

Improvement of Productivity for Aqueous Biphasic Hydroformylation of Methyl 10-Undecenoate: A Detailed Phase Investigation

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The overall productivity of the aqueous biphasic hydroformylation of the castor oil-derived methyl 10-undecenoate is increased. To increase the reaction rate, the miscibility of water and the fatty compound is increased by addition of the green solvent 1-butanol as co-solvent. For the first time, the concentration of solvents, substrate, and product within the reaction process is experimentally examined in a biphasic system under 20 bar pressure of synthesis gas and 140 °C. A reactor to get samples of both phases is developed to determine the quaternary mixture of the reaction system presented in a four-dimensional tetrahedron diagram. With the knowledge gained about the reaction and its drivers, it is possible to increase the efficiency of the reaction process reported so far. With simultaneously high reaction rates (turn over frequency = >5000 h⁻¹), the space–time yield of the reaction reaches values of >120 g L⁻¹h⁻¹ and can be improved significantly without negatively affecting catalyst leaching.

Practical Applications: Most polymers are made of petrochemicals. Here, the development of a highly efficient process for the formation of bifunctional molecules starting from technical grade methyl 10-undecenoate made from castor oil in an aqueous biphasic reaction system is presented. By rhodium catalyzed hydroformylation, an aldehyde ester is formed which can be used to create alcohols, carboxylic acids, and amines. Subsequently, these molecules can be used as polymer precursors in polycondensation reactions.

derivatives thereof having a carboxyl function and their long hydrocarbon chain with double bonds bears a large functionalization potential.^[2] Methyl 10-undecenoate (M10U), for example, is made from castor oil plants (lat. *Ricinus communis*), plants that can easily be cultivated even in dry and less nutritious growing areas.^[3] Castor oil consists of more than 85% ricinoleic acid rests. M10U is accessible by initial transesterification of the triglyceride with methanol and subsequent pyrolytic cleavage at 500 °C of the intermediate methyl ricinoleate. *n*-Heptanal is formed as co-product (Scheme 1).^[4] M10U is already used in the chemical industry, for instance, for the formation of Rilsan (polyamide 11).^[5]

For highly selective functionalization reactions (for instance, through hydroformylation reactions), the use of homogeneous catalysts is necessary.^[6] The aldehydes formed in hydroformylation reactions can potentially be transformed into amines by reductive amination, into alcohols by hydrogenation or into carboxylic acids by oxidation (Scheme 2). Thereby, bifunctional molecules are generated which have a potential use in polymer chemistry.^[7]

Since catalyst separation is the major issue for the use of homogeneous catalysts in industrial processes,^[8] different concepts for catalyst immobilization, both on solids and in liquid phases, were developed.^[9] The use of water as immobilization agent seems to be a very suitable idea to get a sustainable process for functionalizations of renewable raw materials.^[10,11] Water is ubiquitous, not hazardous and propitious. However, the biggest barrier of using water are miscibility issues between water and the non-polar fatty compounds. To overcome this limitations, surfactants^[12] or phase transfer catalysts like cyclodextrins^[13] are used. Another concept is the use of co-solvents^[11,14] which leads, however, to a partition of the used solvent between the aqueous and the organic phase. This not only increases the solubility of the substrate in the aqueous catalyst phase, as intended, but also increases the solubility of the water in the organic phase. In a commercial application, this would lead to high catalyst leaching into the organic phase and to a large loss of the co-solvent itself and thus to high costs. Different solvents can be used as co-solvents having a polarity between water and the fatty compound. Besides the chemical

1. Introduction

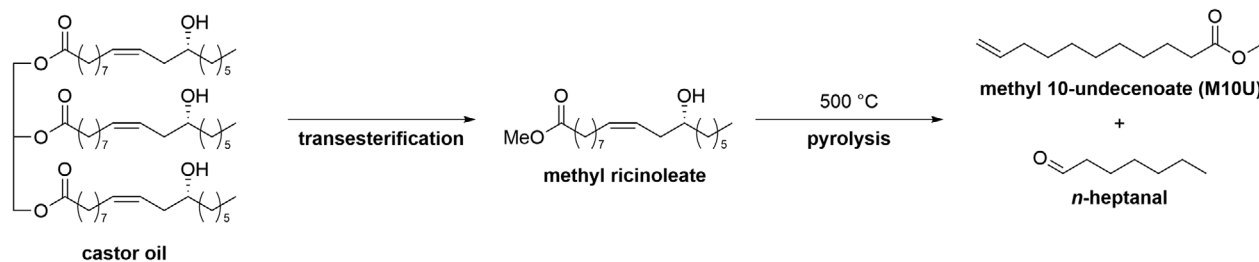
Oleo chemicals are raw materials of great interest for the chemical industry.^[1] Especially, unsaturated fatty acids and

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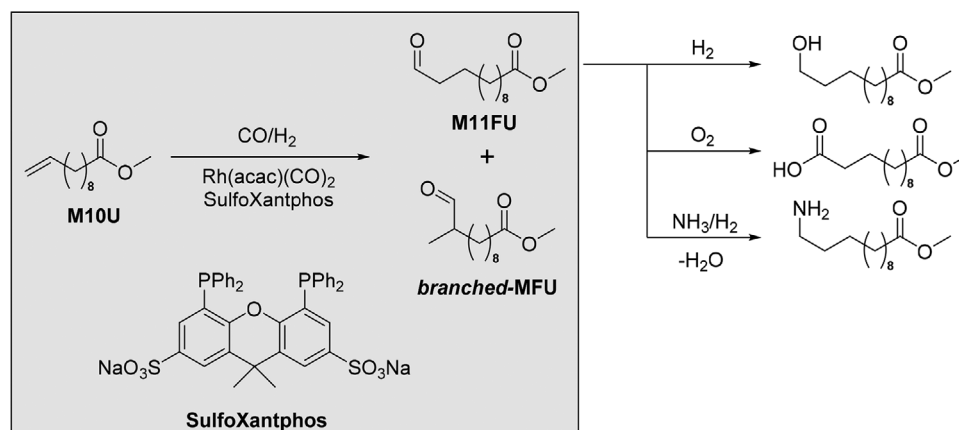
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Scheme 1. Synthesis of methyl 10-undecenoate (**M10U**) from castor oil.^[4]



Scheme 2. Hydroformylation of methyl 10-undecenoate (**M10U**) and subsequent formation to bifunctional molecules as potential polymer precursors by hydrogenation, oxidation, and reductive amination.

properties of the used co-solvent, other properties like the commercial availability and the general sustainability are considered. In particular, alcohols with a short hydrocarbon chain proved to be promising candidates. In the literature, only a few publications using co-solvents can be found.^[14]

In 2016, our group developed an aqueous solvent system for the recycling of the rhodium catalyst in hydroformylation of technical grade **M10U** to methyl 11-formylundecanoate (**M11FU**, Scheme 2) using 1-butanol as co-solvent.^[7] In this case, the ligand SulfoXantphos was used to efficiently immobilize the rhodium catalyst in the aqueous phase. At 140 °C and a pressure of 20 bar synthesis gas, 76% of the linear aldehyde ester (**M11FU**) were formed which corresponds to a turn over frequency (TOF, mole substrate converted per mole of catalyst and time) of 1500 h⁻¹ and a space-time yield (STY, mass of product produced per volume of reactor and time) of 21 kg m⁻³h⁻¹. The TOF was calculated for full conversion. Aim was to create a water-based thermomorphic multiphase system (TMS)^[15] in which a homogeneous reaction system occurs at reaction temperature and the catalyst separation follows after cooling down the reaction system. The used mixture with 1-butanol (46 wt%), water (46 wt%), and **M10U** (8 wt%) did not form a monophasic system at reaction temperature. Because the system still shows thermomorphic properties, it was called “narrow TMS.” The successful transfer to continuous flow process in a miniplant was succeeded over 21 h with stable yields around 70%.^[7]

Besides these very promising initial results, some major issues remain. In batch experiments, 5% of the rhodium leached in the organic product phase due to the relatively high miscibility of water in the organic 1-butanol phase. To prevent this effect, a

make-up of the catalyst would thus be necessary in order to achieve stable operation conditions.

In the described reaction mixture (Scheme 2), **M10U** represents the component exhibiting lowest polarity. For this reason, it is expected that the concentration of **M10U** possesses highest impact on the phase behavior of this system. It is assumed that a higher amount of substrate would lead to lower miscibility between both phases. Further, it is assumed that the formation of the product **M11FU**, having a slightly higher polarity compared to **M10U**, leads to a homogeneous reaction system during the reaction progress and enables high reaction rates. In order to exploit this effect, a low substrate amount of 8 wt% was chosen. However, a detailed investigation on the phase behavior has not been conducted so far.

Whithin the present work, we want to improve the productivity of the presented reaction system. We hypothesize that the productivity can be further increased if a detailed investigation on the phase behavior is available. Particularly, not only the composition of the starting conditions should be considered, but also the change in composition of the whole system in the course of the reaction. Moreover, these investigation need to be performed under “real” hydroformylation conditions, since the effect of syngas also needs to be taken into account. Having detailed insight into this system, we aim at the determination of the maximum reaction rates, represented as TOF. However, not only the reaction rates (TOF) but also the STYs have to be considered for assessing the productivity of a process. We aim at reaching higher STYs by applying higher substrate amounts.

In order to achieve the described goal, it is necessary to investigate the phase behavior of the system under reaction conditions

($T = 140\text{ }^{\circ}\text{C}$, $p_{\text{CO}/\text{H}_2} = 20\text{ bar}$). To do so, a pressure autoclave was specifically equipped with sampling sites. To our knowledge, it is the first time such a detailed investigation has been done experimentally.

2. Experimental Section

2.1. Reagents and Solvents

1-Butanol was received by *Acros Organics* in a purity of 99%. Double distilled water was used for experiments. $\text{Rh}(\text{acac})\text{CO}_2$ was donated by *Umicore*. Sulfoxantphos was synthesized by *MOLISA*. **M10U** was received from *Chemicalpoint* (purity 96%). Synthesis gas in CO/H_2 ratio = 1/1 was received from *Messer*.

2.2. General Procedure for Phase Investigation Experiments

For the phase investigation, 100 g of the simulated reaction mixture containing substrate **M10U**, product **M11FU**, water and 1-butanol were added to the reactor. A catalyst was not used as the catalyst would start reaction and thus strongly influence the phase compositions. Subsequently, 20 bar synthesis gas pressure ($\text{CO}/\text{H}_2 = 1/1$) was applied. Before heating, the four-blade inclined blade stirrer (500 rpm) was started. The reactor was heated by the thermostat for 90 min at a temperature of $145\text{ }^{\circ}\text{C}$. Then, the stirrer was turned off and the reactor was tempered for 2 h at a temperature of $140\text{ }^{\circ}\text{C}$. Samples of the non-polar and then of the polar phase were taken into GC vials through two valves, connected to cannulas, which were led through an ice bath. The samples were analyzed by gas chromatography using a thermal conductivity detector.

2.3. General Procedure for Hydroformylation Experiments

In a typical hydroformylation experiment (example experiment with 25 wt% **M10U**), the precursor $\text{Rh}(\text{acac})(\text{CO})_2$ (0.06 mmol, 15.6 mg) and the ligand sulfoxantphos (0.61 mmol, 473.5 mg) were added into the 300 mL autoclave using standard Schlenk technique. Subsequently, demineralized water (37.5 g) and 1-butanol (37.5 g) were transferred into the reactor by cannula. The reactor was then pressurized with 5 bar synthesis gas and heated to the reaction temperature of $140\text{ }^{\circ}\text{C}$ in a heating block under stirring at 800 rpm using a pitched blade overhead stirrer. Meanwhile, 25 g of **M10U** was filled into a pressure stable dropping funnel with pressure equalization. When the reaction temperature was reached, the substrate **M10U** was added to the reactor using a pressure of synthesis gas of 20 bar (semi-batch). For determination of the reaction progress, samples were withdrawn via cannula connected to a sample valve after different reaction times for GC analysis. After completion of the reaction, the reactor was cooled by an ice bath without stirring and carefully vented.

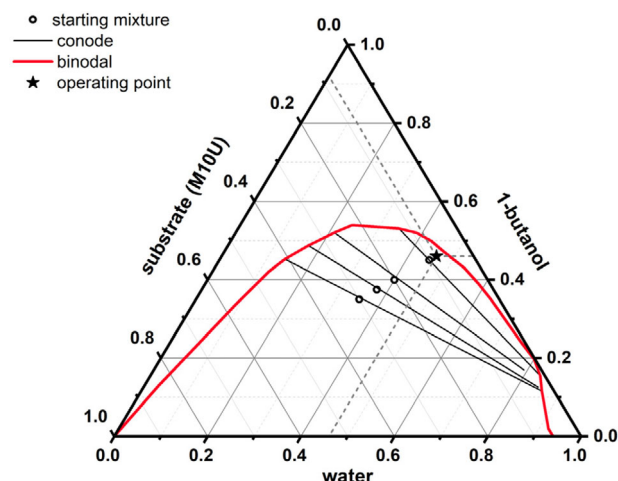


Figure 1. Ternary diagram for the ternary system of 1-butanol, water, and **M10U** at $140\text{ }^{\circ}\text{C}$. The star represents the working point at 8 wt% **M10U** (46 wt% water, 46 wt% 1-butanol). The starting mixtures represent the initial concentrations 10, 20, 25, and 30 wt% of **M10U**. The binodal curve is built by the composition of both phases which were determined via GC. Conditions: $p = 20\text{ bar}$, $\text{CO}/\text{H}_2 = 1$, $m_{\text{total}} = 100\text{ g}$.

2.4. Analysis of Phase Investigation and Reaction Progress

Gas chromatography was performed on a Hewlett Packard 6890 Series GC System gas chromatograph equipped with a thermal conductivity detector, a flame ionization detector and a Hewlett Packard Innovax column (30 m \times 0.25 mm \times 0.25 μm). The external standard quantitation method was used.

3. Results and Discussion

For high productivity, the reaction rate on the one hand and a high STY on the other hand are required. In order to increase the STY, higher substrate amounts and less solvent can be used. With regard to the limitations in substrate amounts described above, it is necessary to investigate the compositions of both phases using higher substrate amounts under reaction conditions. For this purpose, we recorded the ternary diagram (**Figure 1**) of water, 1-butanol, and the substrate **M10U**. The black star represents the operating point of the previous publication at an **M10U** amount of 8 wt% of the total mixture at a CO/H_2 pressure of 20 bar and at a temperature of $140\text{ }^{\circ}\text{C}$. In the diagram, this operating point is very close to the boundary between a biphasic and a homogeneous mixture (binodal). Using higher amounts of substrate **M10U** leads to larger distances between the starting mixture and the binodal. The larger the distance between the starting mixture and the binodal curve, the less “homogeneous behavior” shows the reaction system. This would lead to higher miscibility limitations between both phases and thus a decrease of the reaction rates is expected.

In order to achieve a “more-homogeneous” mixture and thus higher productivity, increasing the reaction temperature generally lowers the binodal curve, the miscibility gap thus decreases. This strategy would lead to a more homogeneously behaving system even with the use of high substrate amounts (higher STY)

Table 1. Determination of the initial mixing temperatures of different reaction mixtures in dependency of the substrate concentration under reaction conditions in a pressure autoclave with a borosilicate window.

Entry	w_{M10U} [%]	$w_{1-Butanol}$ [%]	w_{H_2O} [%]	$m_{1-Butanol}/m_{H_2O}$	T [°C]
1.1	5	47.5	47.5	50/50	135 ± 1
1.2	6	47	47	50/50	141 ± 1
1.3	8	46	46	50/50	149 ± 1
1.4	10	45	45	50/50	158 ± 2
1.5	12	44	44	50/50	168 ± 2

Conditions: $p = 20$ bar, $CO/H_2 = 1$, $m_{total} = 100$ g.

and thus reduces the phase transport limitations (higher TOF). The solution temperatures, at which the biphasic system turns monophasic, for different substrate amounts in the total mixture between 5 and 12 wt% were investigated (Table 1).

Figure 2 shows the different stages occurring during visual investigations of the solution temperature of the system. In the beginning at room temperature, two phases are observed (a). In this case, the substrate M10U and 1-butanol form the upper phase, and water and catalyst form the lower slightly yellow bottom phase. While heating and stirring (b) only the silhouette of the stirrer is visible through the turbid mixture. Once the reaction mixture reaches the solution temperature, it turns clear within a very short period of time (c). The temperature at which this happens is set as solution temperature of the specific composition.

Already the use of 8 wt% of M10U (entry 1.3) leads to a solution temperature of 149 °C. A slightly higher substrate M10U amount of 10 wt% (entry 1.4) leads to a solution temperature of 158 °C. Unfortunately, the stability of the homogeneous rhodium catalyst and its ligand sulfoxantphos limit the increase of temperature.

However, in all cases a vertical movement of the liquid–liquid interface is observed during the heating process, which shows the thermomorphic behavior of the system also under biphasic conditions. Interestingly, the aqueous phase was reduced significantly within the heating process. This behavior matches with the results of the ternary diagram. The variation of both parameters, temperature and substrate amount, only influences the water solubility in the non-polar phase. Meanwhile, the M10U concentration in the aqueous phase has always been very low. Consequentially, the reaction itself does not take place in the aqueous phase.

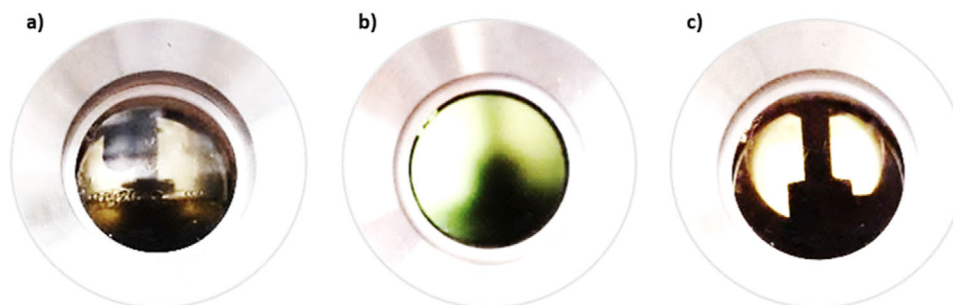


Figure 2. Visual investigation of the mixing temperature in a pressure autoclave under reaction conditions for a given substrate concentration. a) Biphasic system at room temperature, b) biphasic system under stirring while heating, and c) homogeneous system heated to above mixing temperature.

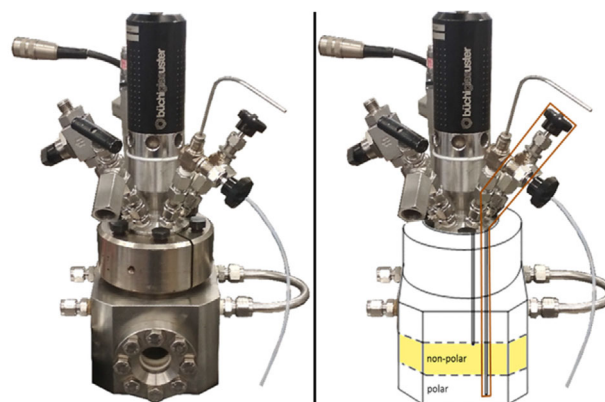


Figure 3. Pressure autoclave with borosilicate window for phase investigation of a biphasic reaction system. Using two independent sampling units, the concentrations in both liquid phases can be determined.

Since the aqueous phase has large influence on the concentration of the catalyst metal and its polar ligand, a high concentration of water in the non-polar phase seems to be necessary. The more the water dissolved in the non-polar product phase, the higher the reaction rates result from the corresponding increased catalyst concentration. Most of all, the productivity of the process would increase. The highest concentration of water in the product phase can be reached in a homogeneous ambience. However, as we reported earlier, high reaction rates were achieved in the reaction using 8 wt% of M10U and starting in a biphasic reaction system. This leads to the assumption that the formation of the product, which is more polar than the substrate, produces a homogeneous mixture quickly after reaction starts and the reaction can therefore proceed without phase transport limitations afterwards. In order to verify this, an investigation of the phase compositions over the reaction progress had to be done.

In order to quantify the composition of both phases as the reaction progressed, we had to modify the reactor to take samples from both phases (Figure 3) and thus determine concentrations of all liquid components under reaction conditions ($T = 140$ °C, $p = 20$ bar). For simplification, by-products such as branched MFU and the hydrogenation product are considered so that a 100% yield (Y) and full conversion (X) is assumed ($X = Y$). The reaction progress was simulated by using different compositions of M10U, M11FU, from $X = Y = 0\%$ (only M10U) to $X = Y = 100\%$ (only M11FU), water and 1-butanol. Additionally, different

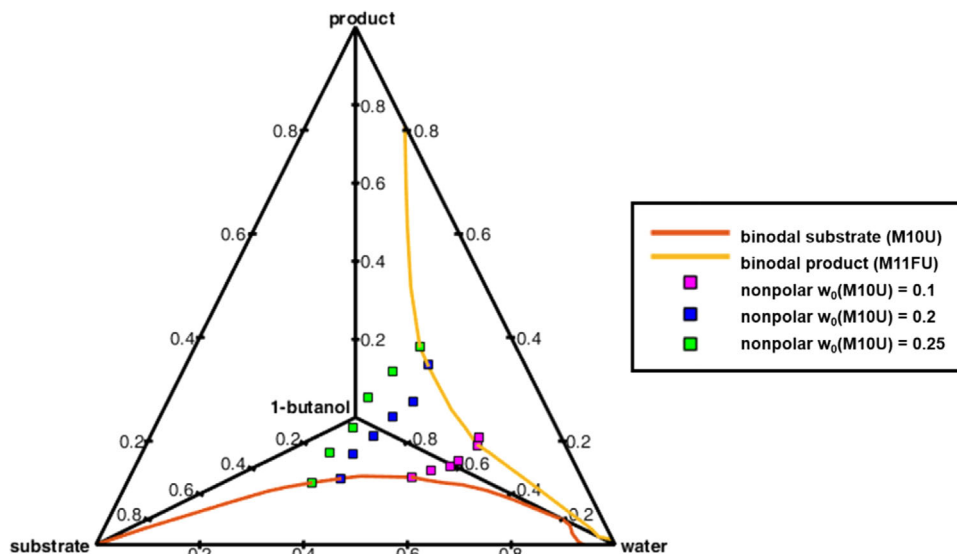


Figure 4. Tetrahedron diagram for the quaternary mixtures of the simulated hydroformylation of **M10U** in water/1-butanol for three different initial amounts of substrate **M10U**. For simplification it was assumed that $X = Y$ and no byproducts were formed. The boxes represent the reaction progress for one initial substrate amount each. Conditions: $p = 20$ bar, $\text{CO}/\text{H}_2 = 1$, $m_{\text{total}} = 100$ g.

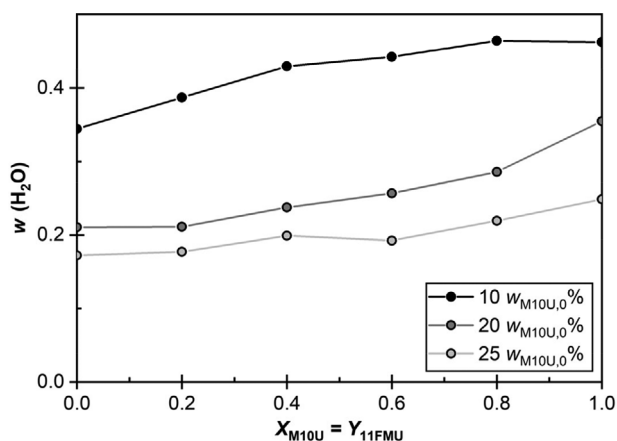


Figure 5. The change of the water content in the non-polar organic phase in relation to the progress of the (simulated) hydroformylation of **M10U**. Conditions: $p = 20$ bar, $T = 140$ °C, $\text{CO}/\text{H}_2 = 1$, $m_{\text{total}} = 100$ g.

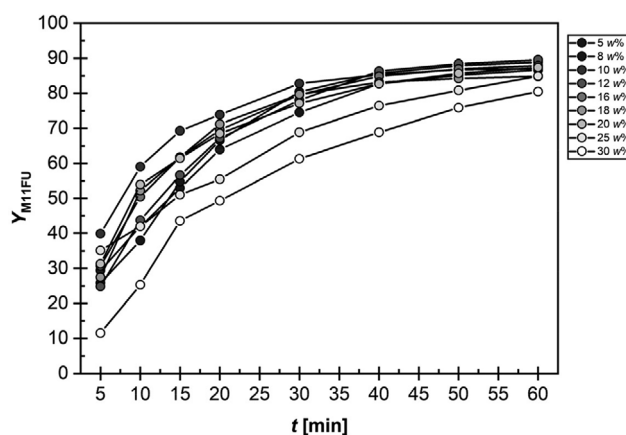


Figure 6. Reaction profile of the hydroformylation of **M10U** for different substrate amounts. Conditions: $m_{\text{total}} = 100$ g, $n(\text{Rh})/n(\text{M10U}) = 1:2000$, $n(\text{Rh})/n(\text{P}) = 1:10$, $p = 20$ bar, $\text{CO}/\text{H}_2 = 1$, $t = 1$ h, $w(\text{water})/w(1\text{-butanol}) = 1/1$, $\text{Rh}(\text{acac})(\text{CO})_2$, SulfoXantphos, $N = 800$ rpm (pitched blade).

starting concentrations of the substrate ($w_0 = 0.1; 0.2; 0.25$) were investigated.

The quaternary mixture is presented in a four-dimensional tetrahedron diagram (Figure 4), in which the aforementioned ternary diagram (Figure 1) is the bottom face of this tetrahedron.

The results show that the assumption previously made did not prove correct. For all different substrate concentrations investigated, the biphasic system remains until the end of the reaction ($X = Y = 80\%$). Nonetheless, we assumed that the water concentration in the non-polar product phase is crucial for the reaction rate. In order to illustrate the influence of the composition of the quaternary mixture (i.e., the conversion of **M10U**) on the water content in the non-polar phase, a two-dimensional cross-section of the tetrahedron diagram is shown in Figure 5. For a substrate **M10U** amount of 10 wt% of the total mixture, the water content in the non-polar phase is already about 35 wt%

in the beginning of the reaction and increases significantly until the end of the reaction. Still, a biphasic mixture is observed at that point.

With regard to increasing the productivity of the reaction, it is important to investigate the water content that is necessary to perform the reaction without the occurrence of phase limitations. We conducted experiments in which the ratio of catalyst to the substrate was consistently kept at 1/2000 ($n:n$). The temperature (140 °C), pressure (20 bar), and $w_{\text{water}}/w_{1\text{-butanol}}$ ratio (1/1) were also kept constant. Only the content of **M10U** was varied between 5 and 30 wt% of the total mixture in order to influence the catalyst and the water contents in the non-polar phase and find possible limitations for the reaction (Figure 6). A decrease in the reaction rates was expected with higher amount (>8 wt%) of substrate **M10U** due to the resulting transport limitations.

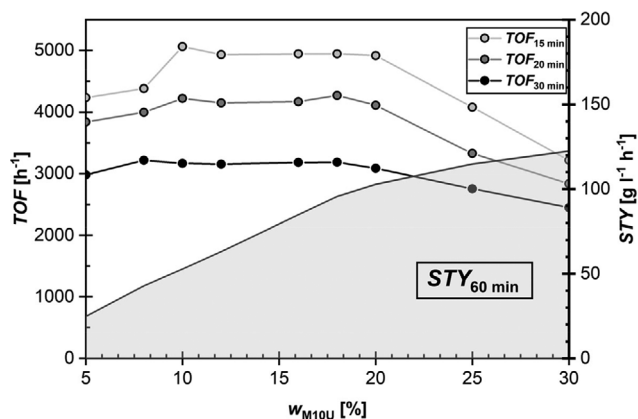


Figure 7. Work zone for efficient hydroformylation of **M10U**. Conditions: $m_{\text{total}} = 100$ g, $n(\text{Rh})/n(\text{M10U}) = 1:2000$, $n(\text{Rh})/n(\text{P}) = 1:10$, $p = 20$ bar, $\text{CO}/\text{H}_2 = 1$, $t = 1$ h, $w(\text{water})/w(1\text{-butanol}) = 1$, $\text{Rh}(\text{acac})(\text{CO})_2$, Sulfo-Xantphos, $N = 800$ rpm (pitched blade).

Surprisingly, the results in Figure 6 deviate from the expectations. The yields in the end of the reaction do not change significantly using weight concentrations of **M10U** between 5 and 25 wt%. Higher amounts lead to a limited reaction rate in the beginning of the reaction. In general, the regioselectivity of hydroformylation represented as l/b -ratio between the linear product **M11FU** and branched **MFU** (Scheme 2) were not influenced by the amount of substrate and stable values about 96/4 were reached in all cases. Side products formed by hydrogenation of the substrate **M10U** (<1%), by isomerization (max. 2%) or the hydrogenation of product **M11FU** (not detectable) were obtained in only very low amount.

For these experiments, the TOF after different reaction times (15, 20, and 30 min) and the STY after 1 hour of reaction time were calculated with respect to the initial substrate concentration in order to assess the productivity of the process (Figure 7).

Interestingly, between 10 and 20 wt% **M10U**, the TOFs at all three selected points of time remain stable, reaching highest values of ≈ 5000 h⁻¹ after 15 min, about 4100 h⁻¹ after 20 min, and around 3100 h⁻¹ after 30 min. Especially in concentration areas using <10 wt%, the highest TOFs were expected, since a more homogeneous system with lower phase limitations should occur. Instead, the mass transport limitations only lead to decreased reaction rates from an initial substrate loading of >20 wt%. Accordingly, a monophasic system is not necessary for an efficient reaction system. The respective STYs increase with higher substrate quantities, as expected. However, the gradient decreases using substrate concentrations between 18 and 20 wt%. For that reason, we defined a work zone between 10 and 20 wt% in which high STYs and high TOFs are combined to achieve a highly efficient reaction process. Notably, the system is not monophasic.

In the final analysis, we had to consider the catalyst leaching in the product phase of the process. If the TOF or STY are increased, but the catalyst leaching of the homogeneous transition metal catalyst is too high, no efficient process can be created. Thus, we checked the rhodium leaching into the organic product phase after reaction and phase separation. It was assumed that the product **M11FU** because of its higher polarity in comparison to **M10U** could influence the leaching significantly when higher

substrate concentrations are used in the beginning of the reaction. In comparison to the reported leaching values for a substrate concentration of 8 wt%, we used the 20 wt% **M10U** because of the high values of TOF and STY. Interestingly, in both cases 5 mol% of the Rhodium was leached after one batch experiment. Since the product has a higher polarity than the substrate, the catalyst leaching could not be reduced despite a lower 1-butanol content, which is acting as mediator in this system. In comparison to the assumption we made in 2016,^[7] the occurrence of a biphasic reaction mixture alone has no negative influence on the reaction performance. The composition of the phases in this particular case the organic phase influences the reaction performance more significantly.

4. Conclusions

Within this work we successfully improved the productivity of the aqueous biphasic hydroformylation of **M10U** using 1-butanol as green and non-toxic co-solvent. It was possible to more than double the STY of the reaction to >120 g L⁻¹h⁻¹ with high TOFs of 5000 h⁻¹. The selectivities of the reaction as well as the leaching of the catalyst were not influenced negatively by these changes in the system. To accomplish this, it was necessary to develop a system for the measurement of phase compositions under reaction conditions ($T = 140$ °C, $p = 20$ bar). This is the first time such a detailed phase investigation under reaction conditions has been presented in a four-dimensional tetrahedron diagram. Using the quaternary diagram it could be shown that for the aqueous hydroformylation of **M10U** not only the simple phase behavior (homogeneous or biphasic) is important, but particularly the composition of the phases influences the reaction behavior. Especially, the water content in the non-polar 1-butanol phase had to be investigated within the reaction progress. This information could also have a major influence on other carbonylation reactions in aqueous media or in purely organic systems, which we will investigate in our future research.

In order to maximize the efficiency of the process, other stirring or reactor concepts should be considered in future work, for example, a jetloop reactor could be used to overcome the solubility limitations between both liquid phases and thus even extend the specified work zone to higher substrate concentrations.

In summary, it was possible to improve the efficiency of the hydroformylation of **M10U** on the way to a sustainable conversion of fatty compounds in an aqueous biphasic reaction system.

Abbreviations

M10U, methyl 10 undecenoate; M11FU, methyl 11 formylundecanoate; STY, space time yield; TOF, turnover frequency

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

green solvents, homogeneous catalysis, hydroformylation, phase behavior, water

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