



Highly integrated reactor–separator systems for the recycling of homogeneous catalysts



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ABSTRACT

Homogeneous transition metal catalysts allow highly selective conversion of reactants at mild reaction conditions. Main drawback of this catalytic method is a difficult recovery of the catalyst, dissolved in the reaction phase. One recovery method is the decrease of the temperature in the reaction phase in order to generate two phases in which the product and the catalyst show different solubilities. This is known as thermomorphic multicomponent solvent (TMS) system. Another method to separate the catalyst directly from the reaction phase is the application of the organic solvent nanofiltration (OSN). For both recovery methods proper operating windows of reaction and separation are necessary to reach a high selectivity and yield in the reaction on one hand and prevent catalyst loss through efficient separation on the other. Only the combination of suitable solvents, reaction conditions and separation methods guarantee a successful performance of the whole catalytic system.

In this work, the method for investigating the interactions between reaction and separation dependent on the different selected unit operations are developed. The application of the TMS system DMF/*n*-decane and the catalyst separation within the hydroformylation reaction is discussed as a case study of industrial interest.

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1. Introduction

Sustainability is one of the great challenges chemists and chemical engineers have to face. Greenhouse gas emission, waste treatment and the exploitation of fossil feedstock need to be minimized to act responsible for a global future. Engineering science can contribute to these goals with the development of efficient processes. The 12 principles of green engineering are an orientation for the sustainable design and improvement of chemical production processes in respect to environmental, economic and social factors [1]. Efficient and selective catalysis is a key technology in the chemical industry, more than 80% of the chemical processes include at least one catalyzed reaction [2]. The application of homogeneous transition metal catalysts offers a highly selective conversion of reactants using mild reaction conditions. Adapting a homogeneous catalyst to a specific reaction

opens up new reaction pathways for the chemical industry. Through this renewable resources are accessible in efficient reactions [3–5].

Main challenge in the field of homogeneous transition metal catalysis is the recovery of the dissolved catalysts, which determines economic feasibility of production processes [2]. Several approaches turned out to be more or less suitable for the recovery of transition metal catalysts, thermomorphic multicomponent solvent (TMS) systems as well as organic solvent nanofiltration (OSN) [6–10]. Apart from these two techniques other recovery methods like adsorption, precipitation, distillation and liquid/liquid-extraction are available [2,11]. In special the techniques using two liquid phases have several occurrences, e.g. systems containing ionic liquids [12], micellar systems [13] and TMS systems [11]. Unfortunately no published method on catalyst recovery turned out to be economically feasible for industrial application.

Process intensification (PI) is a design tool aiming at the development of more efficient processes [14]. PI is targeted to the enhancement of the involved limiting phenomena which

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Nomenclature

Abbreviation

| | |
|---------|--|
| b | Branched |
| CSTR | Continuously stirred tank reactor |
| DMF | <i>N,N</i> -dimethylformamide |
| F | Feed |
| ICP-OES | Inductively coupled plasma optical emission spectrometry |
| l | Linear |
| LLB | Liquid/liquid biphasic |
| MWCO | Molecular weight cut off |
| OSN | Organic solvent nanofiltration |
| P | Permeate |
| PI | Process intensification |
| TMS | Thermomorphic multicomponent solvent |

Symbols

| | |
|-----------|----------------------------------|
| A | Membrane area [cm ²] |
| j | Flux [L/m ² h] |
| m | Mass [g] |
| \dot{m} | Mass flow [kg/h] |
| n | Amount of quantity [mol] |
| p | Pressure [bar] |
| R | Rejection [%] |
| Re | Reynolds number [–] |
| T | Temperature [°C] |
| \dot{V} | Volume flow [m ³ /h] |
| w | Weight fraction [–] |

determine the overall performance of the process [15]. PI can be achieved at different scales which are the (i) fundamental and molecular scale; (ii) phase and transport scale; (iii) equipment and operation; and (iv) process and plant scale [15,16].

One of the approaches of PI at the process plant level is the external integration of at least two different unit operations to solve one common separation task, also known as hybrid separations [17]. The idea behind this integration is to generate synergy effects between unit operations and allow each unit operation to only operate in the operating and separation window in which it outperforms all others [18]. Hybrid separation processes are usually applied for the product purification at the end of the downstream process. Many approaches for the combination of distillation and crystallization are presented in literature. A combination of two separation units is an interesting option for the recycling of homogeneous catalysts, whereas the selection of solvents to significantly improve the separation efficiency is a very important issue.

Hydroformylation is one of the most important industrial applications of homogeneous catalysts for the production of short chain aldehydes, in which many different catalyst separation techniques in processes are suitable [19]. In this paper we discuss the combination of novel techniques for an efficient catalyst recovery in the hydroformylation of long chain olefins, i.e. of 1-dodecene. Typical hydroformylation catalysts are based on cobalt or rhodium. The higher activity of rhodium catalysts leads to mild reaction conditions and savings in energy costs. Due to high rhodium prices highly efficient catalyst recovery is necessary for economical production processes.

2. Separation systems for the continuous recovery of homogeneous metal catalysts

The homogeneous metal catalyst is often not a single molecule but a combination of a precursor and a ligand. Since both are important for reactivity and selectivity both must be recycled back to the reactor (Fig. 1).

Reaction system and separation requirements are characterized by the following specifications:

- Highly diluted systems (concentration of catalysts in mixture <<1 wt.%).
- High recovery of 99.9 wt.%.
- Catalyst is often component of highest molecular weight.
- Catalyst is often component with the lowest vapour pressure.
- Fragile coordination of the ligand to the metal center.
- At atmospheric pressure and moderate temperature the catalyst is solid.

Several separation techniques, based on different separation principles, are suitable for the catalyst recovery (Table 1). The separation efficiency depends on the properties of the product and the properties of the catalyst itself. However, even though the separation principle is promising for catalyst separation, also the phase in which the catalysts will be recovered as well as the operating mode of the separation unit (batch/ semi-batch/ continuous) is important for the subsequent integration of the recovery system. Therefore, the following requirements for a promising integration are summarized: The catalyst containing outlet phase should be liquid while the operational mode of the separation technique should be continuous. Following separation techniques fulfill both criteria: distillation, extraction, organic solvent nanofiltration as well as pervaporation. Since not all separation units may be suitable to recover the metal catalysts in the whole concentration region an integration of different separation techniques may be necessary (Section 2.2).

2.1. Separation techniques for continuous recovery and recycle of metal catalysts

2.1.1. Distillation

Distillation is the most important technique for the separation of liquid mixtures into its components [20,21]. Driving force of this separation technique are different volatilities of involved species. The more volatile component is enriched in the vapor phase and the less volatile component is enriched in the liquid phase. In a continuous distillation process the feed is separated into distillate and bottoms stream. In membrane distillation the membrane acts as a porous barrier providing the interfacial area between gas and liquid. The separation is still based on the different volatilities as in distillation; however, through the use of phobic materials towards the liquid solvent, the membrane hinders the liquid to enter the membrane. Advantages towards the use of distillation systems are the provision of high specific surface area, the potential use of milder conditions at lower pressures while disadvantages are large pressure drops as well as the identification of suitable and stable membrane materials as well as fouling.

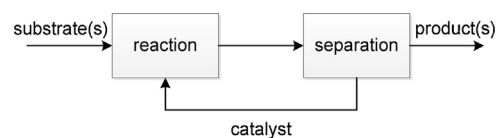


Fig. 1. Block diagram of an optimal homogeneous catalyst recovery.

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