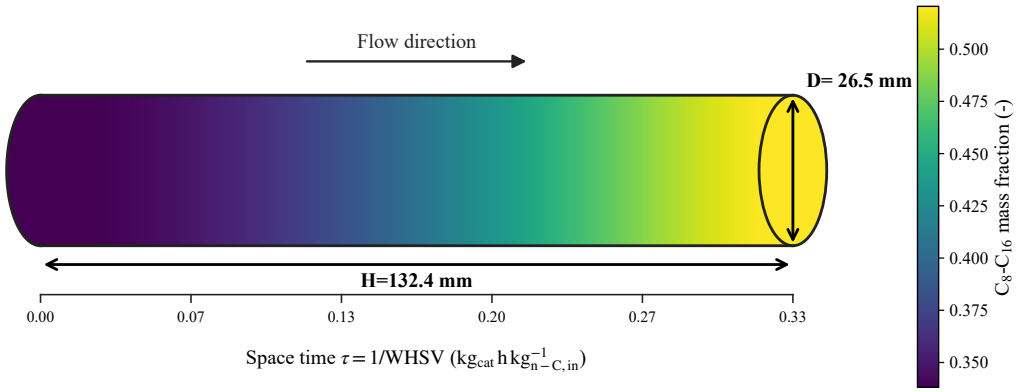


Figure 5: Schematic representation of the cylindrical packed-bed reactor at the recommended operating point (full C_1-C_{70+} ULiège feed, T = 369.3 °C, P = 60 bar, WHSV = 3.00 $\mathrm{kg_{n\text{-}C,in}\,kg^{-1}_{cat}\,h^{-1}}$, H_2/wax = 0.15 kg/kg).

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