Mechanistic Modelling of Reactive Liquid-Liquid Extraction Towers using polar PC-SAFT: Industrial Validation and Optimization of Fat/Oil Hydrolysis

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Biorefineries provide an important alternative for petroleum-based refineries to reduce CO_2 emissions and increase the share of renewable feedstocks for the production of chemicals and fuels. Vegetable oils and animal fats are used as renewable raw materials for the production of oleochemicals. Never before in the history of the oleochemical industry have the changes been more dramatic than in the last decades. The rapid growth of palm oil, the rise of oleochemicals production in Southeast Asian Nations and an increased competition with the biofuel industry for feedstocks form a challenge for the traditional oleochemical players in Europe and North America.[1] This increased competition forces European oleochemical companies such as Oleon NV to diversify the feedstocks they process, ranging from low quality animal fat to higher quality vegetable oils. Operating a continuous installation with a variable feed composition poses significant challenges for process operation and control to ensure resource efficiency, high product yields and excellent product quality. Petroleum refineries regularly use mechanistic and statistical modelling to tackle this challenge of feedstock diversity and adapt process conditions for compositional variability of the incoming crude oil.[2] Applying these techniques to biorefineries, such as for the production of oleochemicals, could aid in utilizing variable bio-based feedstock streams more efficiently, enable the use of lower quality-grade feedstocks and improve adaptability toward future changes in demand and supply.[3]

Fat/Oil hydrolysis is the first step in the production of fatty acids. On an industrial scale, oil hydrolysis is mostly performed in large splitting towers via a counter-current reactive liquid-liquid extraction, as shown in **Figure 1**. The oil feed is introduced at the bottom of the tower and forms the continuous organic phase, while water is introduced at the top and forms the dispersed aqueous phase. The reaction takes place in the organic phase, and the formed glycerol is extracted via the aqueous phase. For fat/oil hydrolysis, important considerations are a high degree of hydrolysis, a high concentration of glycerol in the aqueous phase and a minimal colour degradation of the fatty acids. In the past, related process optimization was typically performed via ad-hoc experiments, neglecting possible adjustments for other feedstocks. This lack of accounting for feedstock variability highly limits an oleochemical plant's flexibility to switch between feedstocks. Although the oleochemical industry is mature, modelling research on oil hydrolysis is scarce, due to the complexity of lipid feedstocks and the lack of data on physical properties.[4] In this work, a comprehensive process model of industrial-scale splitting towers that is able to predict the yield for oil hydrolysis is developed and used to investigate optimal processing parameters for different bio-based triglyceride feedstocks.[5]

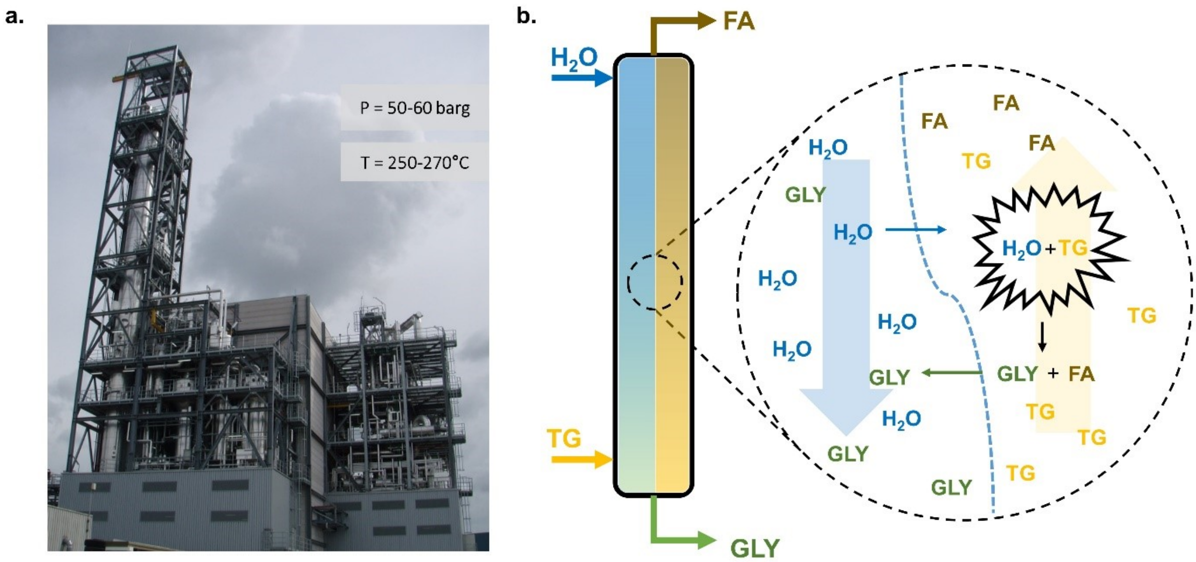

Figure 1. a. Picture of one of the studied industrial-scale splitting towers (Source: Oleon NV). b. Graphical representation of the counter-current reactive liquid-liquid extraction (FA = fatty acids, GLY = Glycerol, TG = Triglycerides).

The splitting tower is represented by a compartmental model, using a cascade of continuous stirred tank reactors and liquid-liquid separators. The developed model extends the state of the art by including a variable glycerol equilibrium ratio, which is a function of the composition and temperature and is calculated using the polar version of the perturbed chain statistical association fluid theory (PPC-SAFT).[6] The group contribution method for PPC-SAFT (GC-PPC-SAFT) is used for all lipid compounds to calculate pure compound properties such as segment number m_i and segment diameter σ_i.[7] The liquid-liquid equilibrium estimated by PPC-SAFT is compared to more traditional property methods UNIFAC_DMD, UNIQUAC and SRK. In addition, the model accounts for the autocatalytic effect of fatty acids in hydrolysis and the isomerization of poly-unsaturated fatty acids.[8, 9] Model validation is performed using process data from three real-life splitting towers covering four feedstock types, i.e., tallow, rapeseed oil, palm oil, and palm fatty acid distillate.

The splitting tower model properly estimates the degree of hydrolysis for tallow, palm, PFAD and rapeseed oil. Composition gradients of the organic phase throughout the tower show that it is crucial to properly account for the changes in the glycerol equilibrium ratio. For the hydrolysis of rapeseed oil, the calculated concentration profiles over the tower show that the reaction is slow at the bottom of the tower due to a low amount of free fatty acids in the organic phase. The reaction rate increases towards the middle, due to a better solubility of water in the organic phase and the autocatalytic effect. At the top, the reaction approaches equilibrium and thus slows down. The importance of feedstock flow rate, water/oil ratio, and temperature profile throughout the tower is analysed and confirmed by sensitivity analysis. Our results show that modifying the temperature profile may shift the reaction equilibrium toward the fatty acid product. In addition, the changed settings result in a reduced steam consumption (-8%), saving water and energy, which is equivalent to a reduction of the climate change impact by 13 kg CO_2eq per tonne hydrolysed rapeseed oil. This knowledge is crucial for improving the energy and resource efficiency of fat/oil hydrolysis, thereby improving its economic and environmental sustainability.

Overall, this work shows how process modelling can deliver a strategic advantage to oleochemical companies for understanding and operating their processes on an industrial scale. For this, the collaboration between academia and industry is essential, as it offers realistic use cases to academia and allows displaying the benefits of new developments and methodologies in process systems engineering to industry.

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