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## Experimental system for cleaning of porous polymer membranes using supercritical fluids

### Introduction

One of possible applications of supercritical fluids, which is currently investigated, is the replacement of organic solvents [Szwest *et al.*, 2008] in the production of porous microfiltration membranes using the TIPS process (temperature induced phase separation) [Berghmans *et al.*, 1996]. In this process, the produced porous membrane is filled with an oil, which has to be removed in order to prepare the membrane for regular use in separation processes.

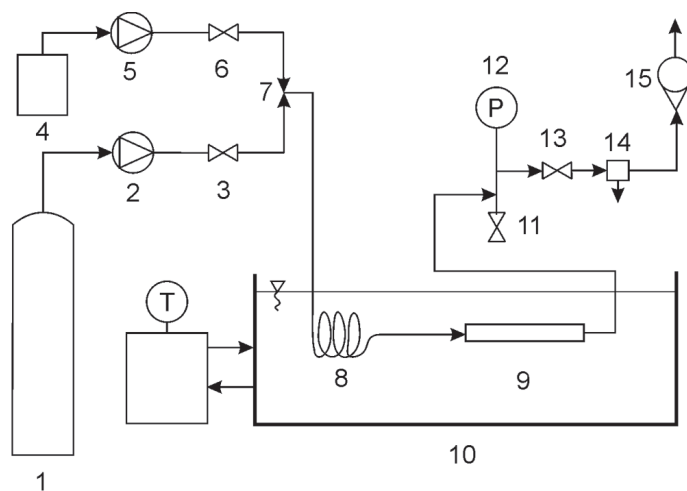
The application of supercritical fluids in the production of porous polypropylene tubular membranes used in microfiltration processes has been investigated before. The influence of addition of small amounts of organic solvents to supercritical carbon dioxide in order to enhance the membrane cleaning process was investigated [Henczka *et al.*, 2012], as well as the influence of supercritical carbon dioxide on structure and mechanical properties of the membranes [Krzysztoforski *et al.*, 2012]. For both investigations, a 1200 ml high pressure reactor (Parr, Inc., USA) was used as high pressure vessel housing the membranes. However, the use of a high pressure reactor for this purpose has some significant drawbacks:

- The reactor is suitable rather for batch processes, than for continuous processes, which are normally used in supercritical fluid extraction due to the possibility of carbon dioxide recirculation.
- The geometry of the reactor is not optimised for use as an extractor. In the case of promising results of future investigations, up-scale of the process would be difficult because a significant change of the extraction vessel geometry would be necessary.
- Hydrodynamic conditions in the reactor are hard to predict and cannot be used for validation of CFD modelling of the process [Krzysztoforski and Henczka, 2012].
- If long pieces of tubular membranes are used in the experiments, they have to be placed in the reactor as a coil. This causes irreversible changes of the membrane structure as the membrane does not regain its original straight form after processing in the reactor.

In this paper, a lab-scale experimental system for investigation of porous polymer membranes cleaning using supercritical fluids is presented, which overcomes the abovementioned drawbacks.

### Experimental system

In Fig. 1, the experimental system is depicted. Carbon dioxide is fed into the system from a cylinder – 1 via a supercritical fluid pump – 2 (SFT-10 pump, *Supercritical Fluid Technologies, Inc.*, USA). An organic solvent is supplied from a storage vessel – 3 using a liquid pump – 4 (HPLC pump *Smartline 1000, Knauer*, Germany). Both streams flow through valves – 5, 6 and are joined in a mixer – 7. The fluid flows through heat exchanger – 8 and flows into the extractor module – 9, which houses one or more tubular membranes. The extraction module is available in 4 versions shown in Fig. 2. The membrane cleaning takes place inside the extraction module. In order to guarantee a constant process temperature, both the heat exchanger – 8 and the extraction module – 9 are placed in a water bath thermostat 10. The fluid containing dissolved contaminants passes a vent valve – 11 and a pressure gauge – 12 and flows through a back pressure regulator – 13, where it undergoes decompression to ambient pressure. Downstream the pressure regulator – 13, a separator – 14 is provided to separate the contaminants and/or



#### Part list:

- |                               |                             |
|-------------------------------|-----------------------------|
| 1. Carbon dioxide cylinder    | 8. Heat exchanger           |
| 2. scCO <sub>2</sub> pump     | 9. Extractor module         |
| 3. Valve                      | 10. Thermostat              |
| 4. Vessel for organic solvent | 11. Vent valve              |
| 5. Liquid pump                | 12. Pressure gauge          |
| 6. Valve                      | 13. Back pressure regulator |
| 7. Mixer                      | 14. Separator               |
|                               | 15. Rotameter               |

Fig. 1. Experimental system

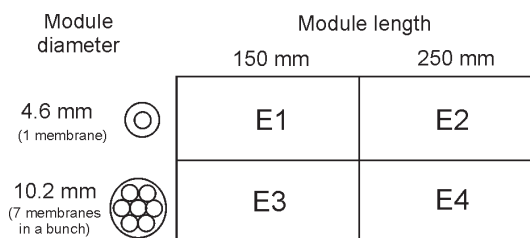


Fig. 2. Extraction modules

organic solvents from the CO<sub>2</sub> stream, depending on the mode of operation (see next chapter). Downstream the separator, a flowmeter – 15 is provided for measurement of the CO<sub>2</sub> flow rate.

The experimental system was designed for investigation of ACCUREL<sup>®</sup> hydrophobic capillary membranes *Type PP S6/2*, manufactured by *Membrana GmbH*, Germany (inner diameter 1.8 mm, outer diameter 2.7 mm, length 1300 mm, porosity 0.7, mean pore size 0.4 μm). For the experimental system, stainless steel elements and valves were used (*DK-LOK*, Korea), which enable easy assembly and modifications of the experimental system.

### Modes of operation

The presented experimental system can be used for carrying out experiments in batch and continuous modes. Four different extractor modules are available for the system (E1, E2, E3, E4, see Fig. 2). The extraction module E1 enables to insert one tubular membrane (length 100 mm) and is suitable e.g. for determination of optimal process conditions. E2 is a longer version of E1 and enables to investigate the co-

urse of cleaning in different parts of the membrane (the membrane can be placed in the system in several pieces arranged axially, which can be investigated separately after decompression). E3 enables to perform a scale up, as it can house up to 7 membrane pieces (see cross-section in Fig. 2), and it can simulate hydrodynamic conditions during cleaning of a bunch of membranes. E4 is the biggest extraction module which can be used if greater amounts of processed membranes are necessary (e.g. for membrane structure investigation). In Tab. 1, available ranges of process parameters of the experimental system are listed.

Tab. 1. Process parameters

Process parameter	Value
Temperature	298÷363 K
Pressure	0.1÷20 MPa
scCO <sub>2</sub> pump flow rate	0.01÷24 cm <sup>3</sup> /min
Liquid pump flow rate	0.01÷50 cm <sup>3</sup> /min

The experimental system can be used for pure supercritical carbon dioxide, an organic solvent, or supercritical carbon dioxide with an admixture of an organic solvent. In this way, the efficiency of supercritical fluid extraction can be directly compared with cleaning results achieved by traditional extraction using an organic solvent, using the same extractor module, i.e. in a system with the same geometry and with similar hydrodynamic conditions. Moreover, due to well-defined hydrodynamic conditions in the extractor module, experimental results obtained with this system can be used for validation of CFD models of membrane cleaning using supercritical fluid extraction.

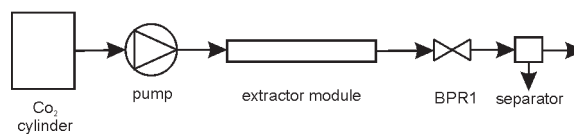
The experimental system was assembled and tightness tests were carried out at high pressure conditions (up to 20 MPa). Preliminary experiments were carried out, in which the E1 extractor module was used and a 100 mm long membrane piece, having the pores filled with soybean oil, was cleaned using isopropyl alcohol. The experimental conditions were as follow:  $T = 313$  K,  $p = 1$  MPa, flow rate: 2 g/min, extraction time: 20 min and 40 min. In these two experiments, 32% (20 min) and 44% (40 min) of the soybean oil was removed during the cleaning process.

### Extension options

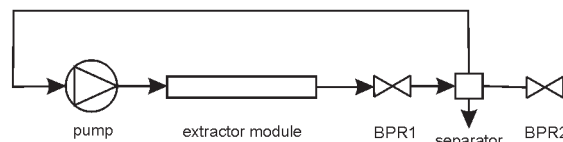
Due to the modular construction of the experimental system, several extension options are available. They include:

- Recirculation of carbon dioxide. In the present state, the experimental system runs without CO<sub>2</sub> recirculation (Fig. 3a). However, by addition of several components, CO<sub>2</sub> can be depressurised and after separation it can be recycled and used again in the process (Fig. 3b).
- The length and/or the diameter of the extractor module can be changed if required, making the experimental system suitable for other applications (e.g. for other tubular membranes or for extraction of substances from solid raw materials).
- Automatic process control can be introduced and time-dependent temperature, pressure and flow rates can be achieved.
- The maximum pressure available at the moment is limited by the liquid pump head (15 MPa) and by the pressure gauge (20 MPa). By replacing these components, as well as the back pressure regulator, pressure values up to 34 MPa can be achieved.

a) without CO<sub>2</sub> recirculation



b) with CO<sub>2</sub> recirculation

Fig. 3. Experimental system – CO<sub>2</sub> recirculation option

### Conclusions

The design of an experimental system for cleaning of porous polymer membranes using supercritical fluids was presented. The system overcomes the main drawbacks of the experimental system used in the previous experiments.

The system allows to carry out batch or continuous cleaning processes, using supercritical carbon dioxide, an organic solvent, or a mixture thereof, at a pressure up to 20 MPa, under stable and repeatable experimental conditions.

Modular construction of the experimental system enables to modify the system so that it allows to recycle carbon dioxide after decompression.

The system can also be adapted for higher pressures (up to 34 MPa) by change of some components of the system.

The presented experimental system will be used for membrane cleaning, as well as for investigation of the influence of supercritical fluids on structure, mechanical and filtration properties of microfiltration membranes.

Due to a well-defined and simple geometry of the extractor modules, the obtained experimental results will be suitable for validation of CFD models of the membrane cleaning process. Moreover, the experimental system is also suitable for investigation of mass transfer in porous media in supercritical conditions, using other porous media as the presented membranes.

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