

# Improving Aqueous Biphasic Hydroformylation of Unsaturated Oleochemicals Using a Jet-Loop-Reactor

Norman Herrmann, Jonas Bianga, Markus Palten, Tim Riemer, Dieter Vogt, Jens M. Dreimann, and Thomas Seidensticker\*

In two case studies, the reaction performance of the aqueous biphasic hydroformylation of two industrially relevant oleochemicals, namely methyl 10-undecenoate (case 1) and methyl oleate (case 2), is significantly improved by the use of a Jet-Loop Reactor concept. Based on previously reported studies, only the two green and benign co-solvents, 1-butanol and isopropanol are applied, respectively, in the absence of any additional auxiliary. Both reactions benefit highly from using this special piece of equipment, specifically designed for improving gas–liquid–liquid mixing to create large interfacial areas with no moving internals. In case 1, the loading of the co-solvent 1-butanol is successfully reduced. For the first time significant yields (>40% after 1 h) are obtained in the absence of any co-solvent, which is very beneficial, since aldehyde products and substrate form a pure product phase enabling straightforward separation. In case 2, the loading of the substrate methyl oleate is successfully increased from 6 to 30 wt% still showing satisfying productivity. At 15 wt%, the yield of the desired internal aldehydes in the jet-loop reactor is increased by a factor of five compared to a stirred tank reactor after 3 h.

**Practical Applications:** The production of aldehydes from hydroformylation of olefins is highly relevant for the chemical industry, since these can undergo numerous subsequent reactions, to form for instance alcohols, amines, and carboxylic acids. Generally, aldehydes from oleochemicals can serve as platform chemicals for gaining access to bifunctional molecules, which are interesting as polymer precursors. Performing hydroformylation with a water-based solvent system enables efficient product separation from the aqueous catalyst phase for the realization of more sustainable processes. By using the Jet-Loop Reactor, the performance of the reaction system can be greatly improved addressing its practical relevance.

## 1. Introduction

Homogeneous catalysts possess a huge potential for functionalizing unsaturated oleochemicals, such as unsaturated fatty acids and derivatives thereof.<sup>[1–3]</sup> As presented in **Figure 1**, aldehydes are accessible by rhodium-catalysed hydroformylation, which can undergo numerous subsequent reactions, to carboxylic acids, alcohols, or amines.<sup>[4,5]</sup> Bifunctional molecules are thus formed potentially having very interesting applications as precursors for polycondensates, lubricants, or surfactants.

However, industrial application of homogeneous catalysts in the transformation of these renewable resources is still limited, although of very high interest.<sup>[6,7]</sup> This can be mainly attributed to separation issues of the catalyst and the product after reaction.<sup>[5]</sup> To date, hydroformylation of oleochemicals in industry is, if at all, conducted under monophasic conditions with subsequent distillation of the high-boiling product under destruction of the catalyst. A more straightforward and sustainable process for recycling of homogeneous rhodium-catalysts in the hydroformylation does, however, exist in industry: Under aqueous biphasic conditions, propene is converted to butanals in the so-called Ruhrchemie/Rhone-Poulenc process operated by OXEA in Oberhausen/Germany.<sup>[8–10]</sup> Efficient immobilization of the catalyst in aqueous solution is achieved by using sulfonated ligands. The butanals

have a much lower solubility in water and thus form a second phase after reaction and can be easily separated. Unfortunately, this elegant process is limited to propene due to its sufficient solubility in water allowing economical productivities.<sup>[11]</sup>

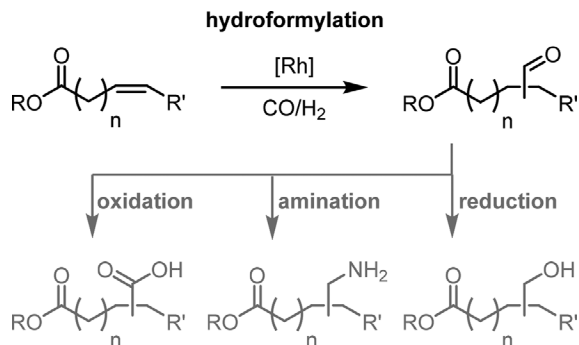
Due to many advantages of water as solvent (nontoxic, environmentally friendly, cheap, abundant, etc.) and its beneficial immobilization properties for homogenous catalysts,<sup>[12–15]</sup> a great effort in also converting longer-chain alkenes under aqueous, biphasic conditions is noticed in literature.<sup>[16,17]</sup> Several approaches in academic research present the application of different additives for either increasing the solubility of the fatty compound in water or phase-transfer catalyst systems to bring the catalyst in the organic phase. Both approaches thus increase the efficiency. Among these examples, are the use of amphiphilic

N. Herrmann, J. Bianga, M. Palten, T. Riemer, Prof. D. Vogt, Dr. J. M. Dreimann, Dr. T. Seidensticker  
Laboratories of Industrial Chemistry  
TU Dortmund University  
Emil-Figge-Straße 66, 44227 Dortmund, Germany  
E-mail: thomas.seidensticker@tu-dortmund.de

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/ejlt.201900166>

© 2019 The Authors. *European Journal of Lipid Science and Technology* published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/ejlt.201900166



**Figure 1.** Hydroformylation of a generic unsaturated fatty acid derivative with potential subsequent reaction of the aldehyde intermediate.

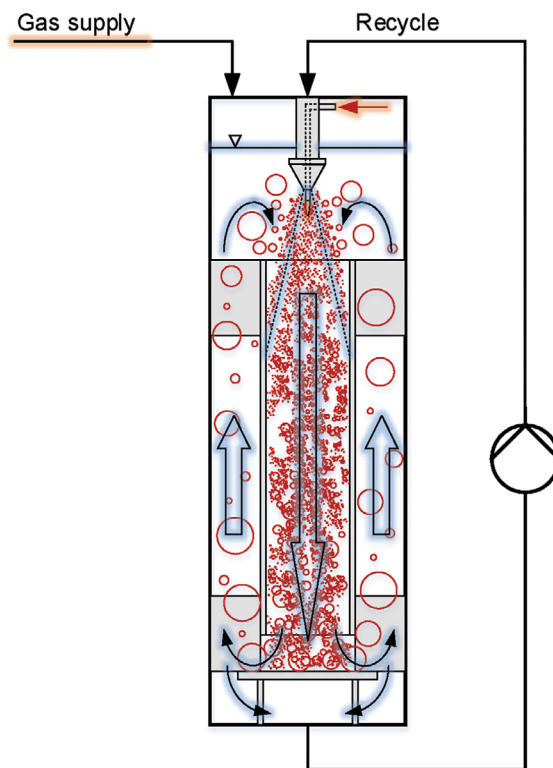
phosphine ligands<sup>[18–21]</sup> and the utilization of additives, such as activated carbon,<sup>[22,23]</sup> surfactants,<sup>[24–30]</sup> cyclodextrins,<sup>[31–33]</sup> alkylimidazolium salts,<sup>[34]</sup> etc.

Surprisingly, reports on the hydroformylation of unsaturated oleochemicals under aqueous biphasic conditions as representatives of long-chain alkenes, are rather scarce. Activated carbon has been used by Monflier et al. in 2012<sup>[23]</sup> and in 2015 the same group used cyclodextrins<sup>[35]</sup> for the hydroformylation of triglycerides, a protocol that is unfortunately not applicable to fatty acid derivatives.

Recently, our group reported on the use of co-solvents in the aqueous biphasic hydroformylation of unsaturated oleochemicals. Short-chain alcohols, namely 1-butanol and isopropanol, have been used as green<sup>[14]</sup> and very effective mediators in the hydroformylation of methyl 10-undecenoate (**M10U**)<sup>[36,37]</sup> and methyl oleate (**MO**)<sup>[38]</sup> respectively. It was shown that by adjusting the solvent ratios accordingly, on the one hand, the selectivity and activity of the chosen catalytic system is maintained, and on the other hand, efficient separation of the organic product phase from the catalyst containing aqueous phase by simple decantation is ensured. Moreover, in both approaches, loss of the applied catalyst was kept at a very low level due to the application of sulfonated ligands (SulfoXantphos for **M10U** (Figure 4), and TPPTS for **MO** (Figure 6)) and consecutive recycling runs of the aqueous phase demonstrated the general feasibility of the concept.<sup>[36,38]</sup>

Nevertheless, two major issues with the presented examples remain: In the hydroformylation of methyl 10-undecenoate (**M10U**), 1-butanol is used as co-solvent in a 1:1 mass ratio which predominantly is present in the organic product phase after reaction. With this, efficient extraction of the product is ensured. However, a considerable amount of water is present in the organic product phase due to apparent miscibility of water in 1-butanol. Hence, the present catalyst is also extracted into the organic product phase, an undesired effect known as leaching. Up to 5% of the initial catalyst loading are thus lost per recycling run.<sup>[36]</sup> It is anticipated, that the reduction of the amount of 1-butanol applied reduces leaching, however, at the expense of the overall productivity of the reaction due to mixing issues.

In the aqueous biphasic hydroformylation of methyl oleate (**MO**), isopropanol is used as co-solvent, which stays in the aqueous phase. Hence, a pure product phase is obtained after reaction with only minimal leaching of both the catalyst and the



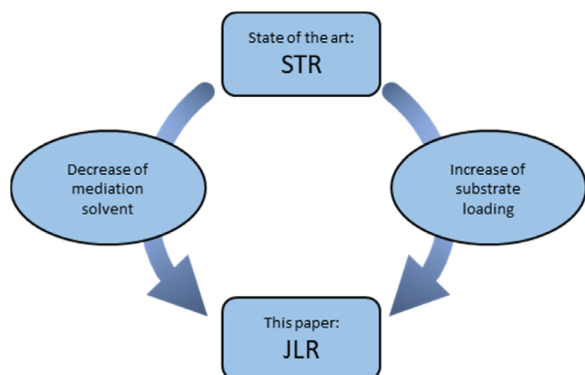
**Figure 2.** Schematic drawing of a Jet-Loop Reactor for intensified mixing.

co-solvent. This behavior is very beneficial, since downstream operations for the purification of the valuable aldehyde product can be virtually omitted. However, this system is limited in terms of substrate concentration and thus in terms of productivity.

Both abovementioned reaction systems have so far only been implemented in stirred tank reactors (STR) in batch mode. However, in order to intensify mixing and thus increase liquid-liquid interfaces in aqueous biphasic hydroformylation of higher olefins, the application of special reactor concepts is an efficient means,<sup>[39]</sup> as recently presented by our group.<sup>[40–44]</sup> 1-Octene was converted in the absence of any additive (so-called *lean hydroformylation*) by means of a Jet-Loop Reactor (JLR) concept.

A Jet-Loop Reactor (**Figure 2**) is a reaction vessel, in which intensive mixing is achieved without any moving or rotating parts.<sup>[45]</sup> From the bottom of the reactor, a liquid reaction stream is withdrawn and reintroduced to the top of the reactor via an external loop. External power input is ensured by a pump in the loop. The feed at the top is introduced via a nozzle underneath the liquid level into a draft tube sucking the gas phase with it thus creating a jet to generate a well-dispersed mixture of the immiscible components. With this, very high interfacial areas can be created. At the end of the draft tube, a baffle is installed which forces the creation of an internal loop additionally helping the intense mixing.

In our ongoing endeavor for developing sustainable processes for homogeneously catalyzed functionalization reactions of unsaturated oleochemicals, our focus is the increase of the productivity of the two presented reactions. On the one hand, by reducing the amount of 1-butanol in the aqueous biphasic hydroformylation of methyl 10-undecenoate (**M10U**) and on the other



**Figure 3.** Concepts for the application of a Jet-Loop Reactor in biphasic hydroformylation of oleo-chemicals.

hand by increasing the substrate loading in the aqueous biphasic hydroformylation of methyl oleate (MO). To address the above-mentioned two limitations and overcome the anticipated mixing issues, we sought to apply the Jet-Loop Reactor concept to these two reaction systems (Figure 3).

## 2. Experimental Section

### 2.1. Reagents and Solvents

See Table 1 for reagents and solvents.

### 2.2. General Procedures

#### 2.2.1. Hydroformylation of Methyl 10-Undecenoate (M10U) in a Stirred Batch Autoclave

Initially, the catalyst Rh(acac)(CO)<sub>2</sub> (8.99 mg, 0.035 mmol) and the ligand SulfoXantphos (272.82 mg, 0.349 mmol) were weighed into the pressure autoclave using standard Schlenk technique and the reactor was closed and evacuated. Subsequently, degassed 1-butanol (46.7 mL, 37.8 g) and water (37.8 mL, 37.8 g) were transferred to the pressure autoclave under vacuum using a capillary. Methyl 10-undecenoate (14.4 g, 69.7 mmol) was degassed and injected into an inert dropping funnel. The reactor was then pressurized with 5 bar synthesis gas and checked for leaks. While the reactor heated up in the heating block, the dropping funnel was mounted. Shortly before reaching 140 °C, the dropping funnel was compressed to 20 bar synthesis gas and expanded into the pressure autoclave at reaction temperature. During the reaction time of 1 h, the stirrer speed was set to 1000 rpm and the synthesis gas pressure was kept constant at 20 bar. For monitoring the progress of the reaction, samples for GC analysis were taken at regular intervals using a capillary

dipping into the reaction solution connected to a valve. After the reaction, the stirrer was switched off, the pressure autoclave was cooled down using an ice bath, carefully vented, and rinsed with argon. The reaction mixture was transferred from the opened autoclave to a separating funnel and the product was separated from the aqueous catalyst phase. For determination of the final conversion after 1 h reaction time, samples were taken from both phases for GC-analysis.

#### 2.2.2. Hydroformylation of Methyl 10-Undecenoate (M10U) in a Jet-Loop Reactor

Initially, the catalyst Rh(acac)(CO)<sub>2</sub> (80.57 mg, 0.312 mmol) and the ligand sulfoxantphos (2.444 g, 3.123 mmol) were weighed under argon into a 100 mL Schott bottle. Then methyl 10-undecenoate (129 g, 0.625 mol), 1-butanol (418 mL, 338.6 g), and water (338.6 mL, 338.6 g) were poured into a 1 L Schott flask. Degassed water was added to the 100 mL Schott bottle and the catalyst ligand suspension was placed in an ultrasonic bath. The contents of the 1 L Schott bottle were stripped with argon and then transferred to the Jet-Loop Reactor using an HPLC pump. The circulation pump was put into operation at 40% power, the external heating was controlled to 140 °C, and a synthesis gas pressure of 5 bar (CO:H<sub>2</sub> = 1) was set in the reactor via the gas distributor. As soon as the reactor content was heated to 80 °C, the catalyst solution was injected into the dropping funnel, which was previously rinsed with argon. To preform the catalyst, the dropping funnel was supplied with 5 bar synthesis gas and the stirrer of the dropping funnel was switched on. As soon as the internal temperature of the Jet-Loop Reactor reached 140 °C, a synthesis gas pressure of 20 bar was applied to the dropping funnel via the gas distributor and the preformed catalyst solution was transferred to the reactor. The circulating pump was set to 90% power immediately after the catalyst was introduced and a constant reaction pressure of 20 bar synthesis gas was set via the main gas line. GC samples were taken at defined intervals via the sampling point installed on the circulating pump.

After 1 h reaction time, the synthesis gas supply was closed, the pump throttled to 30% power, and the heating was switched off. After the system cooled down to below 90 °C, the system was carefully depressurized, then argon was pressed on at a slight overpressure, and the reaction mixture was discharged into a 1 L bulkhead bottle. After phase separation, the product phase was balanced and a sample taken for GC analysis. To examine samples via gas chromatography, a Hewlett Packard 6890 Series GC System gas chromatograph was used, equipped with a thermal conductivity detector (TCD), a flame ionization detector (FID), and a Hewlett Packard Innowax column (30 m × 0.25 mm × 0.25 μm). The injection volume was 1 μL, the split ratio was 1:50. Helium was used as carrier gas with a flow of 1.3 mL min<sup>-1</sup>. The starting temperature of the oven was 40 °C.

**Table 1.** Reagents and solvents (purity values and suppliers in brackets).

Case	Substrate	Solvent	Catalyst	Ligand	Snygas (1:1)
1	Methyl 10-undecenoate (96%) (Chemicalpoint)	Butanol (99%) (Acros)/water	Rh(acac)(CO) <sub>2</sub> (Umicore)	SulfoXantphos (MOLISA)	CO/H <sub>2</sub> (Messer)
2	Methyl oleate (93%) (DAKO AG)	Isopropanol (98%) (VWR)/water	Rh(acac)(CO) <sub>2</sub> (Umicore)	TPPTS (OXEA)	CO/H <sub>2</sub> (Messer)

After 1 min the temperature was increased to 155 °C with a rate of 7 °C min<sup>-1</sup>. The temperature was then increased to 250 °C at a rate of 20 °C min<sup>-1</sup>. This temperature was maintained for 5 min. The external standard quantitation method was used.

### 2.2.3. Hydroformylation of Methyl Oleate (MO) in a Stirred Batch Autoclave

The catalyst Rh(acac)(CO)<sub>2</sub> (113.57 mg, 0.440 mmol) and the ligand TPPTS (2501.8 mg, 4.4 mol) were first weighed into the pressure autoclave using Schlenk technique. Then (47.0 mL, 47.0 g) water and isopropanol (60.3 mL, 47.0 g) were degassed and drawn into the reactor by vacuum. 10 mL isopropanol was mixed with 6.8 mL methyl oleate (MO) (6 g, 17.6 mmol), degassed, and injected into a prepared and inert dropping funnel. 5 bar synthesis gas was injected into the reactor and the tightness of the reactor was checked. The reactor was heated to 140 °C in the heating block. The assembled dropping funnel was brought to the appropriate temperature by means of a heat gun, compressed to 50 bar by means of synthesis gas, and discharged into the reactor when the desired reactor temperature was reached. Stirring was achieved with a pitched blade stirrer for 2 h (1000 rpm) and the synthesis gas pressure was maintained at 50 or 100 bar continuously. A GC sample was taken via a sample valve at various time intervals and made available for analysis. When the reaction was complete, the reactor was cooled by means of an ice bath without stirring. The reactor was carefully expanded, rinsed with argon. The autoclave was cleaned and prepared for the next test.

### 2.2.4. Hydroformylation of Methyl Oleate (MO) in a Jet-Loop Reactor

Initially, the catalyst Rh(acac)(CO)<sub>2</sub> (18.72 mg, 0.073 mmol) and the ligand TPPTS (412.3 mg, 0.725 mmol) were weighed under argon into a 100 mL Schott bottle. Then 53.4 mL methyl oleate (46.5 g, 0.145 mol), isopropanol (467 mL, 364.3 g) and water (334.3 mL, 334.3 g) were poured into a 1 L Schott flask. 30 mL degassed water was added to the 100 mL Schott bottle and the catalyst ligand suspension was placed in the ultrasonic bath. The contents of the 1 L Schott bottle were stripped with argon and then transferred to the jet loop reactor using an HPLC pump. The circulation pump was put into operation at 40%, the heating bands were controlled to 140 °C, and a synthesis gas pressure of 5 bar (CO:H<sub>2</sub> = 1) was set in the reactor via the gas distributor. As soon as the reactor content was heated to 80 °C, the catalyst solution was injected into the dropping funnel, which was previously rinsed with argon. To preform the catalyst, the dropping funnel was supplied with 10 bar synthesis gas and the stirrer was switched on. As soon as the reactor content reached 140 °C, a synthesis gas pressure of 50 bar was applied to the dropping funnel via the gas distributor and the preformed catalyst solution was transferred to the reactor. The circulating pump was set to 90% output immediately after the catalyst was introduced and a constant reaction pressure of 50 bar synthesis gas was set via the main gas line. GC samples were taken at defined intervals via the sampling point installed on the circulating pump.

After 3 h reaction time, the synthesis gas supply was closed, the pump throttled to 30% output, and the heating switched off.

After the system cooled down to below 70 °C, the system was carefully depressurized, then argon was pressed on at a slight overpressure, and the reaction mixture was discharged into a 1 L bulkhead bottle.

## 3. Results and Discussion

As presented in Figure 3, the Jet-Loop Reactor was identified as a highly promising tool to overcome two significant limitations in state of the art aqueous biphasic hydroformylation reactions of oleochemicals. Specifically, the hydroformylation of methyl 10-undecenoate (M10U) and methyl oleate (MO) are considered within this contribution. Previously, the application of the biphasic solvent system consisting of water and 1-butanol for efficient hydroformylation of M10U (Figure 4) and subsequent recovery of the precious catalyst was presented. Herein, the solvent 1-butanol was used as mediator between the aqueous catalyst phase and the substrate.<sup>[36]</sup> In the context of MO hydroformylation, (Figure 6) often low substrate loading of the reaction mixture is described, resulting in low space time yields and therefore, large reactors when thinking about process scale.<sup>[38]</sup>

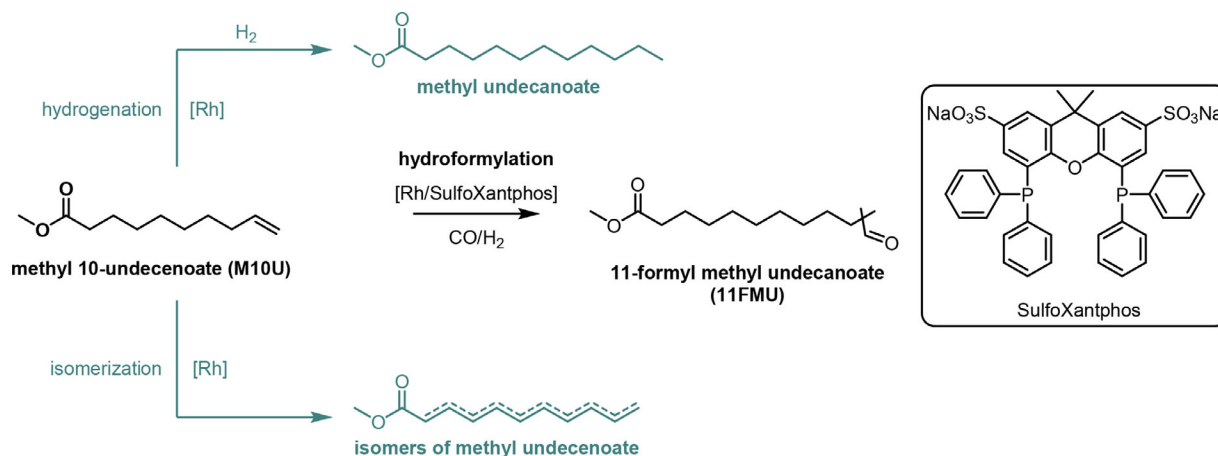
In two case studies, the feasibility of decreasing the mediation solvent content in the hydroformylation of M10U (case 1) and the increase of substrate loading in the hydroformylation of MO (case 2) exclusively being possible with the application of a Jet-Loop Reactor, is presented. For this, hydroformylation experiments have been operated in a standard overhead stirred pressure autoclaves as well as in a Jet-Loop Reactor. Operating these reactors at comparable reaction conditions, reaction profiles were obtained to compare the macroscopic rate of reaction and final yields of the desired aldehyde.

### 3.1. Case 1: Decrease of the Applied Co-Solvent Concentration in Hydroformylation of M10U

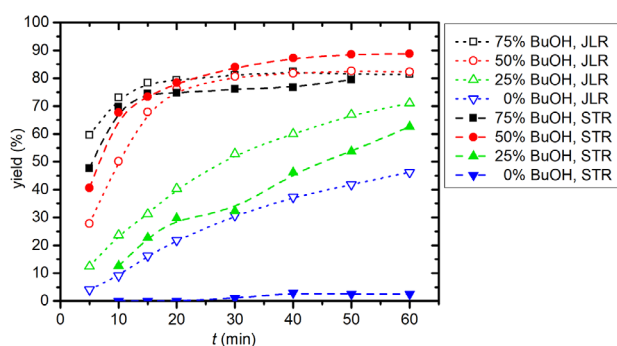
In Figure 4 the hydroformylation of the methyl 10-undecenoate (M10U) toward the preferred 11-formyl methyl undecanoate (11FMU) and competing side reactions are presented. Besides hydroformylation, isomerization of the double bond along the carbon chain is possible, while especially the methyl 2-undecenoate shows a rather stable isomer of the applied substrate. Also hydrogenation of the substrate and its isomers to form the methyl undecanoate is commonly observed. To avoid these side reactions and favor the formation of the linear 11-formyl methyl undecanoate, the so-called Sulfoxantphos ligand is applied with the Rh(acac)(CO)<sub>2</sub> precursor.

As reported, a mixture of 50% 1-butanol and 50% water by weight ensures satisfying yields of the desired 11-formyl methyl undecanoate.<sup>[36]</sup> As decreasing the amount of 1-butanol in the stirred tank reactor leads to poor yields of the desired product, the decrease of 1-butanol in the Jet-Loop reactor is expected to have significantly less impact on the obtained yields.

Thus, it is expected that the reaction performance indicated by achieved yields will be quite similar in the two different reactors at higher 1-butanol loading, since miscibility of both phases is favored. With this, coordination of the substrate at the transition metal catalyst is highly probable. In contrast to that, at lower 1-butanol loading a large difference in the reaction performance



**Figure 4.** Hydroformylation of methyl 10-undecenoate (M10U) to 11-formyl methyl undecanoate (11FMU) and possible competing side reactions using a rhodium SulfoXantphos complex.



**Figure 5.** Reaction profiles of the hydroformylation of methyl 10-undecenoate (M10U) in a stirred tank reactor (STR) and a Jet-Loop Reactor (JLR) with varying proportion of the mediator solvent n-butanol:

Conditions:  $n_{M10U,JLR} = 0.625$  mol,  $n_{M10U,STR} = 0.07$  mol,  $n_{M10U}/n_{Rh(acac)(CO)_2} = 2000$ ,  $n_{SulfoXantphos}/n_{Rh(acac)(CO)_2} = 5$ , 20 bar  $CO/H_2$  (1:1), 140 °C, 1 h,  $V_{total,JLR} = 0.9$  L,  $V_{total,STR} = 0.1$  L.

between a stirred tank autoclave and a Jet-loop Reactor will be expected. In the absence of the mediator in the stirred tank reactor, poor solubility of the catalyst and the product in the counter liquid phase is expected and a small interfacial area between the liquid phases will hinder the coordination of the substrate at the metal catalyst center, so that poor activity will be reached. Meanwhile better separation of catalyst and product is expected. In the Jet-Loop Reactor, rather high yields of the desired product will be expected due to intense mixing. Large interfacial area between the two liquid phases will increase the probability of substrate and catalyst finding each other, although poor mass transfer and low solubility is expected.

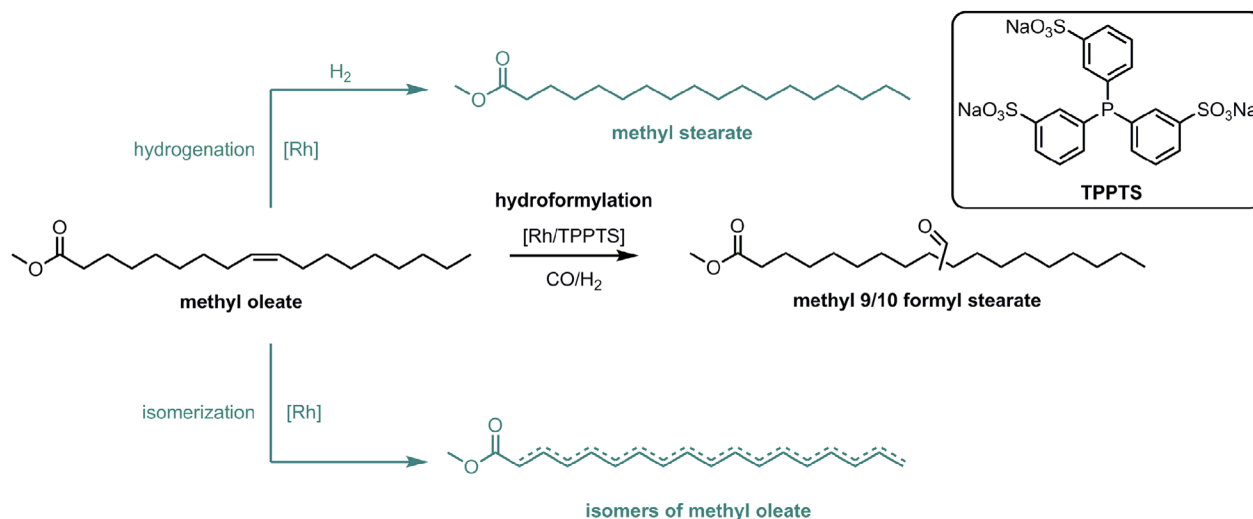
In **Figure 5**, the yields of the desired linear 11-formyl methyl undecanoate (11FMU) obtained at different 1-butanol loadings in the stirred tank reactor and in the Jet-Loop Reactor are presented, respectively. Higher 1-butanol loadings support the reaction performance toward higher rate of reaction. Especially with a solvent ratio of 1-butanol and water of 75:25 by weight (black squares), no significant difference between the STR and the JLR can be identified. Furthermore, at solvent ratio 50:50 (red dots) even the STR outperforms the JLR at given reaction conditions, most probably

since those reaction conditions were identified as most suitable in the STR setup according to Gaide et al.<sup>[36]</sup> As the 1-butanol content is stepwise decreased, the benefits of the JLR reactor can be pointed out. Especially in the absence of 1-butanol (blue triangle) no significant reaction activity can be observed in the stirred tank reactor at all, while nearly 50% yield of the 11-formyl methyl undecanoate can be obtained within 1 h in the Jet-Loop Reactor at the same conditions. In general, the linear aldehydes to branched aldehydes (*l/b*)-selectivities were not influenced by the amount of substrate and stable values about 96/4 were reached in all cases.

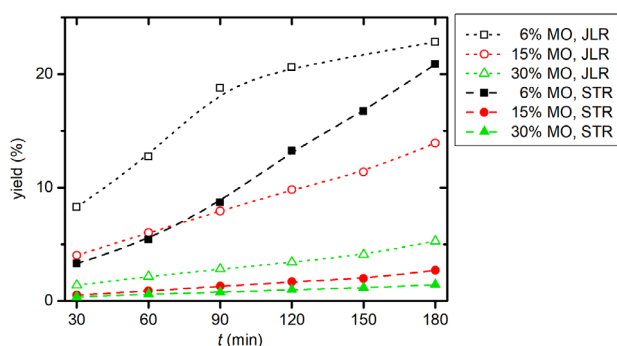
### 3.2. Case 2: Increase of Substrate Loading in Hydroformylation of MO

In **Figure 6** the hydroformylation reaction of methyl oleate (MO) to the desired methyl 9/10 formyl stearate and competing side reactions is presented. As presented in the hydroformylation of methyl 10-undecenoate, isomerization of the CC-double bond along the carbon chain and the hydrogenation of the substrate are not desired. In contrast to the previously described approach, herein the monodentate phosphite ligand TPPTS (Triphenylphosphinitrisulfonate) was applied. The focus here is on the formation of the branched hydroformylation product (methyl 9/10 formyl stearate).

As can be found elsewhere,<sup>[38]</sup> the suitability of a solvent mixture of water and isopropanol is highly beneficial for the hydroformylation of methyl oleate. The strength of that developed system lies in the fact that always a pure organic product phase is observed after reaction at any substrate loading. In order to further improve the productivity of the reaction system, the increase of the substrate loading is favorable. Satisfying yields of the desired aldehydes were obtained at substrate loadings between 6 and 12 wt% in the stirred autoclave. Due to improved mixing of gas-liquid-liquid-mixtures this reaction is anticipated to benefit from the application of the Jet-Loop Reactor. Again, with the creation of large liquid/liquid-interphase the coordination of the substrate at the metal catalyst center is favored, although mass transport is slow and miscibility of both liquid phases is poor. Hence, we compared aqueous biphasic hydroformylation of methyl oleate



**Figure 6.** Hydroformylation of methyl oleate (MO) to methyl 9/10 formyl stearate and possible competing side reactions using a rhodium TPPTS complex.



**Figure 7.** Reaction profiles of the hydroformylation of methyl oleate (MO) in a stirred tank reactor (STR) and a Jet-Loop Reactor (JLR) with varying substrate loading (MO);  $n_{\text{MO}}/n_{\text{Rh(acac)}}(\text{CO})_2 = 2000$ ,  $n_{\text{TPPTS}}/n_{\text{Rh(acac)}}(\text{CO})_2 = 10$ , 50 bar  $\text{CO}/\text{H}_2$  (1:1), 140 °C, 3 h,  $m_{\text{IPrOH}}/m_{\text{H}_2\text{O}} = 1$ ,  $V_{\text{total,JLR}} = 0.885$  L,  $V_{\text{total,STR}} = 0.1$  L.

in a stirred tank reactor and a Jet-Loop Reactor at three different substrate loadings. We selected 6, 15, and 30 wt% for present investigations, since 15 wt% is right above 12 wt%, previously reported as the maximum substrate loading, and at 30 wt% only poor yields were obtained.

In **Figure 7**, the yields of the methyl 9/10 formyl stearate obtained from the hydroformylation reactions operated in the stirred tank reactor and the Jet-Loop Reactor are presented. In all cases, significantly higher yields of the desired product can be obtained with the application of the Jet-Loop Reactor. Although the reaction performance decreases with higher substrate loading in the stirred tank reactor as well as in the Jet-Loop Reactor. As expected, the improvement of the reaction performance at 6 wt% (black squares) is less pronounced by the application of the Jet-Loop Reactor as with the other two. Interestingly, the reaction benefits most at 15 wt% (red dots), which is represented by a fivefold yield after 3 h, since the substrate concentration was right above the previously found reaction optimum. At highest loading of 30 wt% (green triangles) methyl oleate,

still significantly higher yields of the product can be obtained when applying the Jet-Loop Reactor, as almost no reaction was observed in the stirred tank reactor at same conditions. The regioselectivity remained constant with hydroformylation occurring only at position 9 and 10 of the carbon chain.

For the first time, the significant increase of the reaction performance in the hydroformylation of methyl oleate by using a Jet-Loop reactor was demonstrated. With this strategy formation of aldehydes was possible even at substrate loading of 30%. Optimization of the reactor design and reaction parameters such as temperature, pressure, circulation flow capacity are promising for future process development.

## 4. Conclusions

The reaction performance of the aqueous biphasic hydroformylation of two industrially relevant oleochemicals, namely methyl 10-undecenoate and methyl oleate, was significantly improved. By the application of a JLR, both reactions highly benefit from the improved gas–liquid–liquid mixing, compared to standard STR. Therefore, two case studies were investigated.

In case 1, the hydroformylation of methyl 10-undecenoate using  $\text{Rh(acac)}\text{CO}_2$  as precursor and sulfoxantphos as ligand, the feasibility of reducing the co-solvent 1-butanol was demonstrated. The results in the first case show no significant difference between STR and JLR at a solvent ratio of 1-butanol and water of 75:25 wt%. The advantages of the JLR reactor were unraveled by gradually reducing the 1-butanol content. Especially in the absence of 1-butanol, no significant yield of the desired aldehyde was observed by using the STR, whereas in the JLR yields exceeding 40% of 11-formyl methyl undecanoate were achieved within 1 h under comparable conditions. Additionally, the formation of a pure product phase in the absence of 1-butanol thus containing only aldehyde products and substrate is highly beneficial, since straightforward separation from the aqueous catalyst phase is enabled.

In case 2, the hydroformylation of methyl oleate using Rh(acac)CO<sub>2</sub> as precursor and TPPTS as ligand, higher yields of the desired aldehyde products at increased substrate loadings are achieved by using the JLR compared to the STR. As expected, the reaction performances decrease with higher substrate loading in both, the STR and the JLR. However, at highest substrate loading of 30 wt%, significant yields of the product were observed using the JLR, whereas no reaction was observed in the STR under comparable conditions. Moreover, the product always separates from the aqueous catalyst phase after reaction enabling their straightforward decantation, independent from the chosen substrate concentration.

The JLR thus identifies itself as a very efficient tool for the conversion of oleochemicals under aqueous biphasic conditions as demonstrated by hydroformylation. Compared to conventional stirred tank reactors, the Jet-Loop Reactor enables a significant decrease in co-solvent loading and a significant increase in substrate loading to improve overall reaction performance by intensified gas-liquid-liquid mixing. The implementation of the presented concepts in a continuous process including product separation and the recycling of the aqueous catalyst phase is currently under investigation in our laboratories. Moreover, the JLR will be used for further homogeneously catalyzed functionalization reactions of unsaturated renewables under biphasic conditions.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

The authors gratefully acknowledge the financial support from the German Research Foundation (DFG) within the Collaborative Research Center/Transregio 63 "Integrated Chemical Processes in Liquid Multiphase Systems" (InPROMPT/TRR63). The authors also thank Umicore Co KG for the donation of precious metal catalysts, OXEA for donating TPPTS, and DAKO AG for the supply of technical grade methyl oleate.

## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

biphasic catalysis, hydroformylation, Jet-Loop Reactor, methyl 10-undecenoate, methyl oleate

Received: August 14, 2019

Revised: October 1, 2019

Published online: October 29, 2019

[1] A. Behr, A. J. Vorholt, *Homogeneous Catalysis with Renewables*, Springer, Berlin 2017.

[2] T. Seidensticker, A. J. Vorholt, A. Behr, *Eur. J. Lipid Sci. Technol.* 2016, 118, 3.

- [3] A. Behr, T. Seidensticker, *Einführung in die Chemie nachwachsender Rohstoffe: Vorkommen, Konversion, Verwendung*, Springer Spektrum, Berlin 2018.
- [4] R. Franke, D. Selent, A. Börner, *Chem. Rev.* 2012, 112, 5675.
- [5] A. Behr, P. Neubert, *Applied Homogeneous Catalysis*, Wiley-VCH, Weinheim, Germany 2012.
- [6] T. Vanbésien, E. Monflier, F. Hapiot, *Eur. J. Lipid Sci. Technol.* 2016, 118, 26.
- [7] A. Behr, *Catalysis, Homogeneous*, Wiley-VCH, Weinheim, Germany 2010.
- [8] J. Hibbel, E. Wiebus, B. Cornils, *Chem. Ing. Tech.* 2013, 85, 1853.
- [9] G. Frey, G. Dämbkes, *75 Jahre Oxo-Synthese: 75 Years of Oxo Synthesis*, Klartext, Essen, Germany 2013.
- [10] B. Cornils, *Org. Process Res. Dev.* 1998, 2, 121.
- [11] S. Rothstock, *Isomerisierung und isomerisierende Hydroformylierung von Fettstoffen*, Cuvillier Verlag, Göttingen, Germany 2008.
- [12] B. Cornils, W. A. Herrmann, *Aqueous-Phase Organometallic Catalysis*, Wiley-VCH, Weinheim, Germany 2004.
- [13] J. M. Dreimann, M. Skiborowski, A. Behr, A. J. Vorholt, *ChemCatChem* 2016, 8, 3330.
- [14] D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehada, P. J. Dunn, *Green Chem.* 2016, 18, 288.
- [15] T. Rösler, T. A. Faßbach, M. Schrimpf, A. J. Vorholt, W. Leitner, *Ind. Eng. Chem. Res.* 2019, 58, 2421.
- [16] L. C. Matsinha, S. Siangwata, G. S. Smith, B. C. E. Makhubela, *Catal. Rev.* 2019, 61, 111.
- [17] B. Bibouche, D. Peral, D. Stehl, V. Söderholm, R. Schomäcker, R. von Klitzing, D. Vogt, *RSC Adv.* 2018, 8, 23332.
- [18] A. Solsona, J. Suades, R. Mathieu, *J. Organomet. Chem.* 2003, 669, 172.
- [19] H. Fu, M. Li, J. Chen, R. Zhang, W. Jiang, M. Yuan, H. Chen, X. Li, *J. Mol. Catal. A: Chem.* 2008, 292, 21.
- [20] M. S. Goedheijt, B. E. Hanson, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* 2000, 122, 1650.
- [21] B. E. Hanson, H. Ding, C. W. Kohlpaintner, *Catal. Today* 1998, 42, 421.
- [22] N. Kania, B. Léger, S. Fourmentin, E. Monflier, A. Ponchel, *Chem. - Eur. J.* 2010, 16, 6138.
- [23] J. Boulanger, A. Ponchel, H. Bricout, F. Hapiot, E. Monflier, *Eur. J. Lipid Sci. Technol.* 2012, 114, 1439.
- [24] G. La Sorella, G. Strukul, A. Scarso, *Green Chem.* 2015, 17, 644.
- [25] L. Wang, H. Chen, Y.-E. He, Y. Li, M. Li, X. Li, *Appl. Catal., A* 2003, 242, 85.
- [26] A. Rost, M. Müller, T. Hamerla, Y. Kasaka, G. Wozny, R. Schomäcker, *Chem. Eng. Process.* 2013, 67, 130.
- [27] M. Müller, Y. Kasaka, D. Müller, R. Schomäcker, G. Wozny, *Ind. Eng. Chem. Res.* 2013, 52, 7259.
- [28] T. Hamerla, A. Rost, Y. Kasaka, R. Schomäcker, *ChemCatChem* 2013, 5, 1854.
- [29] M. Illner, D. Müller, E. Esche, T. Pogrzeba, M. Schmidt, R. Schomäcker, G. Wozny, J.-U. Repke, *Ind. Eng. Chem. Res.* 2016, 55, 8616.
- [30] M. Schwarze, T. Pogrzeba, K. Seifert, T. Hamerla, R. Schomäcker, *Catal. Today* 2015, 247, 55.
- [31] E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, *Angew. Chem., Int. Ed. Engl.* 1995, 34, 2269.
- [32] D. N. Tran, F.-X. Legrand, S. Manuel, H. Bricout, S. Tilloy, E. Monflier, *Chem. Commun.* 2012, 48, 753.
- [33] F. Hapiot, S. Manuel, H. Bricout, S. Tilloy, E. Monflier, *Appl. Organomet. Chem.* 2015, 29, 580.
- [34] S. L. Desset, D. J. Cole-Hamilton, D. F. Foster, *Chem. Commun.* 2007, 299, 1933.
- [35] T. Vanbésien, E. Monflier, F. Hapiot, *ACS Catal.* 2015, 5, 4288.
- [36] T. Gaide, J. M. Dreimann, A. Behr, A. J. Vorholt, *Angew. Chem., Int. Ed.* 2016, 55, 2924.

- [37] T. Gaide, J. M. Dreimann, A. Behr, A. J. Vorholt, *Angew. Chem.* **2016**, 128, 2977.
- [38] N. Herrmann, J. Bianga, T. Gaide, M. Drawing, D. Vogt, T. Seidensticker, *Green Chem.* **2019**, 21, 6738.
- [39] M. Schrimpf, J. Esteban, T. Rösler, A. J. Vorholt, W. Leitner, *Chem. Eng. J.* **2019**, 372, 917.
- [40] J. Esteban, H. Warmeling, A. J. Vorholt, *Chem. Ing. Tech.* **2019**, 91, 560.
- [41] H. Warmeling, R. Koske, A. J. Vorholt, *Chem. Eng. Technol.* **2017**, 40, 186.
- [42] H. W. F. Warmeling, T. Hafki, T. von Söhnen, A. J. Vorholt, *Chem. Eng. J.* **2017**, 326, 298.
- [43] H. W. F. Warmeling, D. Janz, M. Peters, A. J. Vorholt, *Chem. Eng. J.* **2017**, 330, 585.
- [44] H. Warmeling, A.-C. Schneider, A. J. Vorholt, *AIChE J.* **2018**, 64, 161.
- [45] H. Warmeling, A. Behr, A. J. Vorholt, *Chem. Eng. Sci.* **2016**, 149, 229.