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Investigations on the behaviour of ceramic micro- and mesoporous membranes at hydrothermal conditions

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ABSTRACT

Hydrothermal processes can be used for extraction, reaction or analytical purposes. In combination with membrane technologies, energy consumption of such processes can be reduced considerably in terms of a nearly isobaric and isothermal regeneration of the hot and pressurized fluid. However, investigations on the performance of this hybrid process concept require experimental data on the use of membrane processes under hydrothermal conditions.

Consequently, the main objective of this work is the determination of characteristics such as permeation and filtration behaviour for several ceramic, asymmetric micro- and mesoporous membranes (TiO_2/ZrO_2) with average pore diameters from 0.9 to 3.0 nm at hydrothermal conditions. Performed studies are comprised of experimental investigation of pure water permeance and organic model substance retention in dependence on feed pressure (200–375 bar), feed temperature (40–140 °C) and transmembrane pressure (5–25 bar). All investigations were carried out in a newly developed stainless steel membrane separation apparatus.

Due to seriously corrosive hydrothermal conditions, a degradation of the glass coated membrane end seals and the membrane separation layer at temperatures above 140 °C has been observed. Subsequently, an inorganic and more stable end seal has been designed. Moreover, this work gives a first promising approach for stabilizing the membrane separation layer by Y_2O_3 modification. As a result, pure water permeance has been found to be independent of feed and transmembrane pressure, but showed an almost linear dependence on feed temperature.

In a following step, the filtration characteristic towards organic model substances such as Inulin and Neohesperidin dihydrochalcone (NHDC) has been studied. Experimental results showed retention up to 88% for Inulin and 75% for NHDC.

1. Introduction

As an environmentally friendly alternative to a variety of organic, hazardous solvents for reaction and extraction processes, water at elevated temperatures and pressures has been in the focus of researchers for more than 30 years [1]. As a so-called "Green Solvent" water is physiologically harmless, non-toxic, inexpensive, available in large quantities and requires usually no treatment prior to disposal. Due to high reactivity, hot water provides a favourable environment for many chemical synthesis and reaction processes such as oxidation, hydrogenation or hydrolysis. A main advantage derives from an increasing solubility for many nonpolar, organic compounds with increasing temperature due to a decreasing dielectric constant. Besides the dielectric constant, further physical and chemical properties such as density, viscosity or ion product can be easily adapted to the process requirements in a wide range by variation of temperature and pressure, especially close to the critical point of water (T_c = 374 °C, p_c = 221 bar).

In terms of the presented work, this hydrothermal phase is defined as a single, liquid phase with a temperature between 100 °C and 374 °C and a pressure higher than the corresponding vapour pressure. In general, the phase is also referred to as Pressurized Hot Water (PHW), Hot Compressed Water (HCW), Liquid Hot Water (LHW), Superheated Water or Subcritical Water [2–4].

Besides reaction, synthesis and analytical applications, a major area of interest is the extraction under hydrothermal conditions. On the one hand, focus is on removal of organic pollutants i.e. from contaminated soils (near-/supercritical state) usually coupled with a subsequent degradation by Supercritical Water Oxidation (SCWO) [5]. On the other hand, a major goal of

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hydrothermal/subcritical state extraction processes is to increase selectivity of separation of valuable substances from plant materials. For that reason, an important market can be seen in the hydrothermal extraction, isolation and analysis of pharmacologically active, bioactive, antioxidant or anti-carcinogenic components/food additives such as polyphenols, phytosterols or carotenoids [6,7]. Another area of intense research is the separation of mono-, poly- and oligosaccharides from hemicellulose by hydrothermal extraction, which can be found in many forms in wooden biomass. The resulting components, such as xylose, arabinose or galactoglucomannan can provide important renewable feedstocks for the food, textile and cosmetics industry as well as for paper production or biofuels and medical applications [8,9]. The separation of the aforementioned substances mainly takes place at temperatures in the range of 100–250 °C. Since the majority of cited literature on this topic dates from the last 10 years, the growing interest in hydrothermal separation processes is clearly indicated [4].

However, to offer new applications to hydrothermal extraction and reaction applications, an efficient technique for a selective separation of hydrothermally dissolved substances is of general advantage. For that purpose, inorganic membrane technology presents an efficient and promising separation pathway under hydrothermal conditions to isolate extracts for fractionation or to remove reaction products to shift reaction equilibria. Furthermore, solvent recycling at conditions almost similar to extraction temperatures and pressures for the main amount of the fluid provides considerable savings of energy costs. Finally, desired components are obtained by decompression of a rather small amount of solvent where conventional phase separation can easily take place. This results in a significant increase in process efficiency and presents a major step in process intensification. Fig. 1 illustrates example hybrid concepts involving a membrane unit operation for two potential applications.

The combination of membrane technology by methods with near/supercritical fluids, mainly supercritical CO_2 and water treated with organic or hybrid (organic/inorganic) membranes, is part of research for about 20 years. In a large number of studies, implementation of membrane processes can advantageously affect the process and its efficiency by purification, fractionation or phase contact formation [10–16].

However, processing in a liquid and hydrothermal regime requires highly resistant membrane materials that can withstand these harsh mechanical, chemical and thermal conditions. Therefore, inorganic membrane materials are most suitable compared to polymeric membranes to resist hydrothermal conditions on a long-term basis at water temperatures above 100 °C. Compared to organic membranes, no swelling caused by dissolved fluid inside the membrane matrix occurs. Furthermore, inorganic membrane materials show a high resistance to compression forces induced by higher pressures. Both properties (no swelling, no compaction) lead to a constant pore size and pore size distribution during changes in process parameters [17].

Former investigations of membrane filtration under hydrothermal and even up to supercritical water conditions have been performed by using metal, organic, inorganic ceramic or hybrid systems with macro- and mesoporous membranes. Contrary to the presented work, investigated conditions included steam, steam based gas mixtures and/or binary mixtures of water and organic solvents [18–25].

Still, by now no studies dealing with porous, oxide ceramic micro- and mesoporous membranes (minimum pore size 0.9 nm) under hydrothermal conditions (single liquid phase) and elevated pressures have been published yet.

Hence, the presented study investigates for the first time the behaviour of oxidic, ceramic micro- and mesoporous membranes for water temperatures up to 140 °C and pressures up to 375 bar. In order to perform these investigations, a new membrane separation apparatus has been developed and built.

In particular, the investigations studied the pure water permeance depending on feed-pressure, feed-temperature and transmembrane pressure. Moreover, filtration characteristics have been analysed with two organic model substances, namely Inulin and Neohesperidin-dihydrochalcone (NHDC).

Because of hydrothermal membrane degradation at higher temperatures, a first approach to enhance hydrothermal membrane stability up to 160 °C is presented.

2. Experimental set-up

2.1. Micro- and mesoporous ceramic membranes

In the study, oxide ceramic micro- and mesoporous membranes with average pore diameters from 0.9 nm to 3.0 nm have been investigated. The majority of the tested membranes were nanofiltration membranes produced by *Fraunhofer Institute for Ceramic Technologies and Systems IKTS (Hermsdorf, Germany)*. The employed membranes were designed in tubular configuration with a length of 250 mm (outer/inner diameter 10/7 mm) and an asymmetric structure. A macroporous layer of α-Al_2O_3 supports several mesoporous intermediate layers formed of ZrO_2 and/or TiO_2. Finally, the

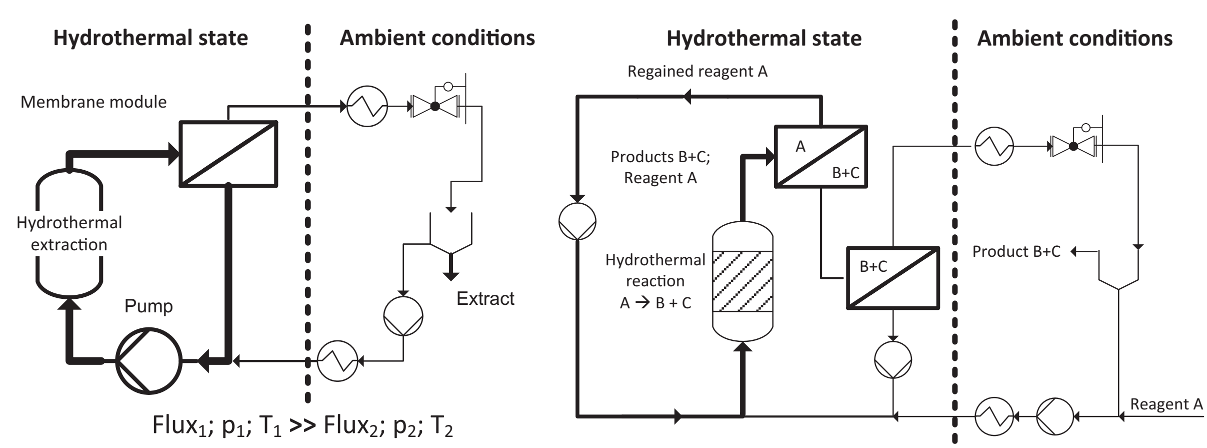

Fig. 1. Left: Principle of hydrothermal extraction coupled with membrane separation step to regenerate the main part of the solvent. Right: Hydrothermal reaction coupled with membrane separation steps to shift reaction equilibria and separate reaction products from solvent under hydrothermal conditions.