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**HYDROFORMYLATION OF 1-DODECENE IN  
MICROEMULSIONS: OPERATION AND VALIDATION OF  
LAB RESULTS IN A MINIPLANT**

**HYDROFORMYLOWANIE 1-DODEKANU W  
MIKROEMULSJACH: WARUNKI I MOŻLIWOŚCI  
STOSOWANIA WYNIKÓW BADAŃ LABORATORYJNYCH  
W MINI-INSTALACJI**

**Abstract**

A method of hydroformylation to convert long- chained olefins, using tunable microemulsion systems, tests were conducted on a mini-plant at the center InPROMPT/TRR 63. Surfactant allowing a quasi-homogeneous reaction of olefin in aqueous Rhodium catalyst solution.

*Keywords: hydroformylation, microemulsions, mini-plant, long term operation*

**Streszczenie**

W pracy przedstawiono metodę hydroformylowania w celu konwersji długołańcuchowych olefin, z wykorzystaniem przestrajalnych układów mikroemulsji, badania przeprowadzono na mini-instalacji w ośrodku InPROMPT/TRR 63. Stosowano surfaktant umożliwiający quasi-jednorodną reakcję olefin 1- dodecenu w wodnym roztworze katalizatora rodowego.

*słowa kluczowe: hydroformylowanie, mikroemulsje, mini-instalacja*

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## 1. Introduction and Motivation

Within the chemical industry, hydroformylation is one of the main reaction processes used in the formation of aldehydes, a major class of base chemicals used for polymer or solvent products, flavourings, and detergents [1]. The reaction itself was discovered in 1938 by Otto Roehlen [5]. Nowadays, the application is usually realised as a homogeneously catalysed process – this offers advantages with regard to high product selectivity and mild reaction conditions [2-4]. Here, olefins react with hydrogen and carbon monoxide in the presence of transition metal catalysts (cobalt, rhodium) towards the linear aldehyde and branched byproducts (Fig. 1).

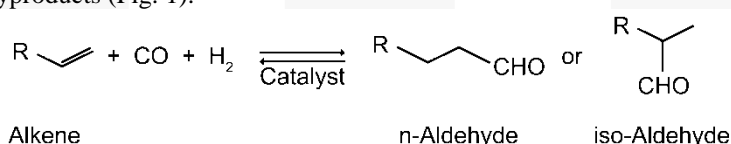


Fig. 1. Reaction equation of the hydroformylation reaction, R denotes an alkyl group [6,7]

Recently, industrial applications have focussed upon rhodium-based catalysts in which the modification of the metal complex with tailored ligands offers higher degrees of selectivity and activity [1, 8]. As a major drawback, the increasing costs of catalysts necessitate efficient catalyst recovery. Dissolving the catalyst in an aqueous phase and thus enabling a biphasic process concept tackles this obstacle. Highly active catalyst-ligand complexes maintain high reaction rates, while catalyst recovery is efficiently achieved through basic phase separation (see the Ruhrchemie-Rhône Poulenc Process, described in [3]). However, with the increasing chain length of the applied olefin, the miscibility of the oily reactant phase and the aqueous catalyst solution decreases. Additionally, the reaction rates decrease, as the interfacial area between the reactants and the catalyst is reduced. Therefore, state of the art biphasic process concepts are not applicable in case new feedstocks, such as bio-based long-chained olefins, are to be used.

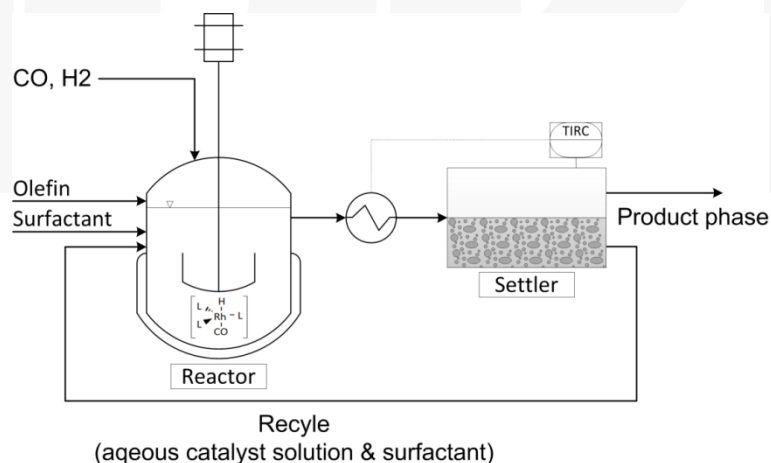


Fig. 2. General process concept for the hydroformylation in microemulsions, derived from [10]

In this contribution we examined a new process concept for the hydroformylation of long-chained olefins in microemulsion systems, which is currently investigated within the collaborative research centre InPROMPT / TRR 63 in Germany. Here, a surfactant is used to increase the miscibility between the nonpolar reactants and the aqueous catalyst phase by the formation of micelles. Again, a water-soluble ligand-modified rhodium catalyst is used to achieve good reaction performances, as described by Hamerla et al. in [9]. After the reaction step, the thermomorphic behaviour of micellar systems is exploited to separate and collect a pure product containing oily phase, while the catalyst and the surfactant are recycled back into the reactor [9, 10]. The general process concept is depicted in Fig. 2.

In the scope of this study, an integrated process development approach was carried out. This consisted of initial lab scale experiments to determine suitable reaction conditions, the phase separation behaviour, and the general component and fluid properties. In addition, a mini-plant was constructed to investigate the technical and economic feasibility.

Besides tackling the main challenges (homogenous reaction and stable phase separation) of this novel process concept, also the applicability of early stage laboratory scale results on the technical system are of interest. For that, preliminary lab results of the reaction performance and the phase separation are presented.

From this data, an operational set point for the mini-plant has been derived and operated during a 200 hour campaign. The resulting data is then discussed in comparison to previous findings to highlight additionally needed investigations on the laboratory scale.

## 2. Background Information

In this section, the constitution of surfactant containing multiphase systems and occurring phenomena are discussed. Moreover, information on the applied component system and the constructed mini-plant is given.

### 2.1. Microemulsion systems

Microemulsion systems are formed with the addition of a specific amount of surfactant to a mixture of polar and nonpolar components. In a thermodynamically favourable state, micelles are formed as microscopic scale structures trapping either oil (nonpolar component) or water (polar component). As a consequence, the interfacial area between oil and water is increased. On a larger scale, this multiphase system can be regarded as homogeneous, thus enabling efficient catalytic reactions.

The formation of micelles and additional excess phases of either oil or water is influenced by the concentrations of the components in the system and the temperature of the system. Here, different phase separation states are possible, which could be exploited in a phase separation step. For the description hereof, Kahlweit's fish diagram, a cross-section of Gibb's phase prism at a constant oil to water ratio of 1:1, is used.

Relating to Fig. 3, it is obvious that the phase distribution and the emulsion state depends on temperature and surfactant concentration. Regarding the process concept a pure oil phase (light grey in Fig. 3) containing the reaction product and a catalyst rich aqueous phase (dark in Fig. 3) for efficient catalyst recycling are desirable. Therefore, only the three phase (3) and the two-phase region (2) are feasible for the plant operation. As described by

Pogrzeba et al. [13], the phase separation dynamics show a distinct reduction of the time needed to achieve full separation in the three-phase region; therefore, an operational temperature interval is given for the settler operation.

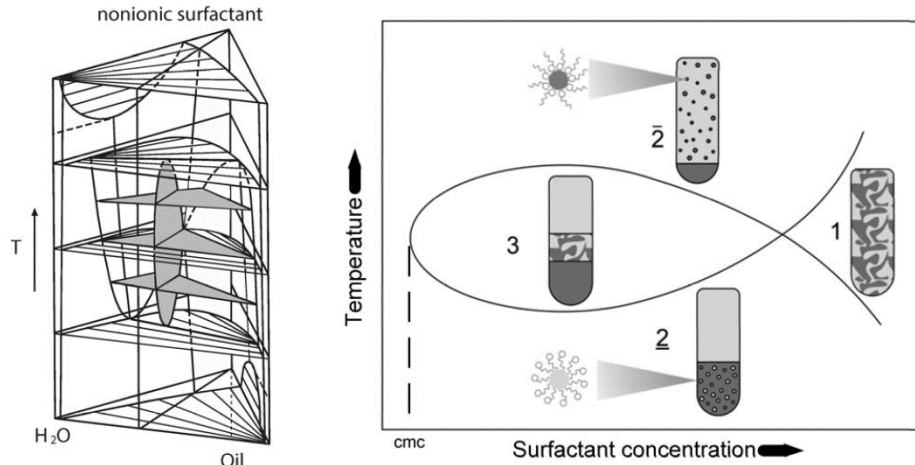


Fig. 3. Left: Temperature dependent Gibb's phase prism for an oil, water, and non-ionic surfactant mixture, taken from [11], Right: Kahlweit's fish [12]

## 2.2. Mini-plant Set-up

The constructed mini-plant at the Process Dynamics and Operations Group at Technische Universität Berlin consists of three main sections, as depicted in Fig. 4. The feed section contains tanks for the long-chained olefin, catalyst solution, surfactant, and synthesis gas containers. Piston pumps deliver a maximum alkene feed of 840g/h to the reaction section. Herein, a stirred tank reactor with 1.5 L total and 0.8 L liquid volume, gassing stirrer, and gauge glass, as well as the self-constructed settler are located. The latter is equipped with knitted wire internals to enhance phase separation and offers quick volume and functionality adaption through a modular design [14]. The heating of both units is regulated by thermostats. In the product section a part of the oil phase is purged from the process and stored for further processing.

The plant is fully automated by the process control system SIEMENS PCS7. Operators are supplied information from more than fifty sensors and may enforce operation trajectories through twenty actuators. Here, pumps for liquid flows, thermostats for temperature control and control valves for gas and product streams are selectable.

To provide additional information, especially for component concentrations inside the settler and the reactor two offline gas chromatographs are employed; additionally, an ICP-OES is used to determine the rhodium concentration in the product phase. For online-concentration measurements the Raman spectroscopy is carried out. Sampling positions and Raman probe locations are indicated in Fig. 4.

The plant was constructed to meet ATEX Explosion Zone 2 specifications.

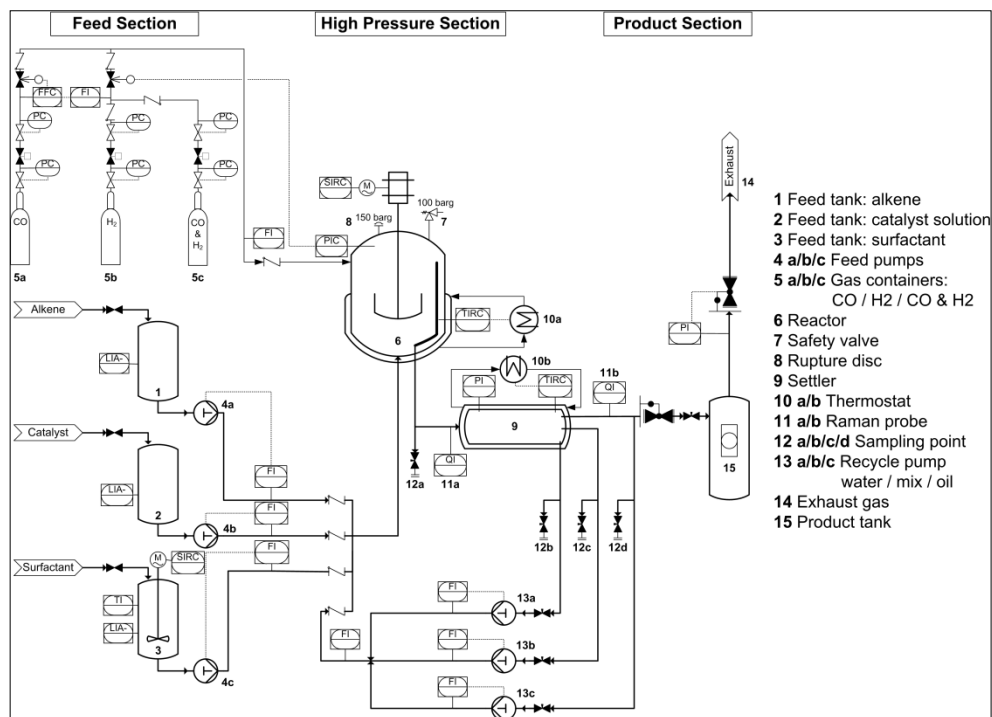


Fig. 4. Simplified P&ID of the mini-plant for the hydroformylation of long-chained olefins

### 2.3. Applied substances

For preliminary laboratory experiments and mini-plant operations, an exemplarily multiphase system was used in this study.

As a long-chained olefin 1-dodecene (C<sub>12</sub> alkene) was used. The synthesis gas was set to a composition of 1:1 vol.-% of CO:H<sub>2</sub> with a purity of 5.0. The applied catalyst complex was aggregated from a Rhodium precursor [Rh(acac)(CO)<sub>2</sub>] (CAS: 14874-82-9), sponsored by Umicore N.V., and the water soluble ligand SulfoXantPhos (sulfonated form of XantPhos, CAS: 161265-03-8, Molisa GmbH). To maintain a microemulsion system, the non-ionic surfactant Marlipal 24/70 (CAS: 68439-50-9), sponsored by Sasol Germany GmbH, was applied. Additionally, small amounts of Na<sub>2</sub>SO<sub>4</sub> (1 wt.-%) were used to enhance the phase separation.

Expected products according to the reaction equation in Fig. 1 are 1-tridecanal and its isomers. Additionally, isomers of 1-dodecene and dodecane as a hydrogenation product were expected as by-products.

### 3. Preliminary investigations

The proposed novel process concept poses two major challenges: maintaining a reaction step which meets the advantageous features of a homogenous catalysis; maintaining a fast and robust phase separation. Although the overall mixer-settler set-up is comparatively simple, these major aspects need to be faced in advance on a smaller scale.

#### 3.1. Reaction kinetics

Determining the reaction set point also requires detailed investigations on the influence of reactor operation parameters such as educt and surfactant concentration, synthesis gas pressure, and temperature.

For this purpose, various experiments were carried out to identify the overall aldehyde yield, reaction selectivity regarding all products, and the n/iso selectivity, marking the fraction of linear to branched aldehydes. As an example, the influence of pressure and temperature were examined in this study. Laboratory results are depicted in Table 1 and Fig. 5 and are subsequently discussed.

The concentrations of educt (Oil content) and surfactant for these experiments and accordingly, the mini-plant operation are fixed to

$$\text{Oil content: } \alpha = \frac{m_{\text{Oil}}}{m_{\text{Oil}} + m_{\text{Water}}} = 0.46 \quad (1)$$

$$\text{Surfactant content: } \gamma = \frac{m_{\text{Surfactant}}}{m_{\text{total}}} = 0.08 \quad (2)$$

using mass fractions of 298 g/g Rh(acac)(CO)<sub>2</sub> and 4530 g/g SulfoXantPhos(see [9, 15, 16]).

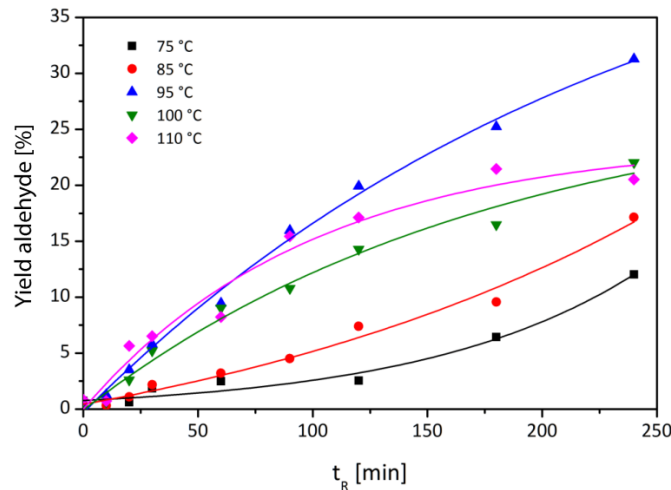


Fig. 5. Temperature influence on the yield of 1-tridecanal at 15bar and a reaction volume of 50mL, results taken from [16].

Table 1

**Experimental results of kinetic experiments at 95°C reaction temperature for the above given component composition after 240 min in a reaction volume of 50mL, results taken from [16]**

Reaction pressure	Aldehyde [wt-%]	Selectivity [%]	Selectivity [n/iso] aldehyde	TOF <sub>Ald</sub> [h <sup>-1</sup> ]
3 bar	15.9	83.1	97/3	94
15 bar	19.2	89.5	97/3	102
20 bar	20.4	87.5	99/1	106
30 bar	21.7	89.0	98/2	114
40 bar	15.7	82.6	97/3	77

Obviously, a reaction temperature of  $T_R = 95^\circ\text{C}$  is desirable, as the highest 1-tridecanal yields could be achieved. The decreasing aldehyde yield and changing curvature for other reaction temperatures is mainly due to changing catalyst selectivity and activity [15].

Regarding the pressure influence, there is a payoff between maximum yield and reaction selectivity. Given the results in Table 1  $p_R = 15$  bar is favoured given the high total selectivity, n/iso selectivity, and high aldehyde yield at a low pressure level.

At this point, operation conditions can be fixed for the reaction step of the mini-plant. Using the given temperature and pressure set point for a mini-plant, a product yield of roughly 30 % after 240 minutes could be expected in batch mode.

### 3.2. Phase separation

To maintain a stable phase separation in a microemulsion system, a specific optimal operation temperature needs to be applied, as described in section 2.1. A systematic approach for phase separation system investigations, model development and equipment design is given by Müller et al. [14]. Following this guideline, a systematic mapping of the three-phase region is achieved, which can be implemented into empirical correlations. Fig. 6 depicts a set of collated experimental data, whereas the upper and lower temperature limit of the desired three-phase region was tracked with respect to the surfactant concentration.

By also taking the product content  $X$  as 1-tridecanal yield and the oil content  $\alpha$  into account, parameterised empiric correlations could be introduced (see Eq. 3 and 4). Fitting the parameters  $P_i^{max/min}$  to experimental data enables the prediction of the settler temperature during the mini-plant operation based on the concentration data from GC samples at position 12a in Fig. 4.

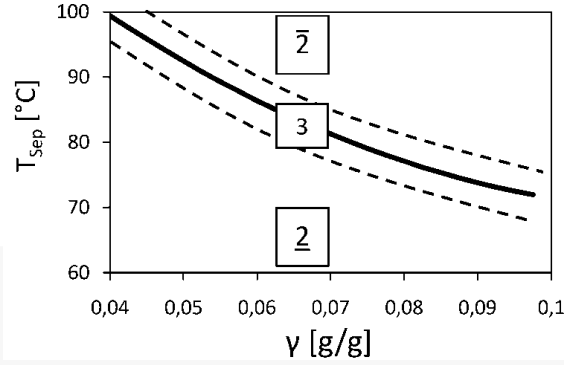


Fig. 6. Optimal separation temperature (solid line) and lower and upper limit (dashed lines) for maintaining the three-phase state, dependent on surfactant concentration  $\gamma$ . Oil content  $\alpha$  was kept constant at 0.5 g/g, aldehyde yield was set to  $X = 0\text{g/g}$ .

$$\begin{aligned}
 T_{max} = & P_1^{max} + P_2^{max} \cdot \alpha + P_3^{max} \cdot \gamma + P_4^{max} \cdot X \\
 & + P_5^{max} \cdot \alpha^2 + P_6^{max} \cdot \gamma^2 + P_7^{max} \cdot X^2 + P_8^{max} \cdot \alpha^2 \cdot \gamma^2 \\
 & + P_9^{max} \cdot \alpha \cdot \gamma + P_{10}^{max} \cdot \alpha \cdot X + P_{11}^{max} \cdot X \cdot \gamma
 \end{aligned} \quad (3)$$

$$\begin{aligned}
 T_{min} = & P_1^{min} + P_2^{min} \cdot \alpha + P_3^{min} \cdot \gamma + P_4^{min} \cdot X \\
 & + P_5^{min} \cdot \alpha^2 + P_6^{min} \cdot \gamma^2 + P_7^{min} \cdot X^2 + P_8^{min} \cdot \alpha^2 \cdot \gamma^2 \\
 & + P_9^{min} \cdot \alpha \cdot \gamma + P_{10}^{min} \cdot \alpha \cdot X + P_{11}^{min} \cdot X \cdot \gamma
 \end{aligned} \quad (4)$$

#### 4. Results and Discussion: Long-term mini-plant operation

Before detailing the measurement data from long-term mini-plant operations, the operational conditions and pursued schedules are outlined. Reaction data concerning product and by-product formation and an evaluation of the phase separation state and success is given and connected to the operation schedule.

##### 4.1. Process Conditions and Schedule

In accordance with section 3.1 the reaction pressure is set to 15 bar gauge pressure, the reaction temperature is kept constant at 368 K. Depending on the emulsion state, the stirring speed is varied between 700 and 1200 rpm. Gassing is always ensured in this range.

Over a 200-hour period of operation, several operational modes were applied to investigate the dynamic process behaviour in terms of reaction performance and phase separation robustness. For these modes, the feed rate for the continuous operation and the internal recycle streams for the surfactant and the catalyst solution were adapted. Table 2 presents the main operational parameters of the three investigated modes SP1-3.



Table 2

**Mini-plant operation schedule overview with operational conditions and modes for different set points (SP)**

	SP1	SP2	SP3
<b>Duration</b>	50 h	10 h	60 h
<b>Residence time reactor</b>	0.45 h	2.6 h	2.6 h
<b>Residence time settler</b>	0.55 h	3.2 h	3.2 h
<b>Alkene feed</b>	100 g/h	0 g/h	30 g/h
<b>Operation mode</b>	Continuous	Full recycle	Continuous

The reaction started once synthesis gas was introduced into the process. This is marked as operation hour 0 in the following figures. Following the start up a steady state was obtained and operated in a continuous plant operation mode (SP1). Afterwards, a new set point was approached with a full recycle mode in SP2, without any alkene feed. SP3 again marks continuous operation. In this mode, the feed rate and the internal recycle were reduced to increase the residence times in reactor and settler and achieve a higher aldehyde yield.

#### 4.2. Reaction yield and selectivity

In this section, the reaction performance within the mini-plant operation is shown regarding overall product yield and selectivity of the reaction. Depicted diagrams are sorted by the operation modes SP1-3, in terms of constant residence time and alkene feed rate.

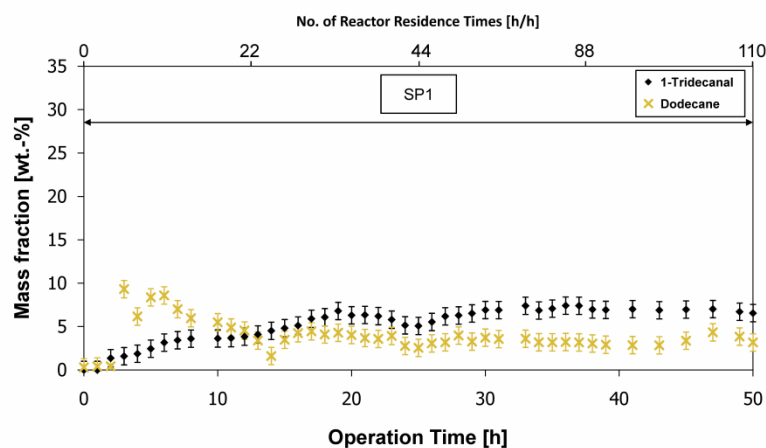


Fig. 7. Results for the main product (1-tridecanal) and one by-product (dodecane) as mass fractions in the reactor for mini-plant operation state SP1

With regard to product formation Fig. 7 and Fig. 8 confirm a significant formation of 1-tridecanal. A steady state concentration was achieved in all continuous operation modes. Due to the different residence times, a maximum mass fraction of roughly 7wt.-% for SP1 and 20wt.-% 1-tridecanal for SP3 are reasonable. In the qualitative comparison to the reaction performance in Fig. 5 a minor reduction in product yields is obvious, which is caused by the different geometric set up (scale-up) and non-ideal mixing in the reactor.

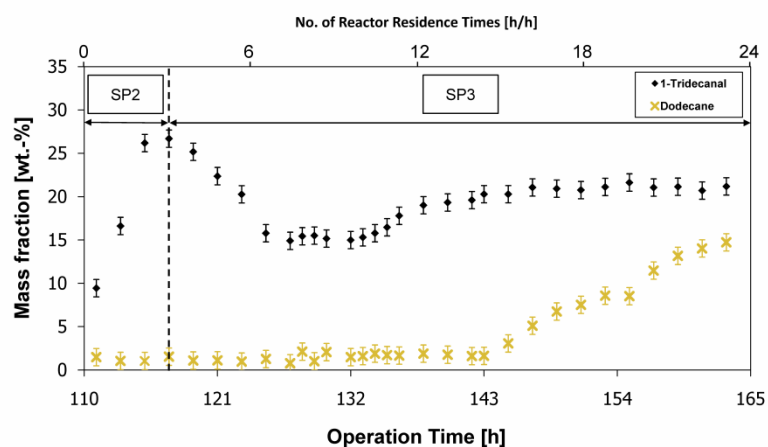


Fig. 8. Mass fractions of main the product (1-tridecanal) and one by-product (dodecane) in the reactor for mini-plant operation modes SP2 and SP3

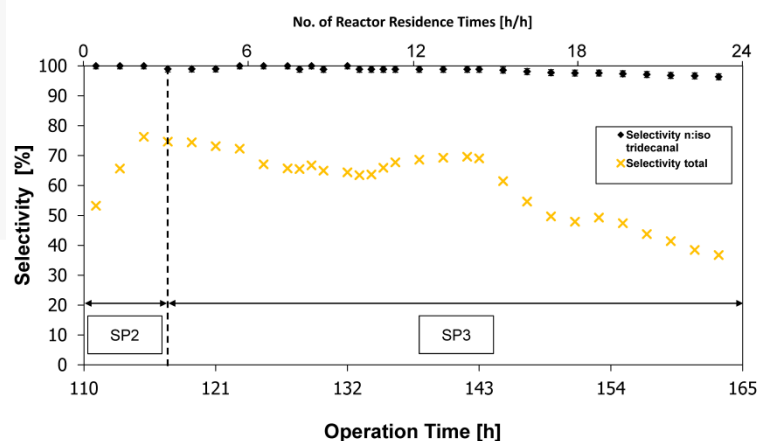


Fig. 9. Selectivity of the reaction expressed as the fraction of linear to branched aldehydes (n/iso) and the total selectivity towards 1-tridecanal. Data is given for the for mini-plant reactor at operation states SP2 and SP3

However, large quantities of the undesired by-product dodecane are also produced. This undesired hydrogenation is dominating for the start-up of the operation at operation time 0 to 10h and reoccurs in mode SP3 beginning with operation time 143 (see Fig. 8). This reaction performance is rather unexpected as only slightly higher hydrogenation was found by Pogrzeba et. al for higher reaction temperatures [16].

Taking a closer look at the reaction selectivities in Fig. 9 the finding described above is emphasised. Table 1 displays a total reaction selectivity of 89.5% for previous batch experiments. In the mini-plant operation, this remains unobtainable with isomerisations further lowering the selectivity. By contrast, the selectivity of linear to branched aldehydes meets prior findings and periodically tops the proposed value of 97% linear aldehyde.

Interestingly, the operational mode has a strong influence on reaction performance and selectivity. This is perfectly clear for the effect of residence time on the expected yield. However, the strong affection on the by-product formation is rather unexpected (compare total selectivity for SP2 and SP3). Given the fact, that the active catalyst species is formed via the addition of a carbon monoxide molecule (see [9]), it is possible that a temporary transformation of the catalyst species occurs within the separation step and the internal recycle which leads to a different reaction performance once the recycled catalyst re-enters the reactor. Consequently, as a feedback to laboratory experiments, operation modes and catalyst conditions need to be investigated regarding by-product formation in order to identify infeasible operation conditions for the mini-plant or conceptual or constructional requirements for improvement.

#### 4.3. Phase separation performance

The phase separation performance is evaluated by the purity of the gathered oily top phase of the settler. For this, sample point 12d (Fig. 4) is used to analyse the total amount of oily components (n/iso-dodecene, dodecane, n/iso-tridecanal) using gas chromatography. The results for operation mode SP2 and SP3 are given in Fig. 10.

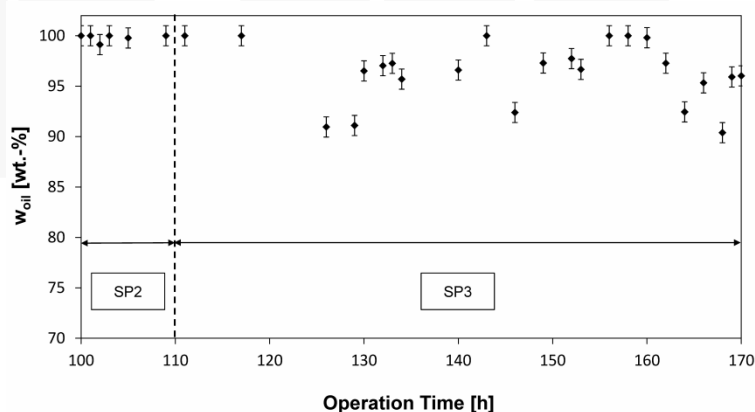


Fig. 10. Phase separation quality embodied by the total amount of oily components in the oil phase of the settler. Data given for operation state SP2 and SP3

In general, the phase separation was successfully achieved for both operation set points as the mass fraction of oily components is permanently higher than 90 wt.%. Periods of perfect phase separation with 100 wt.% oil component mass fraction are achieved for SP2 and around 160 hours of operation. However, reduced oil phase purity is mainly due to the dissolution of larger amounts of surfactant and consequently also traces of the catalyst solution. The corresponding phase separation state is the two upper region, where for a higher temperature, the solubility of surfactant in the oil phase increases [13]. In case of SP3 in Fig. 10, the three-phase region could not efficiently be tracked and operated throughout plant operation – this might be due to concentration shifts caused by the reaction and applied recycle ratios between the recycle pumps 13a-c in Fig. 4. Moreover, the applied model prediction is partly invalid, as the large byproduct formation is not taken into account.

Referring to section 4.2, a possible influence of the settler operation on the catalyst needs to be investigated in terms of the prevention of by-product formation. Here, the reaction performance under varied settler residence times will be investigated. Additionally of interest are the component distribution within the settler phases and possible accumulation of the catalyst and the surfactant in this unit.

## 5. Conclusions and Outlook

In this contribution, a proof of concept for a novel process for the hydroformylation of long-chained olefins is presented with experimental data of a long-term operation of a mini-plant. The applicability of preliminary lab scale results on the plant operation are discussed and future demand for investigations is highlighted.

In general, the main aspects of the developed process concept, a quasi-homogenously catalysed reaction, as well as a stable phase separation could be proven for a long-term operation of a mini-plant. However, some challenges arise from the conducted plant experiments which show a mismatch with preliminary lab experiments. Here, severe by-product formation is present, which drastically reduces the reaction selectivity. This contrasts the economically beneficial homogenous catalysis. Transformations of the active catalyst species are supposed to account for this undesired effect. Additional kinetic experiments and constructional modifications of the mini-plant will be carried out to overcome this issue. The concurrent conduction of lab scale and mini-plant scale experiments show a possible reduction of process development time, as arising obstacles can be tackled at an early stage. Concerning the phase separation, the increased byproduct formation leads to a certain model-plant mismatch. This makes the controllability of the phase separation tedious and shows the complexity of this system. Early stage identification on the influential parameters of the phase separation in a technical system offers a more systematic approach to determining phase separation behaviour.

For further investigations, the described challenges in reaction and separation procedures are to be analysed in the lab to provide updated information for future mini-plant operations. Additionally, advanced process control strategies are to be implemented to enhance controllability and observability of the mini-plant. Advanced (online) analytics,

such as Raman spectroscopy, are to be tested for fast and reliable concentration identification for in situ tracking reaction and phase separation.

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