CHEMICAL ENGINEERING TRANSACTIONS
VOL. 70, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

ISBN 978-88-95608-67-9; **ISSN** 2283-9216
DOI: 10.3303/CET1870147

Lab Scale High-Pressure Equipment for Supercritical Drying

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This paper is devoted to the development of high-pressure laboratory equipment for supercritical drying processes. Conducting processes under supercritical conditions requires appropriate high-pressure apparatus. High-pressure apparatus' working part design was developed on the basis of the results of supercritical carbon dioxide hydrodynamics mathematical modeling. To do this, modern computer simulation methods, based on principles of computational fluid dynamics (CFD), were used. Such methods allow to calculate velocity, pressure, physico-chemical properties fields within the apparatus at arbitrary boundary conditions. In addition, it is important to develop process flowsheets that include high-pressure vessels, high-pressure pumps, separators, intermediate tanks, complex shut-off and control valves, a set of instrumentation and automation. The developed laboratory equipment was realized and successfully commissioned. Proposed equipment can be used for studying the kinetics of the supercritical drying process. Such studies are necessary for resource and energy saving, efficiency increasing and scale up.

1. Introduction

Modern scientific society is focused on improving the hardware design of technological processes from the standpoint of energy and resource saving, environmental safety and reliability of chemical processes and industries. One of the actively developing areas is the introduction of technologies utilizing supercritical fluids (SCF), an important advantage of which is compliance with all the requirements of "green" chemistry. Supercritical processes include: supercritical fluid chromatography, supercritical fluid micronisation, supercritical extraction, supercritical adsorption, supercritical drying. SCF has a high penetrating ability, low viscosity, high solubility its physicochemical properties can be set within wide limits with changes in external parameters, such as temperature and pressure. Idham et al. (2017) used supercritical extraction of red colour extract from Roselle. Özbakır and Erkey (2015) produce aerogels based on silica using supercritical drying.

On the market there are companies that produce equipment for supercritical drying of various scale, both laboratory and industrial. For example, Applied Separations manufactures a system called Helix Supercritical Fluid Systems with high-pressure vessels of 300, 500 and 1,000 mL capacity that can withstand pressures up to 69 MPa. WATERS produces units with high-pressure apparatus with the volume of 100-5,000 mL, pressure up to 60 MPa. Laboratory series of NATEX company include high-pressure equipment with a volume of 20-500 mL, pressure up to 40 MPa, and also high-pressure vessels with a volume of 2-10 L and pressure up to 32.5-70 MPa. In the world, there are only a few companies that manufacture semi-industrial and industrial equipment for supercritical drying. AMAR manufactures equipment for supercritical drying with high-pressure devices up to 1,000 L. NATEX is developing and manufacturing equipment for supercritical drying of semi-industrial and industrial scale. Semi-industrial scale Installations include high-pressure vessels with a volume of 200 to 800 L. In most cases, such installations consist several high-pressure vessels connected in parallel. Industrial-scale installations, created by this enterprise, include high-pressure vessels with a volume exceeding 5,000 L. The production of equipment for supercritical drying is handled by a small number of companies represented on the market. Therefore, the development of equipment for the process of supercritical drying is an urgent task, which is especially true for laboratory scale equipment.

An important task in the development of new equipment is the selection of the most effective parameters for process control and its design features. To solve these problems, the best method is mathematical modeling.

Please cite this article as: Tsygankov P.Y., Khudeev I.I., Lebedev A.E., Lebedev E.A., Menshutina N.V., 2018, Lab scale high-pressure equipment for supercritical drying , Chemical Engineering Transactions, 70, 877-882 DOI:10.3303/CET1870147

At present, there are complex high-precision mathematical models that make it possible to obtain fields of all physical and scalar quantities in the investigated system with arbitrary boundary and initial conditions. CFD can be used to simulate various chemical-technological processes. The application of this method, as shown by Lebedev et al. (2015) allows us to describe with sufficient accuracy the process evolution in the system under consideration, including medium hydrodynamics, heat and mass transfer in various ranges of temperature and pressure. The use of such an approach makes it possible to increase the efficiency of processes without carrying out costly and lengthy experiments.
Within the framework of this work, the development of high-pressure laboratory equipment for supercritical drying processes is being carried out. First of all, it is necessary to determine the best design of the high-pressure vessel, which will allow to carry out processes with maximum efficiency. For this, modern methods of computer modeling utilizing CFD are used. A flowsheet is being developed for the proposed design of the high-pressure vessel.

2. Design of high-pressure vessels

The development of high-pressure vessels includes the following stages: modeling, design, manufacturing.
The following requirements are imposed on processes under high pressure, the observance of which is necessary for the development of high-pressure vessels:

- Good circulation of supercritical carbon dioxide in the vessel, in order to minimize the possibility of formation of dead zones
- Ensuring reliability, durability and safety during manufacture, installation and operation
- Easy cleaning, material loading and unloading

2.1 Modeling of high-pressure vessels

The design of the high-pressure vessel's working chamber for performing supercritical drying processes was developed on the basis of the results of supercritical carbon dioxide hydrodynamics' mathematical modeling. For this, a mathematical model is proposed, which is based on the fundamentals of continuous media mechanics. Solution of model equations was carried out using the software package ANSYS Fluent. The model equations calculating result is velocity and pressure vector fields, identified at each local point of the studies system under arbitrary boundary conditions. The analysis of calculation results allows to reveal the influence of dead zones, recirculation and bypassing zones on the studied processes' evolution.
The following assumptions were made in the simulation:

- Vessel’s internal volume is totally filled with supercritical carbon dioxide
- Simulation is carried out in a steady-state manner
- Supercritical carbon dioxide is a viscous compressible liquid
- The wall temperature of the high-pressure vessel is considered constant

Mathematical model equations Eq(1) – Eq(2):

$$\frac{\partial(\rho_x v_x)}{\partial x}+\frac{\partial(\rho_y v_y)}{\partial y}+\frac{\partial(\rho_z v_z)}{\partial z}=0 \tag{1}$$

$$\begin{cases} v_x\dfrac{\partial(\rho_x v_x)}{\partial x}+v_y\dfrac{\partial(\rho_x v_x)}{\partial y}+v_z\dfrac{\partial(\rho_x v_x)}{\partial z}=-\dfrac{\partial p}{\partial x}+\mu\left(\dfrac{\partial^2 v_x}{\partial x^2}+\dfrac{\partial^2 v_x}{\partial y^2}+\dfrac{\partial^2 v_x}{\partial z^2}\right) \\ v_x\dfrac{\partial(\rho_y v_y)}{\partial x}+v_y\dfrac{\partial(\rho_y v_y)}{\partial y}+v_z\dfrac{\partial(\rho_y v_y)}{\partial z}=-\rho g-\dfrac{\partial p}{\partial y}+\mu\left(\dfrac{\partial^2 v_y}{\partial x^2}+\dfrac{\partial^2 v_y}{\partial y^2}+\dfrac{\partial^2 v_y}{\partial z^2}\right) \\ v_x\dfrac{\partial(\rho_z v_z)}{\partial x}+v_y\dfrac{\partial(\rho_z v_z)}{\partial y}+v_z\dfrac{\partial(\rho_z v_z)}{\partial z}=-\dfrac{\partial p}{\partial z}+\mu\left(\dfrac{\partial^2 v_z}{\partial x^2}+\dfrac{\partial^2 v_z}{\partial y^2}+\dfrac{\partial^2 v_z}{\partial z^2}\right) \end{cases} \tag{2}$$

with the following boundary conditions Eq(3):

$$\begin{aligned} &\vec{v}(x_{in},y_{in},z_{in})=\vec{v}_0 \\ &\vec{v}(x_{in},\ y_w,\ z_w)=0 \end{aligned} \tag{3}$$

where ρ – density, kg/m^3; $\vec{v}$ – velocity vector, m/s; p – pressure, Pa; $\vec{g}$ – free fall acceleration, m/s^2; $\overrightarrow{S_i}$ – momentum additional source, kg/m^2·s^2; $\vec{v}_0$ – velocity vector at inlet, m/s; μ – viscocity, kg/m·s; variables and values with “in” index relate to the continuous phase inlet of the vessel, with “w” index – to the vessel’s walls.
In Eq (2), the terms on the right of it are responsible for momentum change as a result of the pressure gradient's presence, frictional forces, gravity, and other external forces, respectively.

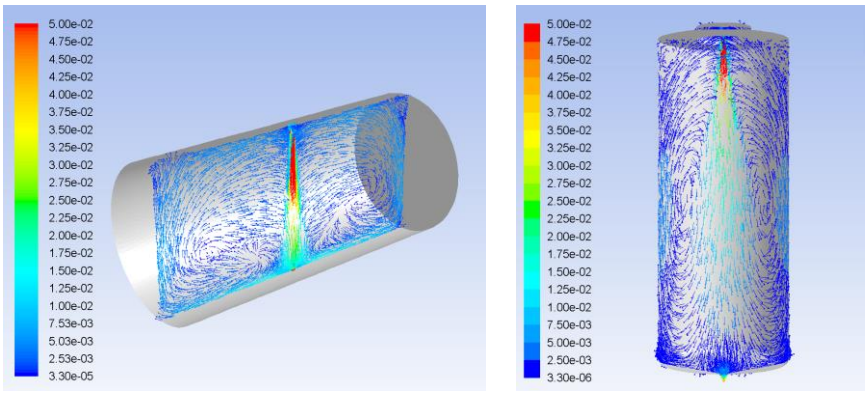
The density of supercritical carbon dioxide is calculated from the Peng-Robinson equation of state (Poling et al., 2011) Eq(4):

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (4)$$

where P – pressure, MPa; T – temperature, K; V – molar volume, m^3/kmol; R – universal gas constant (0.0083144), MPa·m^3/kmol·K; a, b – equation's constant.

Parameter values for calculation: pressure 12 MPa, temperature 313 K, mass flow of carbon dioxide 0.0008 kg/s.

The solution of the model equations system is performed by the finite volume method. Using the proposed model, the most suitable design of the vessel's working chamber was selected. As design options, vertical and horizontal execution of the high-pressure vessel is considered. An important and indispensable stage of the finite volume method is the creation of a calculation mesh. The calculated mesh consist of tetrahedral elements. When constructing the preliminary calculation mesh, it was considered that the obtained variant is satisfactory if the maximum skewness value among all cells is less than 0.9. To increase the accuracy of the calculation, series of calculations were performed with increasing density of the calculated mesh. In order to increase the quality of the mesh with increasing density (with the lowest increase in the calculation time), it is necessary to increase the mesh density only in the most important local areas. These included areas – where the values of the gradients of the calculated values, are significant. The method of such an increase in the density of the mesh is called adaptation. It was carried out after the model equations calculating within the framework of the preliminary mesh. The need for mesh adaptation depends on the key parameter. The key parameter is the average velocity of supercritical carbon dioxide in the volume of the high-pressure vessel. Using the resulting mesh, the model equations are recalculated. Thus, one adaptation cycle is carried out. For each computational mesh constructed, adaptation is carried out, until the relative change in the key parameter after the last adaptation became less than 1%. Thus, the number of cells in the cases considered lies in the range from 500,000 to 1,000,000. Figure 1 show supercritical carbon dioxide velocity fields along crossections of the high-pressure vessel with a volume of 2,000 mL for different designs. The velocity is indicated in m/s.



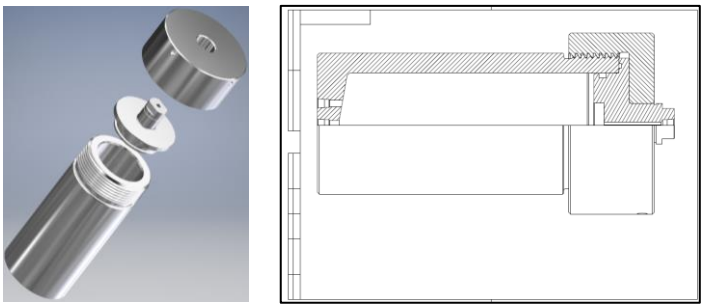
(a) *(b)*

Figure 1: Velocity vector field along crossections of the high-pressure vessel with a volume of 2,000 mL: (a) horizontal design, (b) vertical design

For the 2,000 mL high-pressure vessel, the following parameters were selected: vertical design, length-to-diameter ratio 2.4:1, 1 inlet and 1 outlet 3 mm in diameter. This option is preferred due to the smaller volume of dead zones, recirculation and bypass zones. The number of cells in the calculation mesh for this configuration of the high-pressure apparatus was 743,252.

2.2 Design and manufacture of high-pressure vessels

In the SolidWorks software package, a series of calculations were carried out to determine the required wall thickness, bottom structure, and the cover of the high-pressure vessel. The calculations were carried out using the finite element method. Calculation parameters: the pressure inside the high-pressure vessel is 30 MPa, the temperature is 313 K. At 30 MPa, the maximum deformation that occurs in the bottom is 0.043 mm. It is permissible in the operation of a high-pressure vessel in according with regulations in effect within Russian Federation. Appearance and an assembly drawing of the developed high-pressure vessel with a volume of 2,000 mL are presented in Figure 2.



(a) (b)

Figure 2: Appearance (a) and assembly drawing (b) of the high-pressure vessel with a volume of 2,000 mL

Figure 2 shows the final design of a 2,000 mL high-pressure vessel consisting of a housing, cover and union nut. Based on the detailed drawings, the above-described high-pressure vessel was manufactured.

3. Development of laboratory-scale installations

To operate the supercritical drying plant, in addition to high-pressure vessel, high-pressure pumps, separators, intermediate tanks, complicated shut-off and regulating valves, instrumentation and control equipment are required. Thus, high-pressure laboratory equipment for supercritical drying processes was developed, the flowsheet of which is shown in Figure 3.

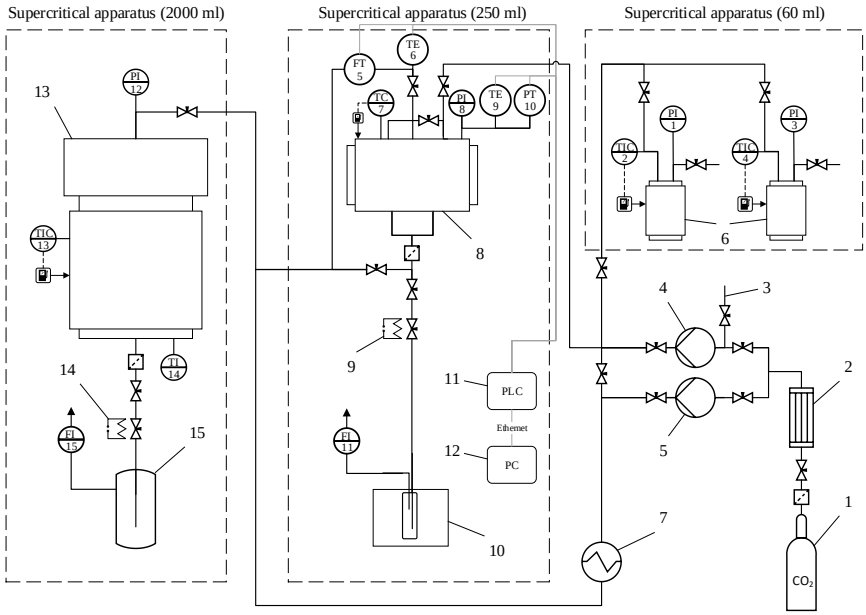
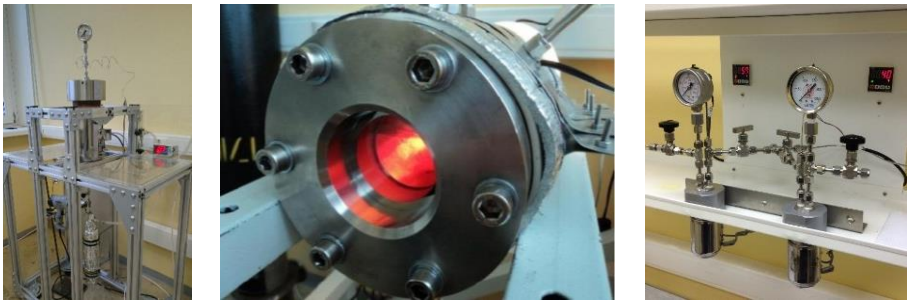


Figure 3: Flowsheet of laboratory-scale high-pressure installation: 1 – vessel with carbon dioxide (6 MPa); 2 – condenser; 3 – co-solvent filling line; 4, 5 – pumps; 6 – 60 mL high-pressure vessel; 7 – thermostat; 8 – 250 mL high-pressure vessel; 9, 14 – heater; 10 – solvent/extract collector with cooling jacket; 11 – PLC; 12 – PC; 13 – 2,000 mL high-pressure vessel; 15 – separator; PI1, PI3, PI8, PI12 – manometers; TIC2, TIC4, TC7, TIC13 – temperature transducers with control loop; FT5 – Coriolis flowmeter; TE6, TE9 – thermocouples; FI11, FI15 – float-type flowmeter; TI14 – temperature transducer

On the flowsheet there are 2 installations for the supercritical drying process, united in a single system of laboratory equipment. In addition, a supercritical adsorption facility is included in this system. Carbon dioxide is supplied from the vessel (1) to the condenser (2), in which the carbon dioxide is cooled down to 278 K to avoid gas phase formation. Then the pressure is increased by the pump (4) from Lewa company (maximum working pressure 25 MPa) or by the (5) G35 pump from Maximator (maximum working pressure 40 MPa). When carrying

out processes in high-pressure vessels (8) and (13), carbon dioxide enters the thermostat (7). Further, supercritical carbon dioxide enters the high-pressure vessels (8) and/or (13). When carrying out processes in high-pressure vessel (6), carbon dioxide enters the high-pressure vessel directly after the pump.
In a supercritical drying installation with a 250 ml high-pressure vessel (Figure 4a) (8) the following instruments are installed: a thermocouple TE6 and a Coriolis flowmeter FT5 at the inlet to the high-pressure vessel, a thermocouple TE9, a pressure transducer PT10, and a manometer PI8 to indicate pressure inside the high-pressure vessel. Coriolis flowmeter allows to accurately measure the consumption of supercritical carbon dioxide. The installation uses a MINI CORI-FLOW ™ M13 Coriolis flowmeter from Bronkhorst. The data from TE6, FT5, TE9, PT10 is transferred to the PLC (11), and then to the PC (12), where the data is displayed and stored. The temperature inside the high-pressure vessel is adjusted via temperature transducer TC7, and heating is carried out using a flexible heating cable located on the housing of the high-pressure vessel. Regulation of the carbon dioxide flow is carried out by a system of valves at the outlet of the high-pressure vessel. The flow rate of gaseous carbon dioxide is indicated be a float-type flowmeter FI11. In addition, it is possible to carry out supercritical processes utilizing a co-solvent in the high-pressure vessel (8). The co-solvent is fed via the pump (4) from Lewa company through the filling line (3). The 250 ml high-pressure vessel is designed similar to the high-pressure vessel of professor Irina Smirnova from Hamburg University of Technology.
In the supercritical drying installation with the 2,000 mL high-pressure vessel (Figure 4b) (13) the following instruments are installed: a temperature transducer TI14 and a manometer PI12 to indicate the pressure inside the high-pressure vessel. The temperature inside the high-pressure vessel is regulated by a temperature controller TIC13, and heating is carried out using an electrical heating jacket located on the housing of the high-pressure vessel. Regulation of the carbon dioxide flow is carried out by a system of valves at the outlet of the high-pressure vessel. The flow rate of gaseous carbon dioxide is indicated on a float-type flowmeter FI15.
In the installation for supercritical adsorption process with two 60 mL high-pressure vessels (Figure 4c) (6) manometers PI1, PI3 are installed. Temperature control inside high-pressure vessels is carried out by temperature controllers TIC2, TIC4, and heating is carried out by electrical heating jackets placed on the housing of high-pressure vessels.



(a) *(b)* *(c)*

Figure 4: Appearance of installations for supercritical processes: (a) with 2,000 mL high-pressure vessel, (b) with 250 mL high-pressure vessel, (c) with 60 mL high-pressure vessels

The developed flowsheet allows to carry out supercritical processes in all high-pressure vessels in parallel mode. In addition, the general block of conditioning and supply of carbon dioxide can reduce capital costs, and its design does not limit the functionality of the installations in any way. The implementation of installations within the framework of a unified system of laboratory equipment makes it possible to simplify research aimed at combining various supercritical processes by simplifying the organization of material flows.

4. Experimental studies using the developed installations

The laboratory equipment presented above has been successfully commissioned and is used for supercritical drying processes. Supercritical drying is the final stage in the production of aerogels. Samples of gels, in the pores of which there is an organic solvent, are placed in a high-pressure vessel. After that, the high-pressure vessel is sealed. The high-pressure vessel is supplied with liquid carbon dioxide at 6 MPa. Further, the step of increasing pressure and raising temperature to the values at which the supercritical drying process occurs. Then, with a constant flow of supercritical carbon dioxide through the high-pressure vessel, the organic solvent is exchanged in the pores of the gel and removed from the volume of the high-pressure vessel within 4-10 h.

After 4-10 h, the supply of carbon dioxide is blocked and the pressure is released at a rate of 0.1-0.3 MPa/min. When the atmospheric pressure is reached, the high-pressure vessel is depressurized.
The supercritical drying process in the installation with the 250 mL high-pressure vessel allows to study the kinetics of the process experimentally. An example of the supercritical drying process kinetics for the production of silica-based aerogel in the form of cylinders is shown in Figure 5. The total volume of the gel was 55 mL.

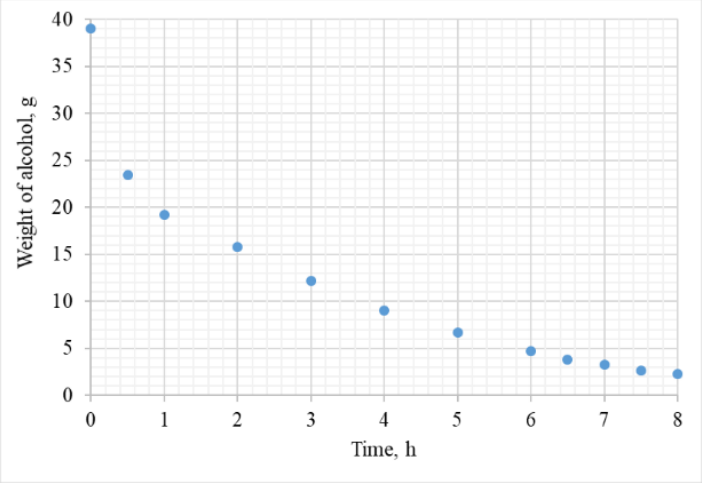


Figure 5: Concentration of isopropanol inside high-pressure vessel during supercritical drying of the silica-based aerogel in the form of cylinders with the pressure of 12 MPa and temperature of 313 K

Based on the kinetics data, the process parameters correction is carried out: time, carbon dioxide flow, pressure and temperature. After selecting optimum values of parameters, the drying process is carried out on larger batches of samples using the 2,000 mL high-pressure vessel. In addition to increase of produced aerogels' volume, the 2,000 mL high-pressure vessel allows drying samples with larger dimensions.

5. Conclusions

The laboratory-scale high-pressure equipment for carrying out supercritical drying process is offered. The stages of 2,000 mL high-pressure vessel development are shown. The stages include: simulation of hydrodynamics of the high-pressure vessel's working chamber using the software package Ansys Fluent, design and manufacture of the high-pressure vessel. A flowsheet for supercritical installations, which are integrated into a single system of laboratory equipment, has been developed. The proposed equipment makes it possible to carry out experimental studies of the supercritical drying process, to obtain experimental batches of aerogel samples.

Acknowledgments

The research is supported by the Ministry of Higher Education and Science of The Russian Federation within the framework of basic component of the State Assignment № 10.4658.2017/ВУ.

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