Modelling and kinetic study of a Fischer-Tropsch reactor for the synthesis of e-kerosene

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Modelling and kinetic study of a Fischer-Tropsch reactor for the synthesis of e-kerosene

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If climate change is evident, society's current ecological transition is also apparent. Renewable energy sources utilisation is paramount to mitigate the anthropogenic environmental impact. However, they present significant drawbacks, including primarily their variability. It implies the necessity to store them in the medium and long term to address this problem, which is possible through the Power-to-X technology. This work specifically focuses on the production of e-kerosene through the low-temperature cobalt-based Fischer-Tropsch synthesis. There are various kinetics in the literature describing this reaction. The overall idea behind this master's thesis is to identify the best kinetic model to be implemented in a reactor model. Ultimately, it will help to understand the interactions between the reaction and the rest of the process.

In this work, the kinetics developed by Ma et al. (2014b,a) are specifically studied. Compared to more classical models, it includes a positive kinetic effect induced by water. A reactor model is developed in Aspen Custom Modeler® in which the kinetics are considered. The reaction stoichiometry is developed following the Anderson-Schulz-Flory theory by accounting for the methane deviation from this ideal model. The implementation of these kinetics and stoichiometry is validated with experimental data (Ma et al., 2014b,a). It is shown that the squared correlation coefficients between the calculated and experimental values exceed 90%. Then, the results yielded by the reactor model are compared with another study (Morales and Léonard, 2022) in which more simple kinetics, following a Langmuir-Hinshelwood expression, are implemented. The model developed in this study concludes that a reactor 2.5 times greater is required to reach an equivalent conversion. A discussion is conducted to explore the origin of this divergence, yielding various assumptions. The general expression and catalyst used to regress both models differing, it probably plays a role in this dissimilarity. A specific interest is also given to the kinetics validity range, which varies depending on the assumptions taken to determine it. A fully numerical approach yields a limiting conversion value of 83.5% in base case conditions, while only considering Ma et al. (2014b)'s experimental data leads to a limiting value of 52%. The validity of these approaches is discussed. Eventually, some sensitivity analyses are conducted to observe the reactor model behaviour when some of its parameters and variables are varied. It shows that proper temperature control of the reaction is crucial for reactor performance and that an appropriate tuning of cooling system parameters should be conducted. These sensitivity studies also reveal that an optimal reactor temperature around 210°C and a syngas ratio slightly above 2 maximise the kerosene fraction selectivity.

The perspectives envisaged for this project are multiple. A particular focus should be given to refining the kinetics validity range and deepening the study of the water kinetic effect, possibly experimentally. Validation of the reactor model with other experimental data seems also relevant. Hopefully, the objective is to conduct those experiments on the future lab-scale installation at ULiège.

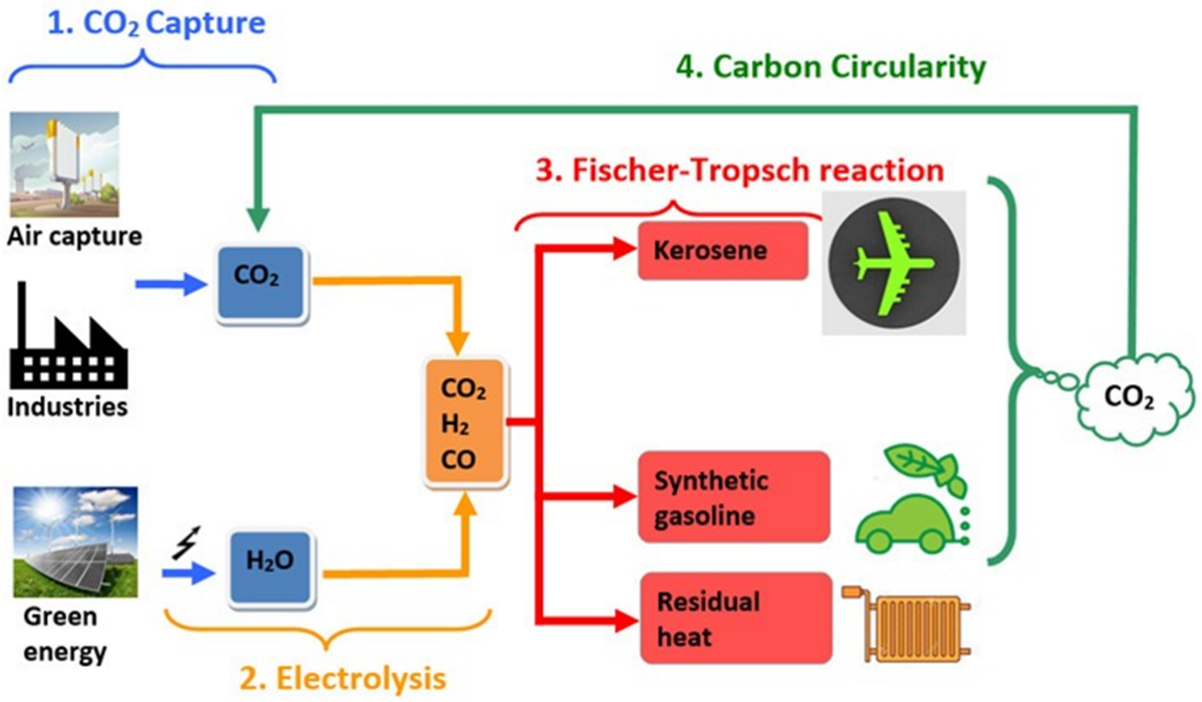

Figure 1: Schematic representation of the Power-to-Fischer-Tropsch technology (Léonard, 2021b)

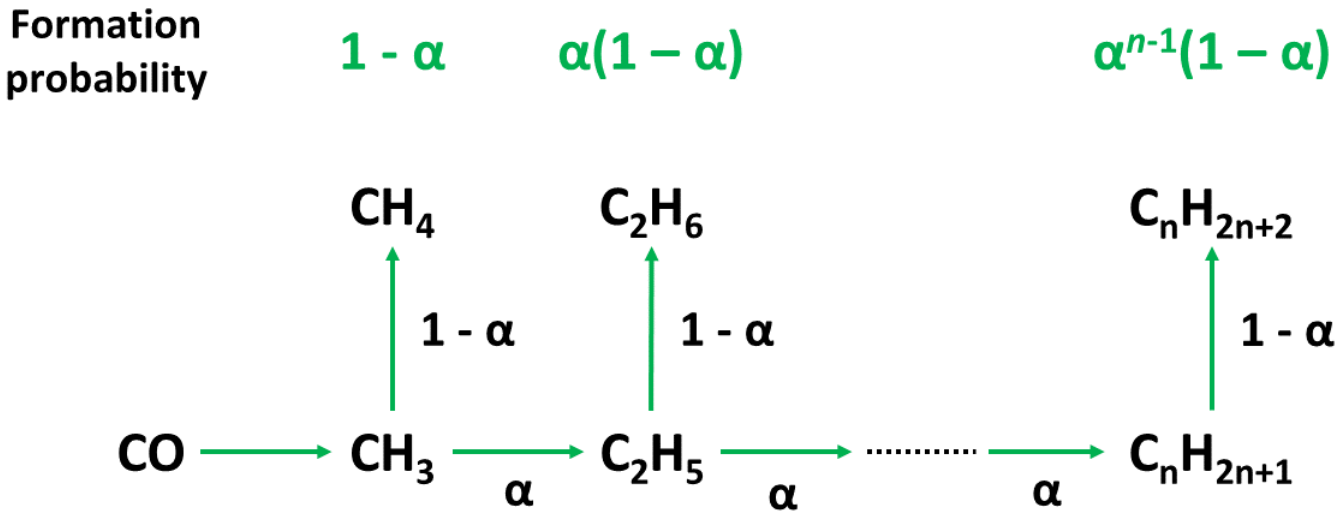

Figure 2: Schematic representation of chain growth probability (inspired by Panahi et al. (2012))

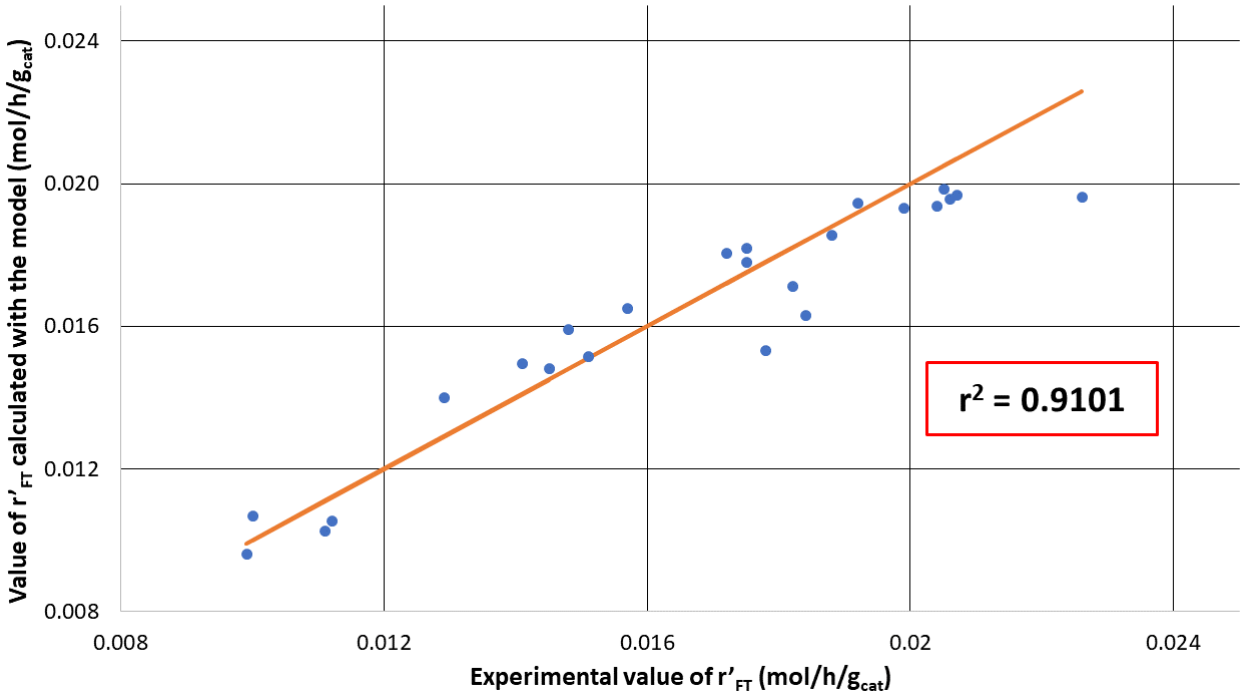

Figure 3: Parity plot for comparison of experimental (Ma et al., 2014b) and calculated Fischer-Tropsch reaction rate r'_{FT}. Their squared correlation coefficient r^2 is also shown

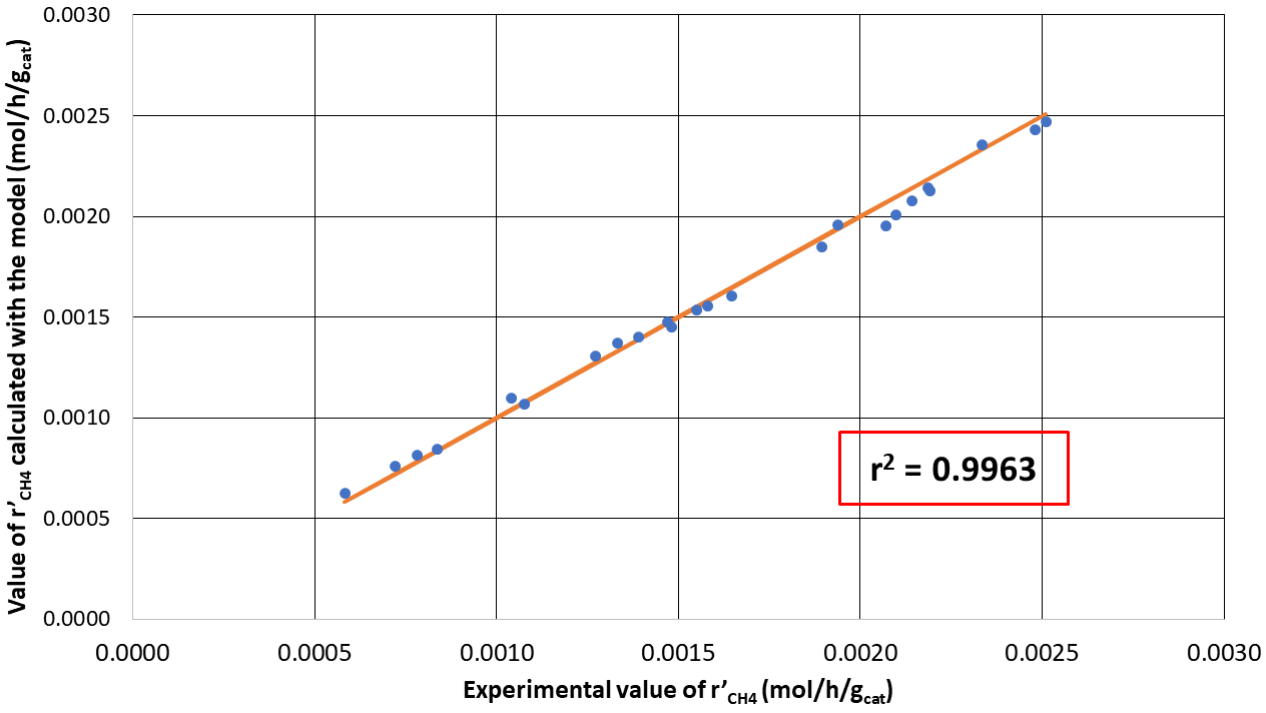

Figure 4: Parity plot for comparison of experimental (Ma et al., 2014a) and calculated methane reaction rate $r'_{\mathrm{CH_4}}$. Their squared correlation coefficient r^2 is also shown

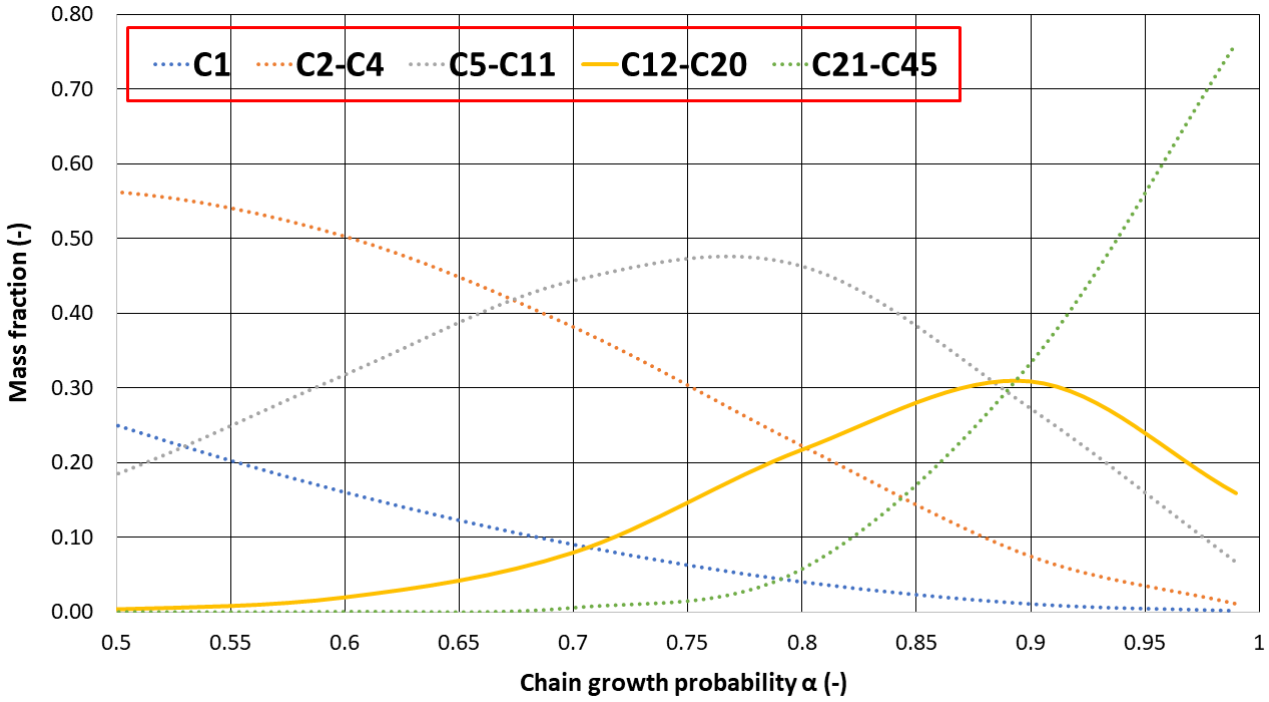

Figure 5: Variation of the mass fraction of Fischer-Tropsch product fractions with chain growth probability α

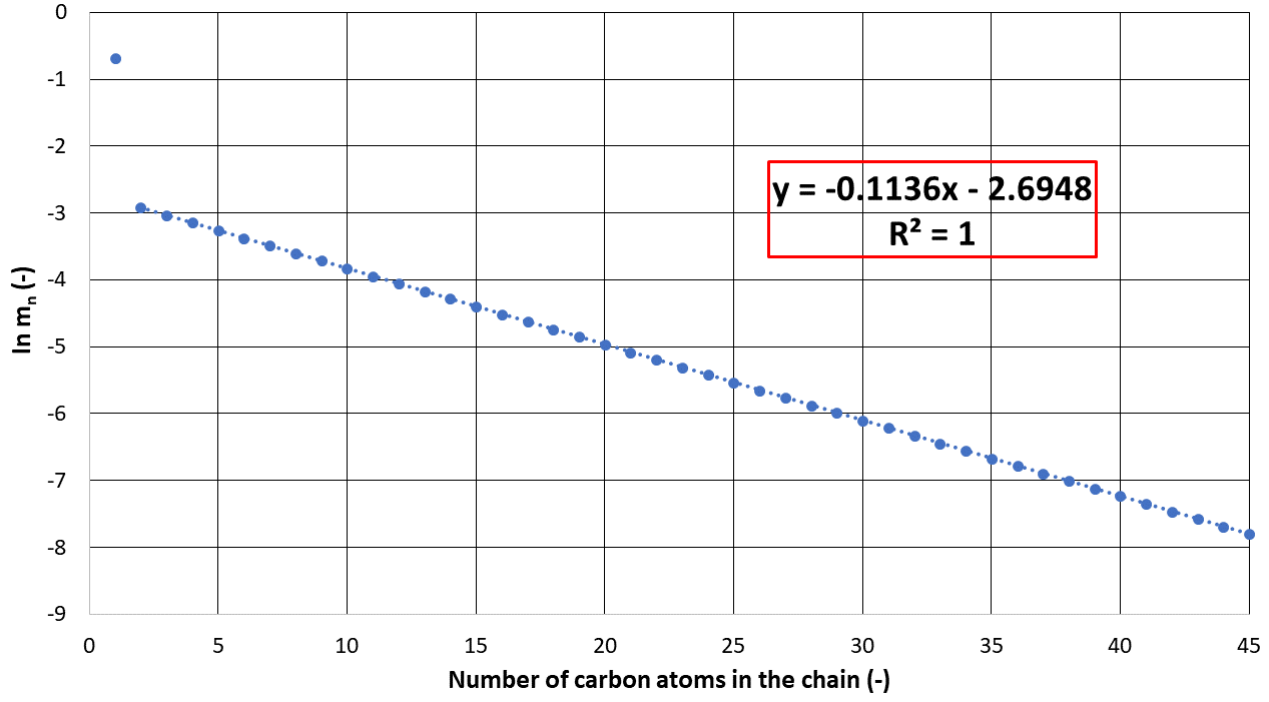

Figure 6: Distribution of Fischer-Tropsch product molar fractions in the product spectrum at the reactor outlet for 1.25 kg of catalyst in the base case conditions

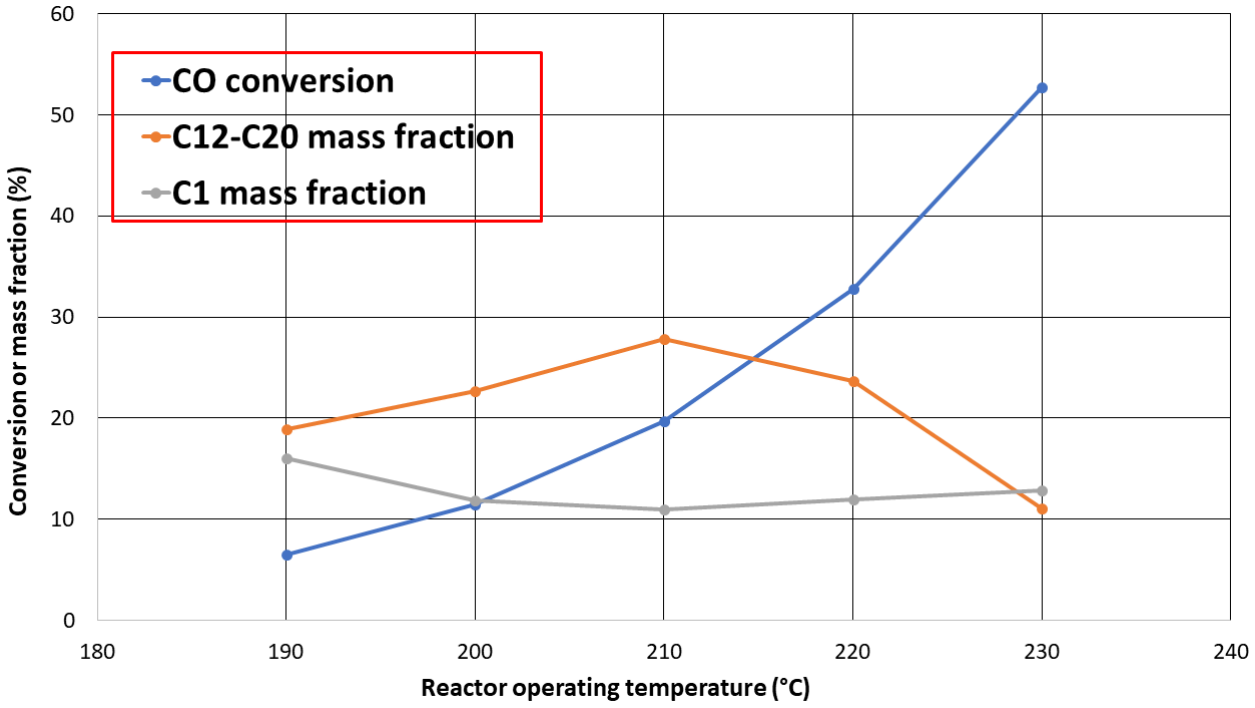

Figure 7: Influence of reactor operating temperature on CO conversion and methane and C12-C20 mass fractions at the reactor outlet for 0.5 kg of catalyst in the base case conditions

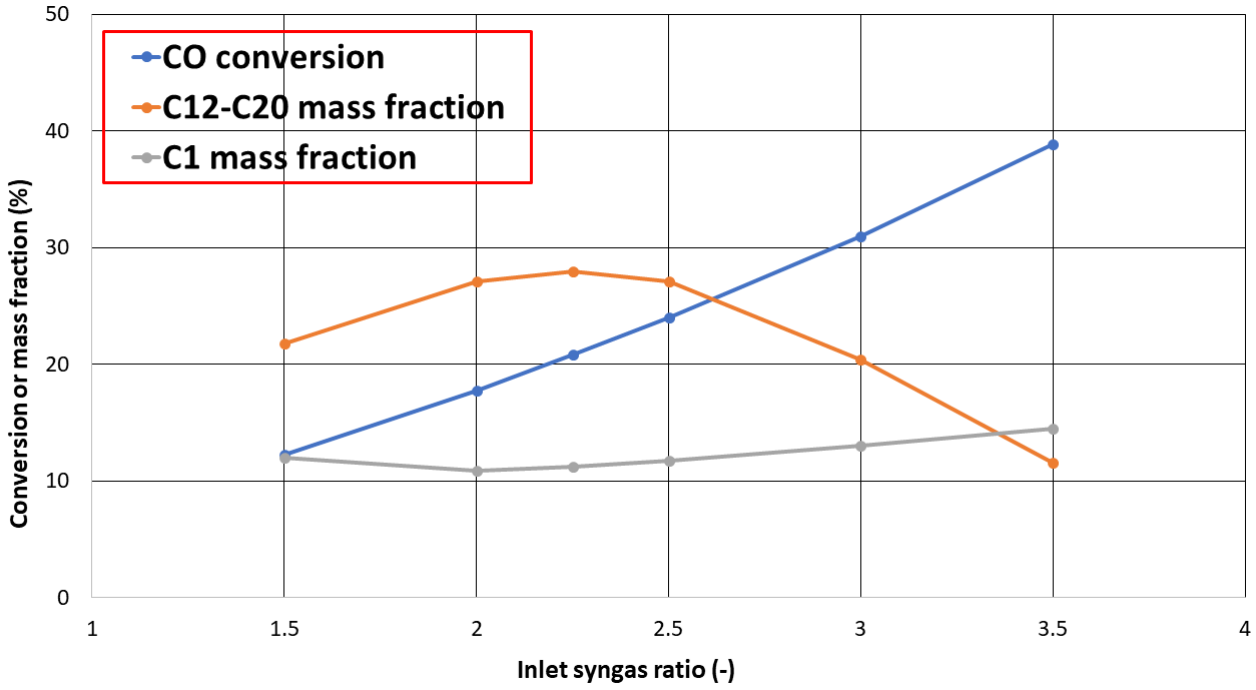

Figure 8: Influence of inlet syngas ratio on the CO conversion and methane and C12-C20 mass fractions at the reactor outlet for 0.5 kg of catalyst in the base case conditions

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