Deliverable report

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Executive Summary

To utilize the unusual selectivity of the REDIFUEL upstream Fischer-Tropsch process and achieve favourable combustion properties, C_5-C_{10} olefins are converted to their corresponding C_6-C_{11} alcohols in the reductive hydroformylation step[1–4]. In this process step within the REDIFUEL concept, a highly active rhodium-based molecular catalyst is used to transform C_5-C_{10} olefins to C_6-C_{11} aldehydes which are subsequently hydrogenated to C_6-C_{11} alcohols. For catalysis in general but especially in the context of fuel production, process cost is heavily influenced by catalyst losses. Despite the high activity as hydroformylation catalyst, rhodium is one of the most valuable metals on earth, even compared to other precious metals (e.g. gold). To achieve an economically viable and competitive process for the production of the proposed 2nd generation biofuel, catalyst losses have to be reduced to a minimum. Two key aspects have to be considered during the process design:

1. **Catalyst activity and productivity**
   Typical catalyst research mostly focuses on improving the performance of a catalyst system in terms of conversion, Turn-Over-Frequency (TOF) and space-time-yields (STY). Improving these parameters usually leads to lower process cost because smaller equipment can be used and less energy input is necessary. We already reported about the activity of two investigated catalyst systems in Deliverable 2.1.
2. **Catalyst stability and recycling**
   When using molecular catalysts, recycling of the catalyst is the most determining step to achieve an economically feasible process.[5] Heterogeneous catalysts, which are usually solid, can often be immobilized in a fixed-bed reactor or separated from the reaction mixture by filtration. In contrast, molecular catalysts are dissolved in the reaction mixture. This enables very high catalytic activity but at the same time generates a separation problem. In Deliverable 2.3 we reported a liquid-liquid biphasic catalyst recycling system. This biphasic system enables an easy and intrinsic catalyst recycling for the molecular catalyst. At the same time this system is susceptible towards mass transfer limitations between the two phases. Careful optimization of process parameters is necessary to balance the catalyst performance and its stability.

A proof of concept for the liquid-liquid biphasic recycling approach was already presented in the results discussed in Deliverable 2.3. In this deliverable, a continuous flow pilot plant has been tested to investigate the stability of the catalyst under industrially relevant process conditions. The hydroformylation was operated in a continuous flow system for up to 50 hours without any addition of extra catalyst while maintaining the activity and selectivity to the desired products. It can be concluded that the catalyst is stable under the chosen reaction conditions also for longer periods of time and suited for continuous operation. The used catalyst concentration is already comparably low and within the continuous operation no noteworthy loss of catalyst in the product phase was measured, resulting in very high utilization of the catalyst. For the first time, the actual product derived from the upstream Fischer-Tropsch process has been successfully converted to alcohols.

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