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Methodology for intensified reactor design applied to the selective hydrogenation of edible oil

Pierre Albrand¹, Florian Veyrine¹, Anne-Marie-Billet¹, Carine Julcour^{1*}

¹ Laboratoire de Génie Chimique, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

*Corresponding author E-Mail: carine.julcour@ensiacet.fr

1. Introduction

The controversy on large-scale palm oil cultivation and, concurrently, the growing concern for cardiovascular illness linked to a diet rich in saturated and/or *trans* fats emphasises the urgent need for suitable edible oil hydrogenation processes. This requires respectful processes towards environment and health (for instance without any risk of nuisance from metal catalyst) as well as selective processes to yield high contents in essential fatty acids, *i.e.* *cis* monoenes. This challenge is played out at the catalyst scale where chemical regime should be enabled, but also at the reactor one with optimal temperature control. Structured heat exchanger-reactors of monolith type (MRHEX) have arisen as promising devices for such a purpose, considering their efficient gas-liquid mass transfer, high available surface area for heat exchange, and plug-flow like behaviour when Taylor flow regime is hosted in the monolith channels [1]. However, recent studies have questioned the homogeneous character of the liquid slugs in Taylor flow [2]. This issue could be even more intricate in the considered case, owing to the high and increasing viscosity of edible oil during the processing. Therefore, a design tool dedicated to this specific application is developed to assess the convenience of these reactors.

2. Methods

A specificity of this work is due to the strong multiphysics interplay coming from the high dependency of viscosity and species diffusivity to oil saturation degree. This requires a reliable model to predict viscosity evolution during the hydrogenation. Then, at the catalyst scale, the kinetic modelling has to account not only for the successive hydrogenated intermediates, but also for the produced isomers. Several mechanisms and rate laws have been proposed to date, but the exact description of the complex effect of pressure and temperature on reaction selectivity remains an open issue [3, 4]. Finally, for the reactor model, these bricks have to be assembled in an adequate simulation environment able to couple all the implied phenomena at the required scale. The developed methodology proposes to examine these crucial points, first separately, then together, by revisiting some of the approaches already applied to the case of edible oils or their main components, triglycerides (TAG). For instance, a contribution group model for TAG viscosity, formerly established by Cerani et al. [5], has been successfully extended to the case of sunflower oil, representing the evolution of its viscosity with respect to the saturation degree and the temperature with an accuracy of +/- 4%. A dedicated experimental campaign has also been performed to evaluate the hydrogenation kinetics for the Pd/Al₂O₃ catalyst present in the monolith wall coating: the catalyst has been used under powdered form in a well-mixed autoclave reactor to remove any mass transfer resistance. Based on the time evolution of species concentration obtained for various operating conditions, a comprehensive kinetic model has been adapted from Grau et al.'s work [3] and optimized to fit the observed selectivity. Finally, following the strategy of Duran-Martinez et al. [6] on the modelling of MRHEX, these models have been associated together to simulate the behaviour of an elementary pattern of the Taylor flow, the so-called Unit Cell, during its progression along the catalytic reactor. Hydrogenation of sunflower oil has been taken as an example. Pressure and velocity of the liquid phase, and concentrations of fatty acids (present in TAG), are computed.

3. Results and discussion

The UC is described in a reference frame travelling along with the bubble, through using a moving wall. During the time-dependent calculations, the geometry, and so the gas-liquid interfacial area, are kept unchanged, but the simulation accounts for the reduction of the gas flow rate, by updating wall velocity. Figure 1a gives an example of the concentration field of fatty acids when the bubble reaches almost half the distance (z) required for the bubble to shrink to a sphere (z_f). In this work, only consecutive hydrogenation reactions are taken into account (*cis* and *trans* isomers being lumped), but essential features of the UC behaviour for a viscous medium are still revealed. Indeed, due to the consumption of polyunsaturated species by the chemical reaction at the wall, sharp C18:2 concentration contrasts are noticeable between the near-wall regions and the rest of the liquid. The zone located at the centre of the slug vortex exhibits a poor exchange with the wall, due to the limited diffusion of the TAG perpendicularly to the streamlines. This gives rise to a segregation phenomenon, with monoene compounds formed at the catalytic wall readily transformed into saturated ones. This situation is highlighted in Figure 1b, showing the evolution of C18:2 and C18:1 bulk molar fractions along the channel, where the maximum proportion of monoene observed – close to the channel entrance – does not exceed 33% whereas more than 70% is predicted by a plug flow model with no mass transfer resistance.

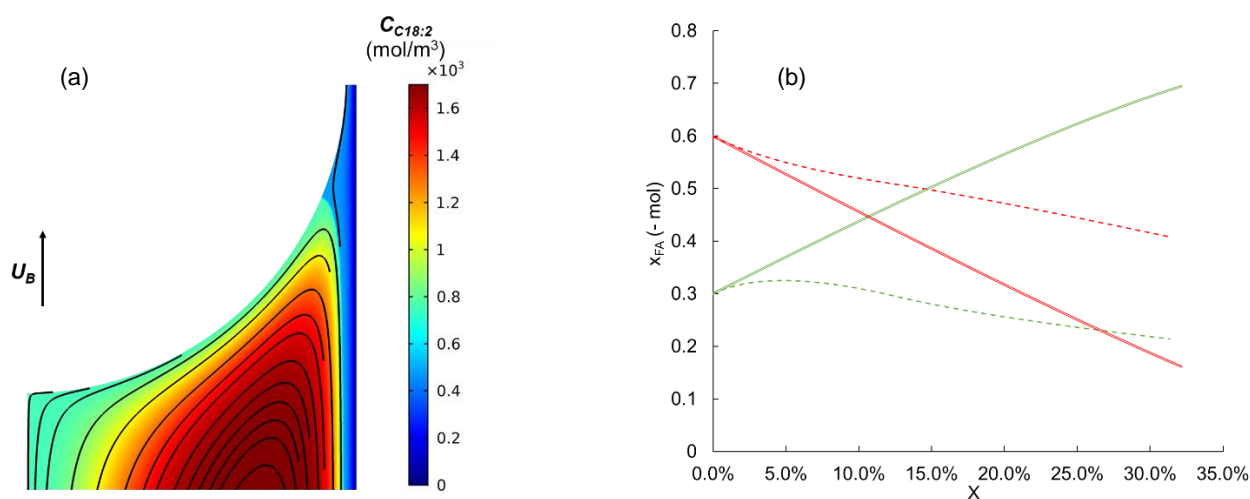


Figure 1. CFD model results: (a) C18:2 concentration field and streamlines at the bubble rear during hydrogenation ($z=0.45 z_f$), (b) Average C18:2 and C18:1 molar fraction in the liquid bulk as a function of the overall oil saturation degree X : C18:2 (red), C18:1 (green), ideal case (plug flow model with no mass transfer resistance) (—), Taylor flow case (---).

4. Conclusions

The CFD model of the monolith reactor allows for questioning the applicability of this technology to edible oil hydrogenation with catalytic washcoat in the channels. This model is extended to the whole reaction scheme, including isomerization, to get a full picture of oil processing. A sensitivity study to the liquid viscosity, catalyst activity, and operating conditions is being performed, and possible internal mass transfer limitations as well as inhomogeneity of fluid distribution at monolith entrance will be taken into account to evaluate the selectivity performance of the MRHEX for various scenarios.

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