

Stability of heterogeneous catalyst for hydrogenation of bio-oils: batch vs. continuous-flows reactor

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1. Introduction

Catalytic hydrogenation of vegetable oils has been studied intensively both in academia and industrial field. Due to their easy availability and valuable composition, bio-oils represent an interesting feedstock for integrated biorefineries for the production of high value-added products. The hydrogenation of these components leads to the formation of the saturated counterparts, which can be employed for the production of cosmetics, pharmaceuticals and bio-based polymers precursors [1]. These reactions are generally performed in the presence of a heterogeneous catalyst constituted of a suitable metal (Fe, Ni, Cu, Zn and Pt group) supported into alumina, silica or carbon. The most common method for performing hydrogenation is in the liquid phase and batch reactor in the presence of high H₂ pressure [2]. This protocol suffers of several drawbacks: the direct utilization of molecular hydrogen at high pressure represents a risk due to its highly inflammable nature and dedicated high-pressure resistant reactors must be employed. For these reasons, a H-Cube system was employed for liquid phase, continuous-flow reactions: due to the scission of water into an electrolytic cell, H₂ is produced *in-situ* and immediately employed for the reaction. The starting material, mixed with H₂, is pumped continuously into a packed catalytic bed containing the solid catalyst. This procedure, not only avoids the storage of pressurized hydrogen, but allows a better control of the temperature and optimal gas-liquid-solid interaction: the small reaction space limits some drawbacks related to the batch system, like diffusional constraint connected to the stirring method, boosting the productivity [3]. Depending on the flow rate, very low contact time (τ) can be employed: in this way it is possible to strongly limit consecutive reactions that might take place in the batch system, increasing the selectivity of the process. Another important aspect of heterogeneous catalysis is the reusability of the catalyst that after one or more cycles can deactivate. The deactivation can be both chemical (poisoning, formation of new phases) and physical (mechanical leaching of the metal caused by attrition, crushing and fouling) [4]. Switching to the continuous flow system can avoid this mechanical stress, increasing the life of the catalyst.

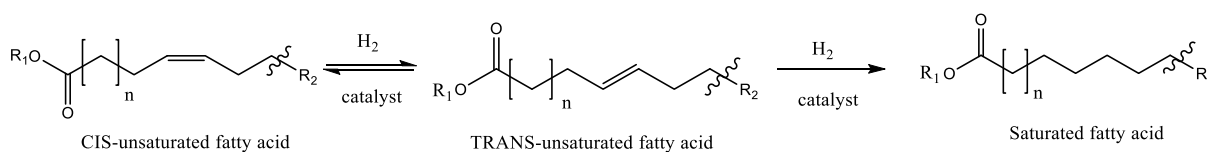


Figure 1: Reaction pathway: the reaction proceeds via a first isomerization of the CIS molecule subsequent complete saturation.

2. Methods

Novamont S.p.A., a leader company in the field of biomass valorisation and production of renewable products, supplied the reaction feedstock consisting of a long chain fatty acids derivative from vegetable oils. For the batch procedure the solution was introduced in a stainless-steel autoclave applying the conditions described in

Fig.2. The H-Cube was employed for the continuous-flow reactions: the solution was diluted for reducing the viscosity of the starting material and pumped through an HPLC pump with the H₂ produced in situ, into the Cat-Cart® containing the metal-supported catalyst. The outgoing mixture was collected and subsequently analyzed via GC-FID analysis after a dedicated derivatisation of the products. A comparison between batch and continuous flow reactor was done, especially regarding the stability of the catalysts after different cycle and/or performing long term reactions.

3. Results and discussion

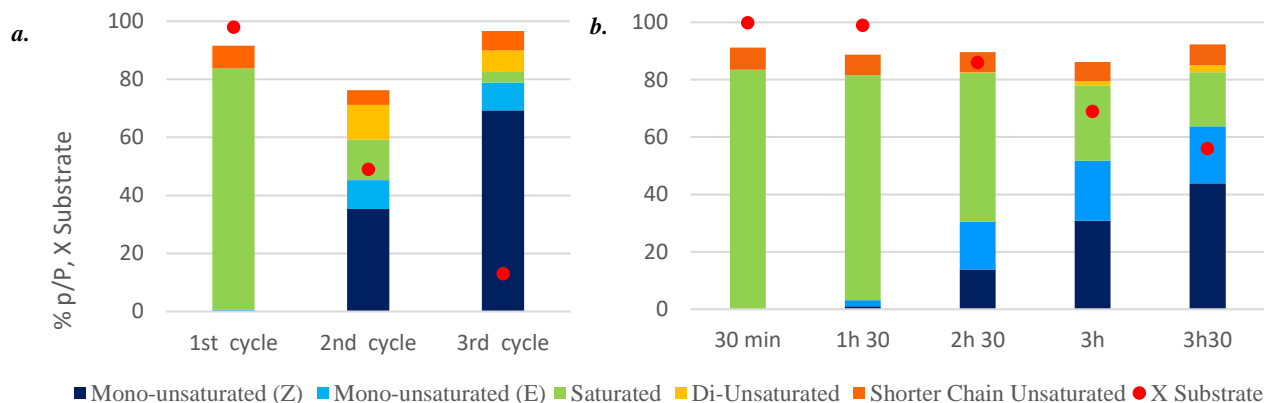


Figure 2: Stability test of Pd/C 0.3% wt **a.** in batch conditions (autoclave), recycling the catalyst for two times [reaction conditions: 15 mL substrate, $t=0.5h$, $T=90^{\circ}C$, $P_{H_2}=4$ bar, 750 rpm, $mPd/m\ substr.=0.05\%$ wt]; **b.** in the continuous flow reactor (H-Cube) collecting the out-flow after 30 min, 1.30, 2, 3 and 3.30 hours [reaction conditions: $T=90^{\circ}C$, $P_{H_2}=20$ bar, flow rate = 1.5 mL/min, $\tau=0.2\ min^{-1}$].

Fig. 2a shows the efficiency of the commercial catalyst employed (0.3wt% Pd/C): even in mild conditions ($90^{\circ}C$, 4 bar) and low metal loading, it is able to convert completely the substrate within 30 minutes. However, the performance dramatically falls after 1 cycle. ICP-AES analysis of the washed catalyst solution show presence of the metal. The decreased activity could be caused by a synergic effect of leaching and fouling of the active sites. In order to explore the stability in other conditions, the same catalyst was tested in the H-Cube flow reactor (Fig.2b). Surprisingly, also at very low contact time, it is noticeable a complete conversion and high selectivity towards desired products. However, also in this case, the deactivation of the catalyst lead to a progressive decline of the substrate conversion. Nevertheless, the applicability of the continuous-flow system for the hydrogenation of these fatty acid derivatives would lead to an enhanced productivity of the process. Further work will be done in order to limit the deactivation phenomena and improve the catalytic system.

4. Conclusions

Commercial catalyst with low metal loading was tested firstly in the batch system: astonishing results in terms of conversion and selectivity were achieved after 30 minutes reaction in very mild conditions. Rapid deactivation was observed so the catalyst was also tested in a continuous flow reactor. Results were promising: complete conversion was achieved for the fresh catalyst with very short contact time ($\tau=0.2\ min$) and deactivation was less prominent, because almost complete conversion was maintained also after 1h 30 minutes. More efforts will be done to understand and limit the deactivation, for enhancing the productivity of the process and make this catalytic system even more efficient.

References

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