



REDIFUEL

Deliverable report

Deliverable No: D2.3
Dissemination level: Confidential (CO)
Title: Catalyst recycling system for the hydroformylation process

Date: 03/03/2020
Version: FINAL
Author(s): Thorsten Rösler (MPI), Sebastian Püschel (MPI), Andreas Vorholt (MPI)
Reviewed by: Gonzalo Prieto (CSIC)
Approved by: Technical Coordinator – Benedikt Heuser (FEV)

Grant Agreement Number: 817612
Project Type: H2020-LC-SC3-RES-21-2018-development of next generation biofuels and alternative renewable fuel technologies for road transport
Project acronym: REDIFUEL
Project title: Robust and Efficient processes and technologies for Drop In renewable FUELS for road transport
Project start date: 01/10/2018
Project website: www.redifuel.eu
Technical coordination: FEV (DE) (www.fev.com)
Project management: Uniresearch (NL) (<http://www.uniresearch.com>)



Executive Summary

Within the REDIFUEL concept the hydroformylation step is the second catalytic process and fulfils the role to transform C₅-C₁₀ olefins generated in the Fischer-Tropsch process to C₆-C₁₁ alcohols. Alcohols are known to significantly enhance the combustion behaviour of diesel fuels.¹⁻³ They significantly lower soot and other emissions (CO₂, NO_x). While being important for a clean combustion, they are at the same time the fuel fraction with the highest value within the mixture and are expected to generate a major share of the total process cost. In order to compete with fossil-based fuels it is of utter importance to keep the process cost as low as possible. In the end further investigation and finally market launch is only reasonable if the fuel can be generated to a price in the same region as fossil-based fuels. Two **main factors** are the driving force for the **process cost** of the hydroformylation step.

1. The productivity and activity of the catalyst and the reaction system:

The activity of the catalyst is important to determine how much of the olefins can be transformed into alcohols and therefore the total alcohol share in the fuel mixture. At the same time a high activity goes inherent with a high productivity and therefore a lower process cost. In Deliverable 2.1 we already reported about two possible very active catalytic systems for the hydroformylation step. A one step process based on amine ligands in combination with rhodium as catalyst metal and a two-step process based on water soluble phosphine ligands again in combination with rhodium as catalyst metal. Especially the phosphine/rhodium-based two-step process shows a very high catalytic activity which is sufficient for an industrial process.

2. The recycling of the precious homogeneous catalyst:

While scientific research is often times focused on catalytic activity and the catalyst recycling and stability is commonly neglected, it is the most important factor for a successful process design. While heterogeneous catalysts (solids) are easily recyclable, homogeneous catalysts, like the one used in the hydroformylation process, are dissolved in the reaction mixture and need to be separated after reaction in order to reuse them. Especially when using precious catalyst metals like rhodium, even losing small amounts of the catalyst after the reaction can skyrocket process costs and make the whole process unfeasible.⁴

A successful concept for the recycling of the homogeneous catalyst is presented in this deliverable. A catalyst consisting of rhodium in combination with water-soluble phosphine ligands (Triphenylphosphine trisodium, TPPTS) was successfully recycled in a biphasic liquid/liquid system with water as the polar (lower) phase and olefin/paraffin as the upper phase. Within this concept, the catalyst metal is immobilized in the water phase by using water-soluble phosphine ligands. The products and substrates on the other hand separate in the upper organic phase. By taking advantage of the different polarities of catalyst and products/substrates, the water phase (containing the catalyst) can be separated and reused.

Before going to the experimental setup, computational calculations of the phase behaviour have been performed. The phase diagrams indicate that the aldehyde products slightly increase the water miscibility in the organic phase. Depending on the aldehyde yield, 4% to 8% of the water phase is lost into the organic phase. While this does not lead to catalyst leaching, it indicates that a water makeup stream will be most likely necessary in the planned miniplant setup. After the theoretical calculations, a recycling setup for a batch-wise recycling of the catalyst was installed. Recycling runs with 1-octene as model substrate together with heptane, mimicking the olefin/paraffin content in the real FT-mixture, have been accomplished.

Within a first set of three runs, it was possible to maintain the catalytic activity, indicating a successful recycling of the catalyst. ICP (Inductive Coupled Plasma) measurements of the organic phase revealed that the amount of rhodium and phosphorus leaching is very low (0.8% rhodium and 0.2% phosphorus), showing that the catalyst is indeed immobilized in the water phase.



Afterwards a larger scale experiment with 10 consecutive runs has been performed. During those experiments a drop of activity in consecutive experiments on the same day was observed, which was successfully restored overnight. The restoration of the activity indicates, again, that the catalyst is held in the water phase. If the recycling of the catalyst is not successful and the catalyst is lost to the organic phase, it would be impossible to restore the initial activity and a steady decrease in activity would be observed for all experiments. The drop-in activity for experiments on the same day can be attributed to a deactivation process during the reaction. The investigation of this phenomena will be part of the next 6 months in order to achieve a stable catalyst system (deliverable 4.2) but is unlikely to occur in a continuous process.

The proof of concept for the catalyst recycling in a biphasic liquid/liquid system for aliphatic substrates in combination with water was shown for 1-octene/heptane as model substrate mixture. A low leaching of under 1% (0.7 ppm) of the initial rhodium metal has been achieved and is expected to be even lower going into continuous process.



Acknowledgement

H2020-LC-SC3-RES-21-2018-DEVELOPMENT OF NEXT GENERATION BIOFUELS AND ALTERNATIVE RENEWABLE FUEL TECHNOLOGIES FOR ROAD TRANSPORT

Acknowledgement:

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

Project partners:

- 1 - FEV – FEV EUROPE GMBH - DE
- 2 - MPI – MAX-PLANCK-GESELLSCHAFT ZUR FORDERUNG DER WISSENSCHAFTENEV - DE
- 3 - CSIC – AGENCIA ESTATAL CONSEJO SUPERIOR DE INVESTIGACIONES CIENTIFICAS - ES
- 4 - VTT – Teknologian tutkimuskeskus VTT Oy - FI
- 5 - RWTH – RHEINISCH-WESTFAELISCHE TECHNISCHE HOCHSCHULE AACHEN - DE
- 6 - OWI – OWI – Science for Fuels GmbH - DE
- 7 - VUB – VRIJE UNIVERSITEIT BRUSSEL- BE
- 8 - NESTE – NESTE OYJ – FI
- 9 – MOL - MOL HUNGARIAN OIL AND GAS PLC - HU
- 10 – INER - INERATEC GMBH - DE
- 11 – T4F - TEC4FUELS - DE
- 12 – UNR - UNIRESEARCH BV – NL

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under Grant Agreement no. 817612

**Disclaimer:**

This document reflects the views of the author(s) and does not necessarily reflect the views or policy of the European Commission. Whilst efforts have been made to ensure the accuracy and completeness of this document, the REDIFUEL consortium shall not be liable for any errors or omissions, however caused.

