Catalysis Today 439 (2024) 114803

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Advancing the aqueous biphasic hydroformylation of oleochemicals in the loop: Continuous reaction and separation using a jet-loop reactor concept

T.F.H. Roth, M. Häusler, D. Vogt, T. Seidensticker *

TU Dortmund University, Department for Biochemical and Chemical Engineering, Laboratory of Industrial Chemistry, Emil-Figge-Straße 66, Dortmund 44227, Germany

ARTICLE INFO

Keywords:
Homogeneous catalysis
Scale-up
Hydroformylation
Renewables
Continuously operated miniplant
Jet-loop-reactor

ABSTRACT

The hydroformylation of renewable oleochemicals in aqueous liquid-liquid multiphase systems was operated continuously using a jet-loop reactor concept, demonstrated in two case studies. The main challenge on this path was to find an optimal compromise between activity and catalyst retention. In Case 1, methyl oleate was converted in an isopropanol/water system with stationary yields of up to 35 % in more than 55 hours of continuous operation at low catalyst loss of only 0.1 %/h and very high selectivity. In Case 2, a reaction system consisting of butanol/water was used to convert methyl 10-undecenoate. Fine-tuning of the substrate loading and separation temperature was required. Under optimised reaction conditions, steady-state yields of >80 % were achieved in a campaign of >55 hours of continuous operation. As little as 16.7 mg of rhodium was leached per kilogram of product formed at excellent selectivities to the linear product. This is the first time a miniplant concept has been presented that enables the hydroformylation of these two renewables in continuous operation.

1. Introduction

Homogeneous catalysis is one of the most valuable methods to achieve highly active and selective chemical conversions, which the 12 principles of green chemistry emphasise especially. [1] Recycling costly transition metal catalysts is essential to make the processes used for these reactions economically competitive. An elegant way to achieve this is using liquid-liquid multiphase systems, for which industrially operated processes already exist, e.g., propene hydroformylation or butadiene telomerisation. [2] In the case of hydroformylation, the catalyst is dissolved in an aqueous phase using water-soluble, sulfonated ligands. The substrate passes through as a gas, partially dissolving in the catalyst phase and allowing the reaction to occur. It is particularly convenient that the resulting products form a second pure phase and can be efficiently removed from the reaction system. [3]

With the increasing pressure to put our value-creation systems on a more sustainable path, the demand to replace petrochemical raw materials with renewable ones, such as fatty acid derivatives, is growing. Since these also exhibit the structural motif of the double bond known from petrochemical raw materials, there is the potential to employ the same chemical methods and catalysts. [4] However, the changing raw materials pose challenges for the process design in which the chemical conversions are embedded, as material properties such as polarity, molecular size, and boiling points change significantly. In general, this has extensive implications for every process stage. However, this challenge is particularly pronounced in reaction systems that use aqueous liquid-liquid multiphase techniques to recycle homogeneous catalysts. While post-reaction separation into two phases is straightforward due to the non-polar nature of the long-chain substances, the reaction is limited by the low solubility of the substrates in the catalyst phase, resulting in low reaction rates.

To overcome these hurdles, several intensification strategies in aqueous multiphase systems have been developed and recently reviewed by the Vorholt group, highlighting the importance of this topic. [5] A particularly promising approach for long-chain substrates such as methyl oleate (MO) or methyl 10-undecenoate ($M_{10}U$) is altering the solubility by adding co-solvents. MO is a renewable raw material that occurs in various plants (rapeseed, sunflowers, safflower, soy) and features an unsaturated double bond. Hydroformylation combines this with synthesis gas to yield aldehydes, which are valuable intermediate products and can be hydrogenated to alcohols, e.g., to form crosslinkers in polymer applications or lubricants (Fig. 1). As it is already available in large quantities from biodiesel production, it is also an interesting substrate from a market strategic viewpoint. Although hydroformylations with methyl oleate have been established in various reaction systems, [6–10] only a few attempts have been made to achieve efficient catalyst

---

* Corresponding author.
E-mail address: thomas.seidensticker@tu-dortmund.de (T. Seidensticker).

https://doi.org/10.1016/j.cattod.2024.114803
Received 26 March 2024; Received in revised form 16 April 2024; Accepted 8 May 2024

recycling. [8,11] In the most promising attempt, a biphasic reaction system using water and isopropanol as catalyst solvent was established, reaching a stable yield of >50 % in 10 consecutive recycling runs. [11] Similar observations were made in the hydroformylation of $M_{10}U$, a renewable raw material obtained from the pyrolysis of castor oil. Due to its terminal double bond, it stands out from many renewable fatty acid derivatives. It is already used industrially in the production of polyamide 11, marketed as Rilsan by the French company Arkema. The hydroformylation reaction now opens routes to polyamide 12 or other polymers based on this renewable raw material, and has already been investigated in a few studies. In a biphasic reaction system using water and 1-butanol as solvents, high TOFs of >5000 h^{-1} were achieved; however, leaching of 5 mol % catalysts to the organic phase was observed. [12] In previous work, a continuous process was also established in a continuously operated stirred tank reactor (CSTR), but only at the cost of a high catalyst loss, which did not allow long-term stable operation. [13]

Another intensification strategy that is promising in liquid-liquid multiphase systems is to increase the surface area by means of extensive mixing. To overcome the limitations of a typical stirred tank reactor (STR) in terms of mixing, new reactor concepts are needed; one widely used concept is the jet-loop reactor (JLR). [14] Here, a liquid circulation stream is pumped from the reactor *via* an external loop to a nozzle at the top of the reactor, re-entering the reaction phase and providing high-energy input without internal moving parts. Although several designs exist, the venturi ejector is the most common nozzle type. [14,15] In this design, a liquid is pumped through a tapered nozzle at high velocity. Due to the resulting pressure drop, gas can be sucked in through a pipe located in the centre, resulting in significant shear rates and liquid/liquid/gas (l/l/g) interfaces (Fig. 3, left). In recent years, this concept has received attention from various fields, from hydrodynamic modelling to fermentation processes.[16–21]

In the aqueous biphasic hydroformylation of 1-octene, high activity and space-time yield were reached in a JLR. [22–25] Even when converting the more challenging, renewable substrates MO and $M_{10}U$ in the described co-solvent mediated reaction systems, high TOFs were achieved. [11,13] While only low substrate loadings could be efficiently converted in the STR during the hydroformylation of MO in the isopropanol/water system, we showed in later work that the substrate loading can be significantly increased when using the JLR. [26] As leaching remained low, these results are promising for a further scale-up. In these studies, we also showed that when $M_{10}U$ is converted in the butanol/water system, higher reaction rates could be achieved with the same butanol content. This gives reason to presume that the butanol content can be significantly reduced by using the JLR without loss of reaction performance, which in turn should significantly lower the previously high leaching. [26] However, an appropriate compromise between reaction performance and catalyst loss must first be found for further investigation.

Despite the promising results in batch experiments, the continuous operation of these biphasic reaction systems in a JLR must first be established to provide a basis for evaluation for a realistic technical application (Fig. 3). Here, particular attention must be paid to an efficient compromise between high productivity and effective catalyst retention in order to provide the framework for a long-term stable process. Various challenges, such as control, foaming, and emulsion formation, to which a reactor concept such as JLR is significantly more sensitive than conventional reactor types, make a continuous operation particularly challenging. Possibly, this is the reason why continuous operation of catalyst phase recycling in liquid-liquid systems for converting renewables in JLR has not been reported hitherto. Herein, we aim to fill this gap by performing two case studies in a continuous miniplant employing a JLR.

The first case study focuses on the hydroformylation of MO in our reaction system consisting of a 1:1 mixture of water and isopropanol as polar solvent, which has proven to be a promising approach in a JLR. The second case deals with the hydroformylation of $M_{10}U$ in our butanol/water reaction system, aiming to ensure effective catalyst retention. Hereby, we would like to demonstrate how combining well-chosen solvent systems and advanced reactor concepts allows the hydroformylation of long-chain renewable raw materials to be efficiently carried out in continuous operation.

2. Materials and methods

2.1. Procedure for batch experiments in a stirred tank reactor

All batch experiments were performed in a 300 mL overhead stirred autoclave with a pitched blade stirrer at 1000 rpm and continuous gassing during the reaction. All substrates were purified over aluminium oxide and then degassed with argon dispersed by a frit in an ultrasonic bath for at least one hour. All liquid chemicals used for the reactions were degassed with argon dispersed through a frit in an ultrasonic bath for at least one hour. The catalyst and ligand are weighed and dissolved in the degassed water using an ultrasonic bath at 40°C for 30 minutes. The reactor is sealed and inertised by repeated evacuations and the application of 5 bar argon. Once the catalyst has been successfully dissolved, the second solvent (isopropanol or butanol) is added, retaining 10 mL. This solution is sucked into the reactor *via vacuo*, and the substrate, together with the retained solvent, is transferred with a syringe in a countercurrent argon flow into a reservoir above the reactor. The system is then pressurised with synthesis gas, and the reactor is heated to 120°C. After the 30-minute preformation time, the reactor is brought to reaction pressure and temperature, and the reaction is initiated by opening the valve between the reactor and the substrate reservoir. At the end of the reaction time, continuous gassing is stopped, and the reactor is cooled in an ice bath to at least 20°C before the stirrer is stopped and degassed. The reactor is then flushed several times with argon. After opening the reactor and separating the phases in a separating funnel, the appropriate analyses were performed. Finally, the reactor was cleaned with isopropanol.

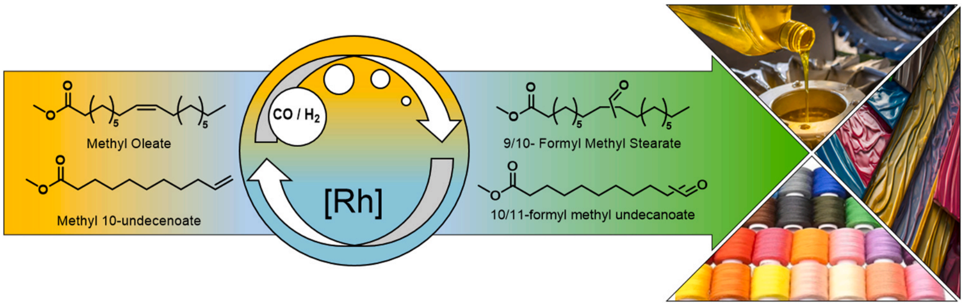

Fig. 1. Conceptual visualisation of the biphasic rhodium-catalyzed hydroformylation of MO and $M_{10}U$ and potential applications of the corresponding products as polymer precursors or lubricants.

2.2. *Procedure for continuous experiments in miniplant*

The commissioned miniplant consists of a 1000 mL jet loop reactor with a venturi ejector (Fig. 2). The reaction mixture is fed into a decanter through a riser tube via a gear pump (Fig. 3). The mixture is separated into the lighter product phase and the heavier aqueous phase. While the latter can flow freely back into the reactor *via* a riser pipe, the product phase can leave the system *via* a flash. As the filling level in the reactor influences the volume-specific energy input and thus the available l/l/g-interface on the one hand and directly influences the residence time on the other, it must be precisely set and controlled. To ensure a constant level in the reactor, the pump feeding the substrate can be operated on feedback of a level measurement placed in an external circulation pipe. Furthermore, both liquid phases must always be withdrawn in the same ratio to prevent one phase's accumulation. For this purpose, all incoming and outgoing streams and their compositions must be controlled, as the components are always distributed over both liquid phases, and any mass loss *via* the product phase must be replaced.

For the startup, the aqueous phase, consisting of Rh precursor, ligands and ultrapure water, is prepared in the absence of oxygen, as in the batch experiments described above. The miniplant is checked for leaks before the experiment and then inerted by repeated vacuum draws and 5 bar nitrogen pressure application. The prepared catalyst phase is transferred to the reactor *via* a capillary tube and vacuum. Preforming is carried out at an H_2/CO pressure of 20 bar and a temperature of 120 °C for 1 hour with the circulation pump running to ensure that gas is introduced into the liquid phase. The catalyst phase is then transferred to the decanter until the level rises to the point where the catalyst phase is returned to the reactor. The reaction pressure and temperature are established, the reactor circulation pump is stopped, and the required amount of substrate is added as quickly as possible *via* a substrate pump. The substrate pump is turned off, and all liquid-carrying valves are closed. A batch experiment is started for 2 hours by restarting the jet loop reactor circulation pump and setting continuous gassing. Continuous operation of the system is then established by opening the valves and starting the gear and substrate pumps. Regular monitoring of the level sensor and visual inspection through the sight glass at the top of the reactor ensure that the level in the reactor is kept constant. Product phase samples and samples for ICP-OES analysis were taken at regular intervals during the operation of the miniplant.

3. Results and discussion

Hydroformylation converts internal or terminal olefins and syngas into linear and branched aldehydes (Fig. 4). The by-product spectrum varies depending on the catalysts and ligands used, but the most relevant side reactions are the hydrogenation of the double bond to saturated species and its isomerisation along the alkyl chain. The internal double bonds formed in this way can, in turn, also be hydroformylated, just as the aldehydes formed can be hydrogenated to alcohols.

In the following case studies, continuous conversion of the renewables MO and $M_{10}U$ with catalyst recycling in a liquid-liquid system in a JLR will now be investigated for the first time to evaluate their long-term stability.

3.1. *Case 1: Hydroformylation of Methyl Oleate*

Technical grade methyl oleate from high oleic sunflower oil was used, in which saturated species (methyl stearate and palmitate) and methyl linoleates are the major impurities (composition in SI). Its conversion under hydroformylation conditions mainly leads to branched formyl methyl stearates (FMS), as the substrate holds an internal double bond (Fig. 5). Observed side reactions are the hydrogenation of the C=C double bond to methyl stearate (MS) and its isomerisation to isomers of methyl oleate (iMO). The retention of the rhodium catalyst, which is applied in the form of $Rh(acac)(CO)_2$, in the aqueous phase is ensured by employing the known monodentate ligand trisodium triphenylphosphine-3,3',3''-trisulfonate (tppts), which exhibits high water solubility.

As small quantities of isopropanol and water are constantly lost via the product flow due to cross-solubility, a make-up feed is installed to prevent a change in the composition or the fill level (solvent stream in Fig. 3). Based on our batch studies, the residence time for continuous operation is set to 6 hours (Fig. 6). In the first 12 hours (marked in grey), the product phase needs to be accumulated in the decanter; thus, no product can be analysed.

A stationary aldehyde yield of up to 35 % at a selectivity of >90 % was achieved after 30 h of continuous operation, corresponding to ca. five residence times. Interestingly, isomerisation only plays a minor role, and aldehydes other than those at the 9- or 10-position are only formed to less than 0.3 %. Hydrogenation is the most prominent side reaction; however, it is to a very limited extent, with yields for MS of approximately 2 %. The technical grade MO used contained small traces of methyl linoleate, which underwent isomerisation; however, the constant amount of different C18:2 isomers indicates that hydroformylation of this species hardly occurs. Although the flow of the reaction mixture to the decanter fluctuated at around 40 h due to a brief malfunction of the mass flow monitor, no adverse effect on process performance was observed. The operating point is maintained for a further four residence

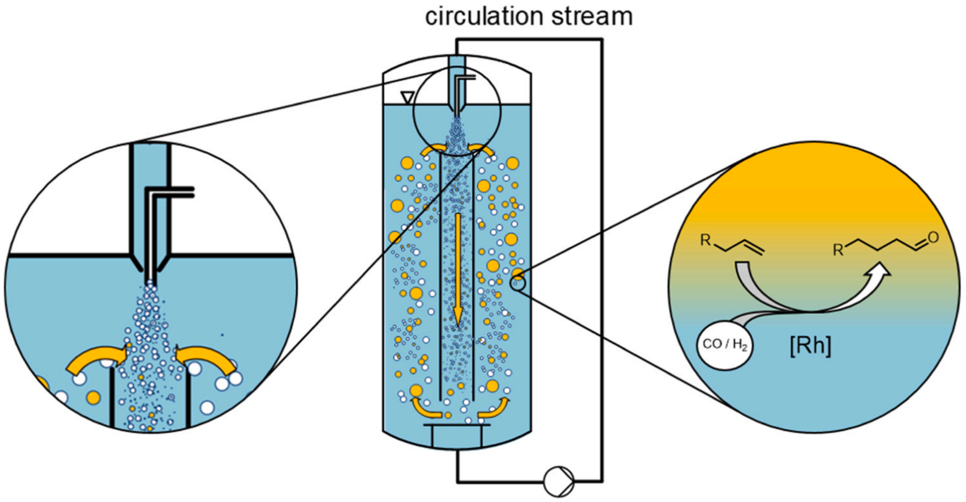

Fig. 2. Concept of a jet loop reactor with venturi ejector (left) and general scheme of biphasic rhodium-catalyzed hydroformylation of a terminal alkene using water-soluble phosphine ligands (right).

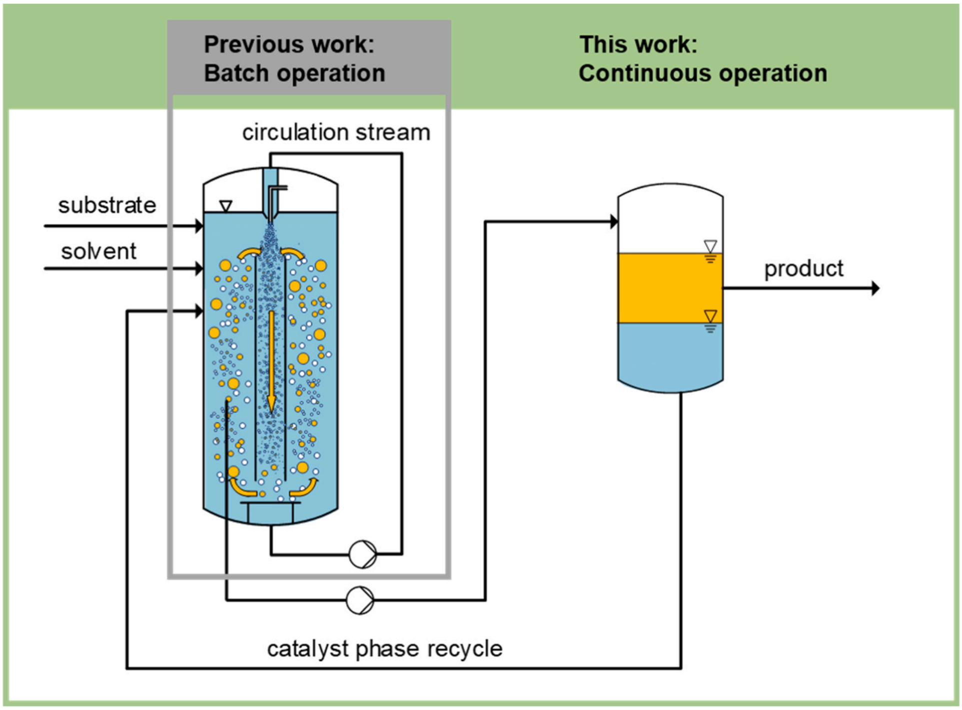

Fig. 3. Relation of this work to the former work of Hermann *et al.* in biphasic hydroformylation. [26] Conceptual flowsheet of the continuously operated jet-loop reactor miniplant in this work.

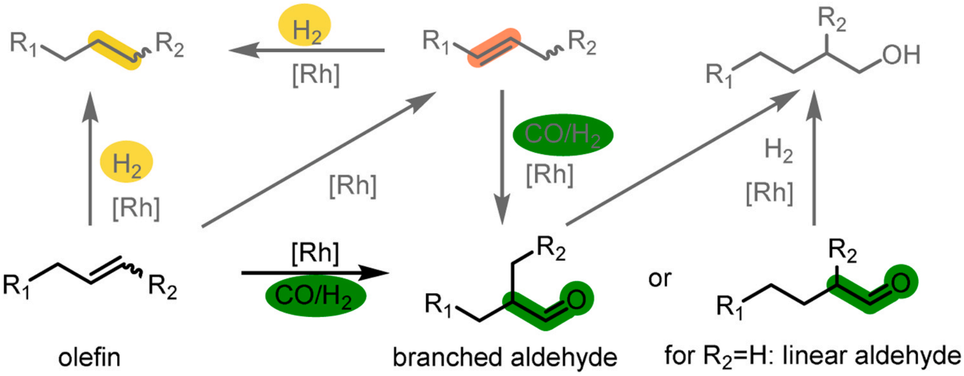

Fig. 4. Fundamental reaction network of hydroformylation and the most relevant side reactions.

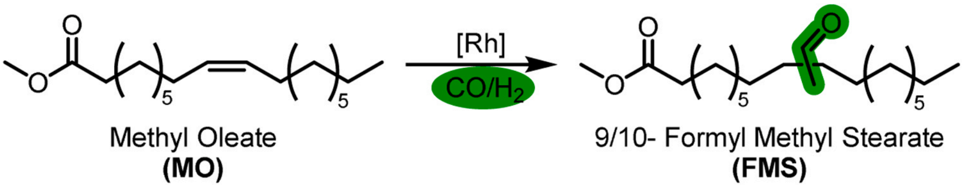

Fig. 5. Hydroformylation of Methyl Oleate.

times, demonstrating that the catalyst can be reliably retained in the aqueous phase. The catalyst loss of 0.1 % of the initial applied amount per hour *via* the product phase does not play a significant role during the time on stream in this experiment, which is remarkable as no catalyst makeup flow was required. Although productivity and rhodium retention should still be improved for an economic process, this one-step separation strategy represents a promising basis and gives hope for a realistic technical application. This case study has thus demonstrated that the renewable raw material MO can be effectively incorporated into the chemical value chain by hydroformylation under technically relevant, continuous operating conditions by using a JLR.

3.2. Case 2: Hydroformylation of Methyl 10-Undecenoate

The hydroformylation reaction of $M_{10}U$ forms linear or branched aldehydes (l-aldehyde, b-aldehyde) as the substrate exhibits a terminal double bond (Fig. 7). The bidentate, sulfonated ligand 4,5-bis(diphenylphosphino)-9,9-dimethyl-2,7-disulfoxanthene disodium commonly

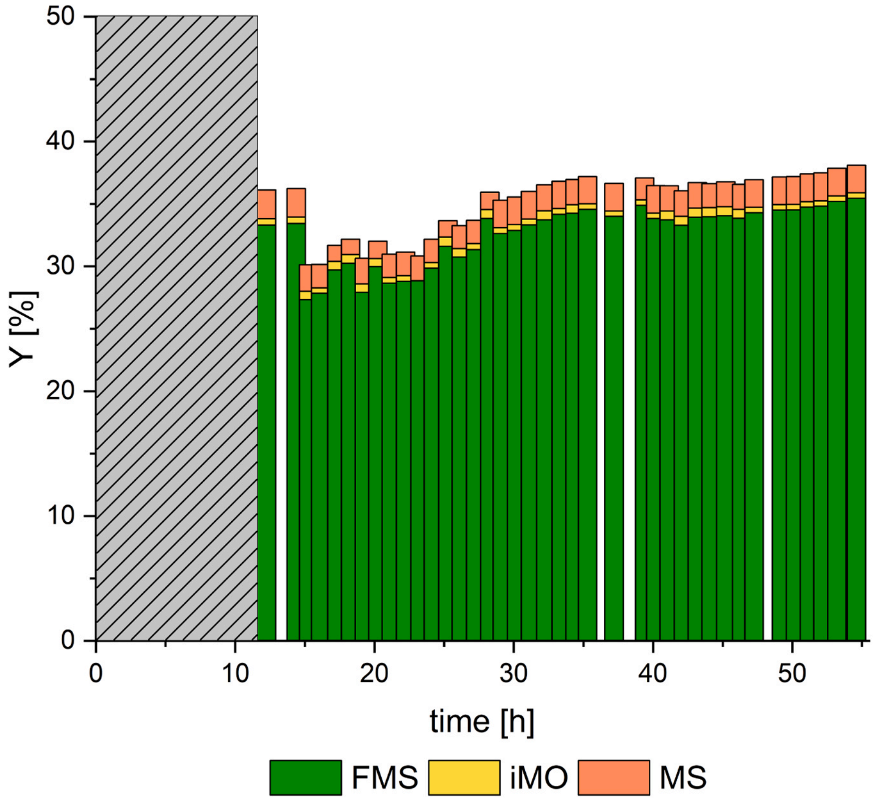

Fig. 6. Yield (Y) during the continuous hydroformylation of MO in a JLR. Conversion (X) equals the sum of all yields (Y). The product stream consisting of substrate, the product spectrum as well as traces of isopropanol and water was analysed by GC-FID using dodecane as an internal standard to calculate yield. Conditions: T_R = 140 °C, p = 50 bar, τ = 6 h, $n_{CO}/n_{H2} = 1$, $c_{Rh(acac)(CO)2} = 0.89$ mmol L^{-1}, $n_{tppts}/n_{Rh(acac)(CO)2} = 10$, $\varphi = 0.06$, $m_{iPOH}/m_{H2O} = 1$, $V_{Reactor}$ = 900 mL, $V_{Circulation}$ = 5.48 L min^{-1}, T_S = 25 °C; Preforming: T = 140 °C, p = 50 bar, $t > 2$ h, $n_{CO}/n_{H2} = 1$.

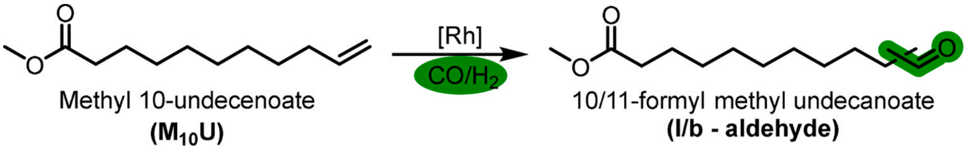

Fig. 7. Hydroformylation of Methyl 10-undecenoate.

known as sulfoxantphos (sxp) enhances the formation of the more desired l-aldehyde. Furthermore, the formation of inward isomerised double bonds (i.$M_{10}U$) and the hydrogenation of the substrate to form saturated methyl ester (sat. $M_{10}U$) are observed.

In addition to the challenges discussed in the first case study when using a JLR, this specific reaction system leaves the reactor as an emulsion. While this does not pose a challenge in batch reactions, it presents significant difficulties in continuous operation. This phenomenon is influenced by various factors, of which interfacial tension, separation temperature and polarity play a pivotal role. Since the butanol concentration also significantly influences the leaching of the catalyst, it was the focus of the initial investigations (further information in SI). Higher concentrations of BuOH show a positive correlation with improved separation performance. In addition, higher BuOH concentrations positively affect the reaction, indicating a potential improvement in the overall efficiency of the process. However, the observed increase in leaching of the catalyst into the product phase calls for a compromise between these opposing effects. The separation temperature was examined as a further parameter on emulsion formation, as this does not directly influence the reaction. With rising separation temperature, the emulsion phase is separated into three phases: 1. an organic, light phase containing mainly solvent, substrate and products. 2. the aqueous heavy phase, containing mainly water, catalyst and ligand, and 3. an emulsion phase between these two, containing all substances in the reaction system. If the separation temperature is increased further, the emulsion phase forms to a lesser extent and separates into distinct organic and aqueous phases. While the influence of the BuOH content on the leaching is linear, the influence of the separation temperature is exponential and more vital with increasing BuOH content, which can also be seen in the corresponding phase diagrams we published earlier. [12] To find operating conditions for the continuous operation of this reaction system, a thorough understanding of the interplay of the various factors influencing emulsion formation is necessary to find a practical compromise between reaction performance and catalyst retention. Based on the preliminary investigations, various promising operating points were identified and examined in a continuous experiment in the miniplant (Fig. 8).

After 16 hours, the first stationary operating point is reached with a high yield of >88 % and high selectivities of >90 %. However, this is at the expense of an expected high catalyst leaching of up to 0.25 %/h, constituting an operation point which can't be sustained due to the high catalyst loss.

The amount of catalyst lost per product produced, a parameter for which reliable values are already known from other recycling systems, is a basis for comparing with other operation conditions. [27,28] Under these starting conditions, 99.2 mg of catalyst are lost per kilogram of

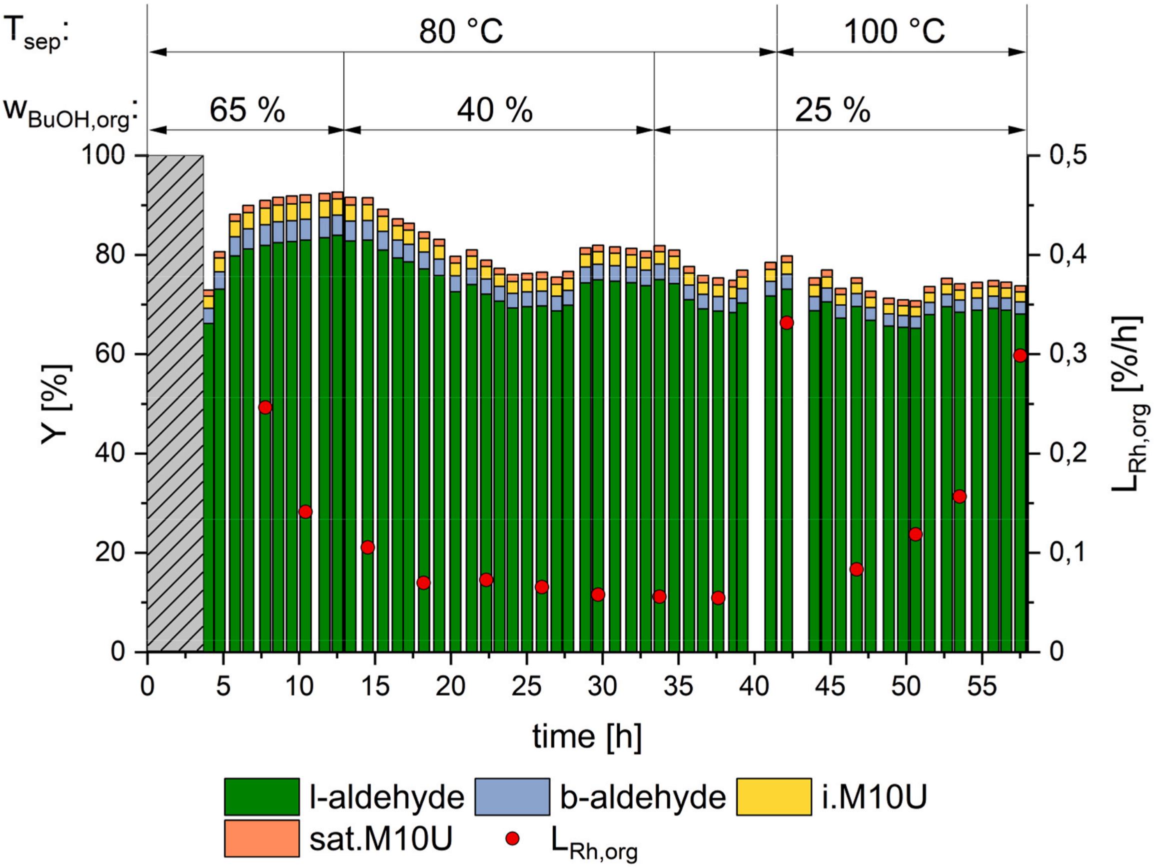

Fig. 8. Reaction performance of the continuous hydroformylation of $M_{10}U$. Conversions equals the sum of all yields. The product stream consisting of substrate, the product spectrum, butanol as well as traces of water was analysed with GC-FID and dibutyl ether as an internal standard to calculate yield. Conditions: $T = 140\ ^\circ C$, $p = 20$ bar, $\tau = 4$ h, $n_{CO}/n_{H2} = 1$, $c_{Rh(acac)(CO)2} = 0.69$ mmol L^{-1}, $n_{sxp}/n_{Rh(acac)(CO)2} = 7$, $\varphi = 0.33$, $V_{Reactor} = 900$ mL, $V_{Circulation} = 5.48$ L min^{-1}; Preforming: $T = 140\ ^\circ C$, $p = 20$ bar, $t > 1$ h, $n_{CO}/n_{H2} = 1$.

product. As the following operation condition, the BuOH content in the organic phase was reduced to 40 wt.- %; since the phase ratio is kept constant, this also corresponds to an increased substrate input, while the separation temperature is kept at 80 °C. As a result, the stationary yield decreases slightly to 80 % while the selectivity remains unchanged at a high level. It is particularly relevant here that the leaching of the catalyst drops to 0.1 %/h and remains stationary. Despite the slight decline in yield, only 16.7 mg of rhodium is lost to the organic phase per kilogram of product. A further reduction of the BuOH content to 25 % leads to emulsion formation in the decanter, which is why no phase separation is possible (Fig. 9). Although a decline in the yields over time is not immediately apparent, long-term operation under these conditions is not advisable as there is a considerable loss of the aqueous catalyst phase *via* the product stream between 37 and 42 hours.

The separation temperature was increased to 100 °C to ensure reliable phase separation, which led to increased catalyst loss. Although the yields still appear stable at first, the sharp increase in catalyst losses shows that long-term operation cannot be guaranteed under these conditions, which is further emphasised by the renewed increase in rhodium loss to 76.9 mg/kg during this period.

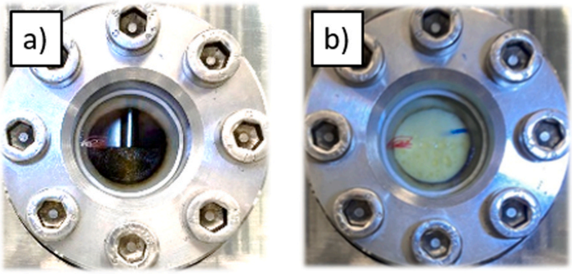

Fig. 9. Phase separation in decanter <37 h (a) and from 37 h to 42 h (b).

Another pragmatic approach to prevent emulsion formation without promoting catalyst loss is to change the polarity of the aqueous phase, e. g. by adding a salt such as sodium sulphate, and at the same time to dispense with an organic solvent, an approach already known from continuous hydroformylations in surfactant systems. [29] Adding 1 % w/w sodium sulphate completely eliminated butanol in batch experiments in the JLR without emulsion formation at the end of the reaction. In subsequent continuous experiments, however, a continuous decrease in yield was observed, which could only be prevented by adding fresh catalyst solution. The reasons for the observed catalyst poisoning are still under investigation. (further information in SI).

4. Conclusions

This work presented the continuous Rh-catalyzed hydroformylation of renewable raw materials using a liquid-liquid system to efficiently separate and recycle the homogeneous catalyst. The well-known demand for an intensification strategy is met using a jet loop reactor, which ensures a high degree of mixing to avoid possible limitations. After the precise planning and construction of the required miniplant, the reaction system from the literature consisting of water and isopropanol was first used to convert the renewable raw material methyl oleate. With the commercially available ligand TPPTS, steady-state yields of up to 35 % were achieved, while side reactions such as isomerisation and hydrogenation only play a subordinate role. To extend the range of applications of the continuously operated jet-loop reactor, the material system consisting of water and butanol for converting methyl undecenoate, also known from preliminary work, was tested in continuous operation using sulfoxantphos as a ligand. The new challenge of emulsion formation, which makes it difficult to separate the product and catalyst phases, was solved by systematically investigating the butanol concentration and separation temperature. This enabled stable yields of >80 % with a low catalyst loss of <0.1 %/h. This corresponds to a loss of only 16.7 mg catalyst per kilogram of product, which promises a possible starting point for further research into potential applications.

CRediT authorship contribution statement

T.F.R. Roth: Writing – review & editing, Writing – original draft, Visualization, Investigation, Data curation, Conceptualization. **M. Häusler:** Investigation. **D. Vogt:** Supervision. **T. Seidensticker:** Writing – review & editing, Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Thomas Seidensticker reports equipment, drugs, or supplies was provided by Dako Aktiengesellschaft. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Data availability

Data will be made available on request.

Acknowledgements

The authors thank the networking program ‘Sustainable Chemical Synthesis 2.0′ (SusChemSys 2.0) for the support and fruitful discussions across disciplines.

We would also like to thank Dako AG for providing the substrate Methyl Oleate.

Furthermore, we are very thankful to the German Federal Ministry of Food and Agriculture (Bundesministerium für Ernährung und Landwirtschaft), represented by the FNR (Fachagentur Nachwachsende Rohstoffe) for financial support of the young research group “Renewlysis” (project number 2219NR355).

Supporting information

Detailed information on the substrate compositions, the investigations of the influence of the butanol concentration and the separation temperature, further investigations with the addition of sodium sulfate, and the analytical methods used are provided.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2024.114803.

References

[1] P.T. Anastas, J.C. Warner, 12 Principles of Green Chemistry - American Chemical Society, Oxford University Press, 1998, p. 30.

[2] A. Behr, P. Neubert, Applied Homogeneous Catalysis, Wiley-VCH, Weinheim, 2012.

[3] C.W. Kohlpaintner, R.W. Fischer, B. Cornils, Aqueous biphasic catalysis: ruhrchemie/Rhône-Poulenc oxo process, Appl. Catal. A *221* (2001) 219–225, https://doi.org/10.1016/S0926-860X(01)00791-8.

[4] A. Behr, T. Seidensticker, Chemistry of Renewables, Springer Nature, Berlin, 2020.

[5] T. Rösler, T.A. Faßbach, M. Schrimpf, A.J. Vorholt, W. Leitner, Toward water-based recycling techniques: methodologies for homogeneous catalyst recycling in liquid/liquid multiphase media and their implementation in continuous processes, Ind. Eng. Chem. Res. *58* (2019) 2421–2436, https://doi.org/10.1021/acs.iecr.8b04295.

[6] O. Roelen (Chemische Verwertungsgesellschaft Oberhausen m.b.H.), Verfahren zur Herstellung von sauerstoffhaltigen Verbindungen, 849 548, 1938.

[7] E.N. Frankel, F.L. Thomas, Selective hydroformylation of polyunsaturated fats with a rhodium-triphenylphosphine catalyst, J. Am. Oil Chem. Soc. *49* (1972) 10–14, https://doi.org/10.1007/BF02545129.

[8] J.P. Friedrich, G.R. List, V.E. Sohns, Hydroformylation of methyl oleate with a recycled rhodium catalyst and estimated costs for a batch process, J. Am. Oil Chem. Soc. *50* (1973) 455–458, https://doi.org/10.1007/BF02639853.

[9] K.F. Muilwijk, P.C.J. Kamer, P.W.N.M. van Leeuwen, A bulky phosphite-modified rhodium catalyst for the hydroformylation of unsaturated fatty acid esters, J. Am. Oil Chem. Soc. *74* (1997) 223–228, https://doi.org/10.1007/s11746-997-0127-8.

[10] E. Benetskiy, S. Lühr, M. Vilches-Herrera, D. Selent, H. Jiao, L. Domke, K. Dyballa, R. Franke, A. Börner, Rhodium-catalyzed nonisomerizing hydroformylation of methyl oleate applying lactame-based phosphoramidite ligands, ACS Catal. *4* (2014) 2130–2136, https://doi.org/10.1021/cs500274n.

[11] N. Herrmann, J. Bianga, T. Gaide, M. Drewing, D. Vogt, T. Seidensticker, Aqueous biphasic hydroformylation of methyl oleate: a green solvent-only strategy for homogeneous catalyst recycling, Green. Chem. *21* (2019) 6738–6745, https://doi.org/10.1039/C9GC02868D.

[12] J. Bianga, N. Herrmann, L. Schurm, T. Gaide, J.M. Dreimann, D. Vogt, T. Seidensticker, Improvement of productivity for aqueous biphasic hydroformylation of methyl 10-undecenoate: a detailed phase investigation, p. 1-7, Eur. J. Lipid Sci. Technol. *122* (2020) 1900317, https://doi.org/10.1002/ejlt.201900317.

[13] T. Gaide, J.M. Dreimann, A. Behr, A.J. Vorholt, Overcoming phase-transfer limitations in the conversion of lipophilic oleo compounds in aqueous media-A thermomorphic approach, Angew. Chem. Int. Ed. *55* (2016) 2924–2928, https://doi.org/10.1002/anie.201510738.

[14] M. Schrimpf, J. Esteban, T. Rösler, A.J. Vorholt, W. Leitner, Intensified reactors for gas-liquid-liquid multiphase catalysis: from chemistry to engineering, Chem. Eng. J. *372* (2019) 917–939, https://doi.org/10.1016/j.cej.2019.03.133.

[15] H. Warmeling, A. Behr, A.J. Vorholt, Jet loop reactors as a versatile reactor set up - intensifying catalytic reactions: a review, Chem. Eng. Sci. *149* (2016) 229–248, https://doi.org/10.1016/j.ces.2016.04.032.

[16] F. Breit, O. Bey, E. von Harbou, Model-based investigation of the interaction of gas-consuming reactions and internal circulation flow within jet loop reactors, Processes *10* (2022) 1297, https://doi.org/10.3390/pr10071297.

[17] A. Behr, M. Becker, J. Dostal, D. Kohlmann, Hydrodynamik und Verweilzeitverhalten eines Düsenumlaufreaktors für den Einsatz in der Mehrphasenkatalyse, Chem. Ing. Tech. *80* (2008) 1501–1508, https://doi.org/10.1002/cite.200800080.

[18] A. Behr, M. Becker, J. Dostal, Bubble-size distributions and interfacial areas in a jetloop reactor for multiphase catalysis, Chem. Eng. Sci. *64* (2009) 2934–2940, https://doi.org/10.1016/j.ces.2009.03.031.

[19] A. Sayyar, H. Zhang, T. Wang, Numerical simulation of the hydrodynamics in a novel jet loop bubble column with helical sieve tapes, Chem. Eng. Sci. *270* (2023) 118491, https://doi.org/10.1016/j.ces.2023.118491.

[20] M. Ughetti, D. Jussen, P. Riedlberger, The ejector loop reactor: application for microbial fermentation and comparison with a stirred-tank bioreactor, Eng. Life Sci. *18* (2018) 281–286, https://doi.org/10.1002/elsc.201700141.

[21] S. Weber, S. Schaepe, S. Freyer, M.-H. Kopf, C. Dietzsch, Jet aeration as alternative to overcome mass transfer limitation of stirred bioreactors, Eng. Life Sci. *18* (2018) 244–253.

[22] H. Warmeling, R. Koske, A.J. Vorholt, Procedural rate enhancement of lean aqueous hydroformylation of 1-octene without additives, Chem. Eng. Technol. *40* (2017) 186–195, https://doi.org/10.1002/ceat.201600383.

[23] H.W.F. Warmeling, D. Janz, M. Peters, A.J. Vorholt, Acceleration of lean aqueous hydroformylation in an innovative jet loop reactor concept, Chem. Eng. J. *330* (2017) 585–595, https://doi.org/10.1016/j.cej.2017.07.152.

[24] H.W.F. Warmeling, T. Hafki, T. von Söhnen, A.J. Vorholt, Kinetic investigation of lean aqueous hydroformylation - an engineer's view on homogeneous catalysis, Chem. Eng. J. *326* (2017) 298–307, https://doi.org/10.1016/j.cej.2017.05.062.

[25] J. Esteban, H. Warmeling, A.J. Vorholt, An approach to chemical reaction engineering and process intensification for the lean aqueous hydroformylation using a jet loop reactor, Chem. Ing. Tech. *91* (2019) 560–566, https://doi.org/10.1002/cite.201800137.

[26] N. Herrmann, J. Bianga, M. Palten, T. Riemer, D. Vogt, J.M. Dreimann, T. Seidensticker, Improving aqueous biphasic hydroformylation of unsaturated oleochemicals using a jet-loop-reactor, p. 1-8, Eur. J. Lipid Sci. Technol. *122* (2020) 1900166, https://doi.org/10.1002/ejlt.201900166.

[27] T.B. Riemer, P. Lapac, D. Vogt, T. Seidensticker, Stable and continuous production of amines via reductive amination in a green switchable solvent system with efficient water removal, ACS Sustain. Chem. Eng. *11* (2023) 12959–12966, https://doi.org/10.1021/acssuschemeng.3c02320.

[28] T. Roth, R. Evertz, N. Kopplin, S. Tilloy, E. Monflier, D. Vogt, T. Seidensticker, Continuous production of amines directly from alkenes via cyclodextrin-mediated hydroaminomethylation using only water as the solvent, Green. Chem. *25* (2023) 3680–3691, https://doi.org/10.1039/D2GC04847G.

[29] T. Pogrzeba, M. Schmidt, N. Milojevic, C. Urban, M. Illner, J.-U. Repke, R. Schomäcker, Understanding the role of nonionic surfactants during catalysis in

microemulsion systems on the example of rhodium-catalyzed hydroformylation, Ind. Eng. Chem. Res. *2017* (2017) 9934–9941.