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DEVELOPMENT OF SEPARATION METHODS FOR A CONTINUOUS HYDROFORMYLATION PROCESS IN A MINI-PLANT SCALE

OPRACOWYWANIE METOD ODDZIELANIA DLA CIĄGŁEGO PROCESU HYDROFORMYLACJI W SKALI MINI-APARATURY

Abstract

In this contribution a novel process concept for the continuous hydroformylation of long chained alkenes to aldehydes in micro emulsion mixtures with the aid of a hydrophilic rhodium–ligand–complex catalyst is discussed. The challenging aspects with regards to the technical and economic feasibility of the process concept are the separation steps to recycle the expensive catalyst. To investigate and optimize the described process concept, a mini-plant is built at the Berlin Institute of Technology. Due to the lack of thermodynamic data, the design of the crucial separation steps, decanter and micellar enhanced ultrafiltration (MEUF), strongly depend on experimental data. Therefore, “small scale” experiments are designed with adequate similarity to the actual units in the plant. The information gained therein leads to improvements for the separation steps and helps to determine operating parameters for the mini-plant.

Keywords: hydroformylation, phase separation, micellar enhanced ultrafiltration

Streszczenie

W artykule niniejszym omówiona zostaje nowatorska koncepcja procesowa dotycząca ciągłej hydroformylacji alkenów łańcuchowych do aldehydów w mieszaninach mikroemulsyjnych za pomocą wodochłonnego katalizatora typu rod–ligand. Wyzwanie w odniesieniu do technicznej i ekonomicznej wykonalności koncepcji procesowej stanowią stopnie oddzielania prowadzące do odzyskania kosztownego katalizatora. W Berlińskim Instytucie Technologicznym zbudowano mini-aparaturę służącą do badania i optyimizowania opisanej koncepcji procesowej. Ze względu na brak danych termodynamicznych projekt najważniejszych etapów oddzielania – wzmoczonej ultrafiltracji dekanterowej i micelarnej (MEUF) – zależy w znacznym stopniu od danych doświadczalnych. Dlatego też eksperymenty prowadzone na „niedużą skalę” przygotowywane są z zachowaniem właściwego podobieństwa do rzeczywistych elementów aparatury. Zebrane informacje prowadzą do ulepszeń w zakresie stopni oddzielania, pomagając określać operacyjne parametry mini-aparatury.

Słowa kluczowe: hydroformylacja, oddzielanie fazowe, wzmoczona ultrafiltracja micelarna

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1. Motivation and introduction

To promote research in the field of substitutable base chemicals and multiphase systems, the German Research Foundation (Deutsche Forschungsgemeinschaft) conceded the Trans-regio 63 collaborative research project in 2009 called “Integrated chemical processes in liquid multiphase systems” (InPROMPT). A part of this project is the investigation of a new process concept for the hydroformylation of long-chain olefins in micro emulsion systems and the subsequent development of separation steps.

The reaction known as hydroformylation is the coincident addition of a hydrogen and a carbon monoxide molecule to a double bond of an alkene in order to produce a linear or branched aldehyde. Fig. 1 displays the general reaction equation.

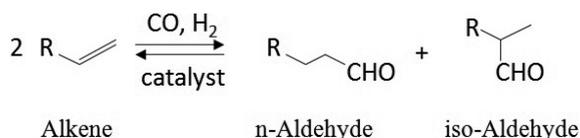


Fig. 1. General hydroformylation reaction equation [2]

Rys. 1. Ogólne równanie reakcji hydroformylacji [2]

In industry, hydroformylation is an important application in the field of homogeneous catalysis and has been established as a standard process for the production of short-chained aldehydes from short-chained alkenes. The resulting aldehydes are used as intermediate base chemicals to produce further products such as alcohols, aromatic compounds, or plastics. Higher alkenes (longer than C12), on the other hand, have not yet been established in industry, mainly due to challenges regarding their hydrophobic character. The longer the carbon chain of the alkene, the less soluble it is in an aqueous phase. Nevertheless, to enable a reaction with long chained alkenes under mild reaction conditions, a water soluble, hydrophilic rhodium-ligand-complex catalyst can be utilized. One possibility to counter the hydrophobic character of the alkene is by applying a non-ionic surfactant. The creation of surfactant micelles has widely been proposed to “solubilize” the reactants above the critical micelle concentration (cmc), to enable the reaction as well as to remove the organic solutes from water [4]. Given the large micelle size, small molecules like organic compounds containing rhodium and tailor-made ligand can be held back by ultrafiltration (UF) membranes.

The afore-mentioned multiphase system offers the possibility to separate the valuable rhodium catalyst comparatively easy from the organic product [1]. In the following the applied chemicals are presented and the novel process concept is discussed.

2. Investigated chemicals

The main chemicals in this study are the educts dodecen and syngas (H₂ & CO), the product dodecanal, the surfactant Marlophen NP9, and the catalyst complex. Of particular interest are the later two, which are described in greater detail.

The non-ionic surfactant used in this study is Marlophen NP9 manufactured by Sasol Germany GmbH. Marlophen NP9 ($\rho_{\text{Surfactant}} = 1.07 \text{ kg/l}$) is an ethoxylated nonyl-phenol alcohol with a chemical structure, as shown in Fig. 2. Its molecules are polydisperse with an average ethoxylation degree of 9. Therefore, this technical surfactant is very soluble in water at room temperature.

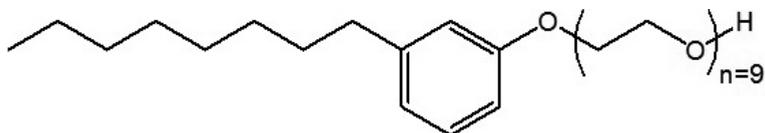


Fig. 2. Chemical structure of Marlophen NP9

Rys. 2. Struktura chemiczna Marlophenu NP9

The catalyst precursor $\text{Rhacac}(\text{CO})_2$ is purchased from Strem Chemicals Inc. Germany and the ligand Sulfo-Xantphos, containing phosphor, is obtained from Molisa GmbH Magdeburg. The educts 1-dodecene and dodecanal are purchased from Merck Darmstadt KGaA in synthesis quality. Their densities are $\rho_{\text{Alkene}} = 0.76 \text{ kg/l}$ and $\rho_{\text{Aldehyde}} = 0.84 \text{ kg/l}$ respectively.

3. The process concept and the challenge

To investigate the described reaction and test the applicability, a mini-plant is built at the Berlin Institute of Technology. The goal is to create a continuous process, in which the C12 alkene is turned into an aldehyde with the aid of the hydrophilic rhodium-ligand-complex catalyst. Fig. 3 shows the novel process concept for the hydroformylation of long chain olefins in a micellar multiphase system.

In the continuously stirred tank reactor, the reagents consisting of alkene, surfactant, and water with dissolved catalyst are mixed. Through the use of the non-ionic surfactant a micro emulsion system is formed and the aqueous phase containing the dissolved catalyst is brought into contact with the organic reagent phase. The hydroformylation reaction

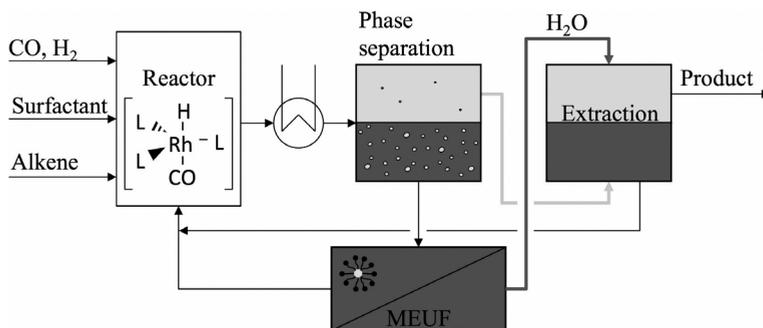


Fig. 3 A novel process concept for the hydroformylation of long chain olefins

Rys. 3. Nowatorska koncepcja procesowa hydroformylacji olefin łańcuchowych

is then initiated by injecting syngas (H_2 & CO) into the micro emulsion system, thus producing the desired aldehyde.

To ensure the economic feasibility of the overall process concept, several separation steps need to be implemented to recycle the valuable rhodium catalyst. Thus, after the reaction, the reactants are fed into a decanter. Due to the phase separation into an aqueous (catalyst-rich), an aqueous surfactant (catalyst-rich), and an organic (product-rich) phase, the greater part of the rhodium catalyst can be separated and recycled. The fact that part of the catalyst is dissolved in the surfactant within the product phase leads to the necessity of a secondary separation step. Therefore, to further reduce catalyst loss, the combination of a micellar enhanced ultrafiltration (MEUF) and an extraction step is implemented.

The almost catalyst free water is used as an entrainer for the extraction step. In consequence, the remaining hydrophilic catalyst in the product phase is absorbed by the water and can thus be recycled back into the reactor.

A systematic approach is necessary to effectively design, combine, and investigate the feasible operating conditions of these separation steps. In the following, two experimental set-ups of the separation steps are investigated. Preliminary results are presented in this work.

4. Application of a systematic approach for equipment design and process operation

Given the lack of thermodynamic data for micro emulsion mixtures, the design of the crucial separation steps strongly depends on experimental results. To tackle this challenge, an approach has been developed to identify relevant design parameters and operating conditions for the mini-plant. The approach, presented in [3], involves the analysis of the general phase separation behavior, the investigation of the phase separation dynamics, and in the last step the set-up of “small scale” experiments for specific process units. In this contribution the latter is discussed. In order to achieve an adequate similarity with the actual units in the mini-plant, the experiments are separately carried out as continuous processes. Therefore, two experimental set-ups are realized: the decanter and the MEUF.

4.1. Continuous phase separation in the decanter

The goal is to test the applicability and analyze the continuous phase separation within the decanter. The quality of the phase separation strongly depends on several variables. Among these are the concentrations of surfactant (γ , eq. 1), water (α , eq. 2), and product (λ , eq. 3). Three symbols are introduced regarding the composition of the investigated mixture.

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{alkene}} + m_{\text{water}} + m_{\text{surfactant}}} \quad (1)$$

$$\alpha = \frac{m_{\text{alkene}}}{m_{\text{alkene}} + m_{\text{water}}} \quad (2)$$

$$\lambda = \frac{m_{\text{aldehyde}}}{m_{\text{aldehyde}} + m_{\text{alkene}}} \quad (3)$$

It is assumed that the reaction has already occurred and the reactants are led to the separation unit. Therefore, the examined system is free of carbon monoxide or hydrogen. According to preliminary investigations, a turnover of about 50% for a mixture consisting of $\gamma = 0.08$ and $\alpha = 0.5$ has been reached. In other words, for further investigations a micro emulsion system composed of $\gamma = 0.08$, $\alpha = 0.5$, and $\lambda = 0.5$ is prepared and consequently, an experimental set-up for the phase separation is designed.

Figure 4 shows the experimental set-up for the continuous phase separation in the decanter. Beginning on the right hand side in the storage container, the composition of the micro emulsion system mentioned above is mixed and heated. A pump feeds the micro emulsion system into a heated glass decanter, where the heavier phases, the catalyst rich aqueous and the surfactant rich middle phase, are discharged together. The lighter organic phase on the other hand is removed separately. Investigations presented in [3] show 71°C as an adequate operating temperature for phase separation without catalyst. For the next investigations a catalyst concentration of 0,46 wt% is added. Due to its influence on the thermodynamics of the system, the temperature of interest increases to 83°C. Of particular interest for the following separation step are the concentrations of alkenes, aldehydes, and surfactant in the two product containers.

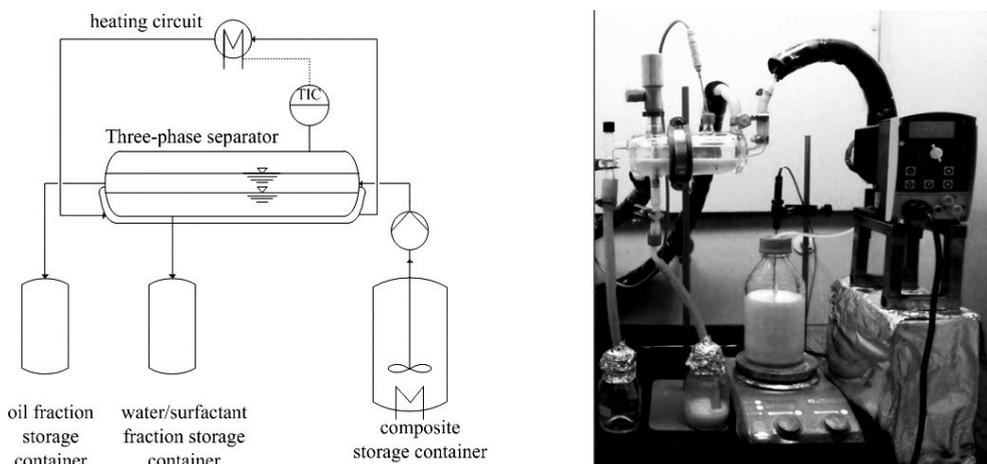


Fig. 4. PFD diagram of the experimental set-up of the decanter (left), picture of the set-up of the continuous separation of a three phase micellar multiphase system (right)

Rys. 4. (L) Diagram PFD doświadczalnego układu dekantera, (P) obraz układu ciągłego oddzielania w trzyfazowym systemie micelarnym

Table 1 shows the experimental results of the concentrations (in mass percentage) of the reaction participants before (original mixture) and after the phase separation in the two product containers. These results are obtained using a Gas Chromatograph (GC) and a High Performance Liquid Chromatograph (HPLC).

Experimental results: concentrations after phase separation in the decanter; *calculated

Container	w_{Alkene}	w_{Aldehyde}	w_{NP9}	w_{Water}	w_{Ligand}	V	ρ
	[wt%]	[wt%]	[wt%]	[wt%]	[wt%]	[ml]	[kg/l]
Original Mixture	22.90	22.90	7.93	45.81	0.46	770	0.90
Oil fraction	39.34	39.80	3.10	17.75*	0.01	30	0.83
Surfactant fraction	15.04	9.62	15.13	59.98*	0.23	350	0.93

Based on these results the following conclusions can be drawn: The continuous phase separation for the analyzed micro emulsion system is applicable for the mini-plant, the aqueous-surfactant phase contains a low amount of product, and the bulk of the ligand stays in the surfactant phase. Furthermore, optimizations regarding the design of the decanter for the mini-plant are taken into consideration, inter alia a height-modifiable product drain for the heavier phases and an inspection hole to determine a possible shift in height of the phases due to different velocities of the liquid streams.

At this point it has to be mentioned that the value for the concentration of the ligand does not directly represent the concentration of rhodium or of the catalyst complex. The ligand value is used due to its convenient identifiability in the HPLC. The ligand itself undergoes a reaction with the rhodium and thus the catalyst complex is formed. In the HPLC the retention time of the catalyst complex differs from that of the ligand. This is a partial explanation of why neither oil nor surfactant fraction have a higher ligand concentration than the original mixture. Furthermore, it is obvious that the mass balance is violated. The reasons for this deviation are that a certain amount of the original mixture remained in the composite storage container and in the decanter after the experiment.

4.2. Continuous separation in the meuf

Consequently, with the information gained from the decanter experiment, operating parameters for the MEUF are determined. The ultrafiltration experiments were carried out using a batch stirred cell obtained from Schleicher & Schuell (SC 75) with a volume capacity of 75 ml. This test cell is made of stainless steel and borosilicate glass. The set-up is shown schematically in Fig. 5.

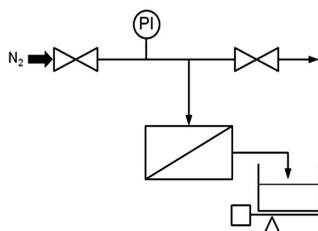


Fig. 5. Flow-diagram for dead-end ultrafiltration experiments

Rys. 5. Blokowy schemat działania eksperymentalnej ultrafiltracji zamkniętej

To analyze the separation performance, asymmetric hydrophilic flat membranes made of polyether sulphone (PES) with a nominal molecular weight cut-off (MWCO) of 5000 u, manufactured by Microdyn-Nadir GmbH, are used. The effective membrane area (A_{membrane}) is $1.39 \cdot 10^{-3} \text{ m}^2$. For the experiment, the membrane is soaked in distilled water overnight to clean the membrane surface and saturate the pores before it is inserted into the test cell. The speed of the magnetic stirrer in the test cell is then set to 200 min^{-1} . All experiments are carried out at 20°C with a nitrogen pressure (Δp) of 3 bar.

The ultrafiltration consists of two steps. Firstly, the pre-filtration with distilled water is carried out until steady state conditions in the membrane are reached. For the ultrafiltration with rhodium catalyst solubilized in the micellar solution the feed solution is prepared as follows: Rhacac(CO)₂ and Sulfo-Xantphos (ligand) are dissolved in water with a molar ratio of catalyst to ligand of 1:5 and then added to water containing the NP9. The feed solution has a similar composition as the lower aqueous phase leaving the decanter.

During the filtration, the permeate sample is collected until the end of the filtration experiment. The collected mass of permeate (m_p) is measured over the time (Δt) and then analyzed regarding its concentration of rhodium ($c_{\text{Rh},p}$) and phosphor ($c_{p,p}$) by an inductively coupled plasma atomic emission spectroscopy (ICP-AES). Furthermore, the surfactant concentration is determined by UV-vis-spectroscopy at 277 nm.

Using the following equations the permeability P and the rejection of rhodium (R_{Rh}), phosphor (R_p) and also NP9 (R_s) are calculated for the given concentrations in the feed solution and in the permeate phase:

$$P = \frac{m_p}{A_{\text{membrane}} \cdot \Delta t \cdot \Delta p \cdot \rho} \quad (4)$$

$$R_{\text{Rh}} = \left(1 - \frac{c_{\text{Rh,Permeate}}}{c_{\text{Rh,Feed}}} \right) \quad (5)$$

$$R_p = \left(1 - \frac{c_{p,Permeate}}{c_{p,Feed}} \right) \quad (6)$$

$$R_s = \left(1 - \frac{c_{s,Permeate}}{c_{s,Feed}} \right) \quad (7)$$

The steady state fluxes are achieved within a few minutes, so that the permeate flux at that time is valid for the steady state ultrafiltration process. The permeability of the micellar aqueous solution through the MEUF is found to be much lower than that of pure water, which can be seen in Fig. 6. Moreover, the membrane PES5 reject 91% rhodium, 89% phosphor (i.e. Sulfo-Xantphos), and 97% surfactant NP9. For future analyses, important parameters like transmembrane pressure or temperature will be investigated to determine the effectivity of the membrane.

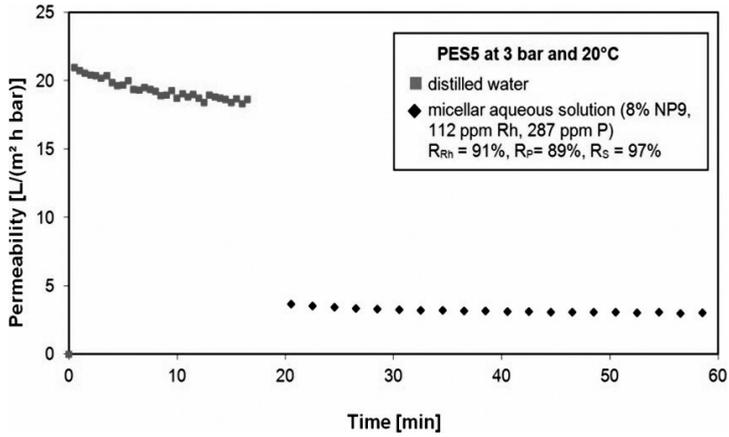


Fig. 6. Separation performance of the membrane polyether sulfone with MWCO 5×10^3 u

Rys. 6. Szybkość oddzielania sulfonu polieteru membranowego przy MWCO 5×10^3 u

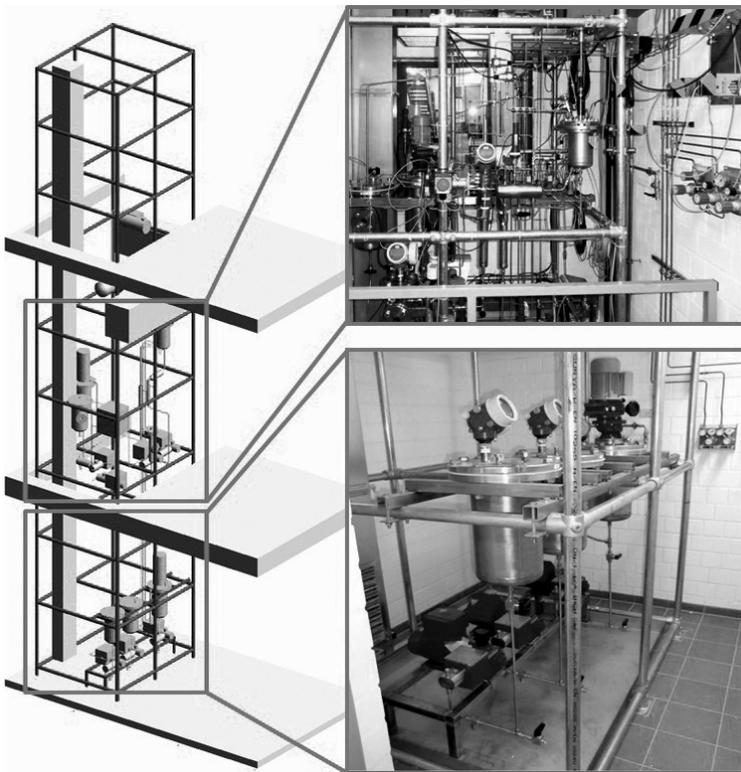


Fig. 7. Mini-plant at the Chair of Process Dynamics and Operation

Rys. 7. Mini-aparatura w Katedrze Dynamiki i Działania Procesowego

4.3. Implementation in the mini-plant

With the gained information, the mini-plant at the Chair for Process Dynamics and Operation at the Berlin Institute of Technology is designed and modified. Fig. 7 shows a 3D image and two pictures of the actual plant. In the top photo the reactor and the decanter are displayed. The MEUF is yet to be implemented. The bottom photo shows the three reagent containers containing the alkene, the surfactant, and the catalyst.

5. Conclusion

Recycling the valuable rhodium catalyst is the challenging aspect of the hydroformylation of long chain alkenes with regards to the technical and economic feasibility. Next to proving the general applicability of the combination of decanter and MEUF, the experimental set-ups help to determine feasible conditions for an integration of both steps into the whole hydroformylation process. The preliminary results show that a high recovery of the rhodium complex could be reached at the investigated conditions.

Symbols

α	–	olefin–water–proportion [–]
γ	–	surfactant–water–proportion [–]
λ	–	aldehyde–olefin–proportion [–]
ρ	–	density [kg/l]
A	–	area [m ²]
c	–	concentration [g/l]
m	–	mass [kg]
p	–	pressure [bar]
P	–	permeability [L/(m ² h bar)]
t	–	time [s]
R	–	rejection [–]
V	–	volume [l]

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