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Classification of Supercritical Drying Methods and a Reactor Design

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Abstract
Although there are many drying techniques in everyday life, most of them are insufficient to protect the structural features of dried products. On the contrary of popular usage of traditional dryings techniques, supercritical drying method provides lots of advantages. Supercritical drying has attracted attention in many areas with superior properties. In this study, supercritical drying methods were investigated and classified. There are basically five types of supercritical drying methods. These are supercritical organic solvent drying, supercritical gas drying, supercritical mixture solvent drying, supercritical gas extraction-drying, and supercritical fluid-assisted spray drying. On the other hand supercritical conditions were specified and a supercritical drying reactor model was created. The model can perform above critical conditions of most substance.

Keywords: Supercritical fluids; drying; supercritical drying; supercritical reactor

1. Introduction

Substances are transformed supercritical fluids (SCF) when they rise above their critical temperature and critical pressure point. Due to their properties, such low viscosity and high diffusivity, SCF's seem like gas phase, besides their high density and resolving power features seem like liquid phase. In the supercritical (SC) area, because of the resolving power is a function of density, a minor change of extraction conditions provides great convenience. Ethylene, ethane, propane, methanol, toluene, water and carbon dioxide (CO_2) are used in supercritical fluid extraction as SCF. If conventional drying methods are used instead of supercritical drying (SCD) during the drying process, this may lead to cause catastrophic failures in the sample structural properties. SCD or supercritical fluid extraction (SCFE) has received considerable attention in the last two decades. In the present study, the SCD methods are classified. Also a reactor design which capable of supercritical conditions (SCC) is realized.

As a short description, SCD is a process to remove liquids (mostly water) from solid materials or solutions with the help of SCF's. SCD process is applied to porous materials with exorable structures in many applications. These are dendrites in aged silica gel (to obtain aerogel), tiny machinery of micro electromechanical devices (to produce micro electro-mechanical systems (MEMS)), cell walls (e.g., to prepare biological specimens for scanning electron microscopy), and so on[1].

As a conventional unit operation, extraction is a contact equilibrium separation process where a solid material containing a solute of interest is brought into contact with a liquid solvent, time is allowed for the equilibrium to be reached and the target component to be transferred from the solid phase to the liquid phase, and, finally, the solid and liquid phases are separated by physical means. This also applies to liquid/liquid extractions but the focus here is on solid/liquid separations. The same principles also apply in the case of supercritical fluid extraction, but the solvent is a supercritical fluid instead of a liquid. Both mass transfer kinetics and equilibrium solubility play a role in dictating the success of the extraction. CO_2 has been chosen in many workouts as SCF for food, medical and health industry due to its moderate critical point of 31°C and 7,4 MPa, allowing extractions to be performed at just above ambient temperatures[2].

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That's obviously seen in figure 1, various types of drying techniques create great damage and some different conditions, drying might cause catastrophic failure on materials structure.

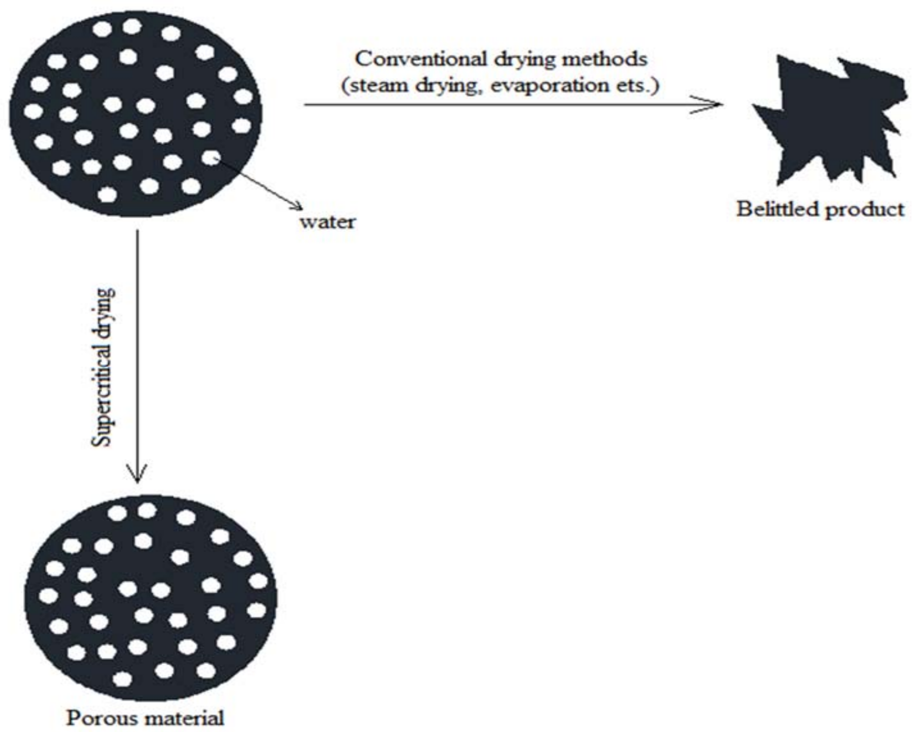

Figure 1.Comparison of ordinary drying techniques with supercritical drying technique.

Figure 1 shows when the ordinary drying techniques are chosen instead of SCD technique, the samples formation changes permanently. SCD protects the volume of the product and it has quite common usage due to its great number of advantages.

If we compare most common drying methods with SCD to obtain porous material, SCD provides at relatively high pressure but proper temperature and relatively short drying time[1].

In the last two decades, supercritical fluid dryings (SCFD) or supercritical dryings (SCD) has attracted growing interests for its increasing applications in various fields.

Because of its effective and any other outstanding properties SCD has a lot of advantage compare to other dryings techniques. There are different physical and chemical properties of each and in this respect they have different phase diagram. Any substance discussed in the pressure-temperature phase diagram of the states of solid-liquid-gas boundary curves with each other, they are in balance. At balanced between gas and liquid states of the substance which we move forward curve in the case of temperature and pressure are increased. Due to thermal expansion as a result, decrease of viscosity of the liquid, density of the gas is increasing. After a while the density of the liquid and gas phases obtain in the same value by approaching to each other. That point indicates the critical point which the density of the two phases to have a common point. If the temperature or the pressure increases over the critical points then it becomes the supercritical fluids (SCF) which has average properties between gas and liquid phases.

The features of the supercritical fluid, viscosity at low rates, high-value propagation, density and resolving powers are similar to both gas and liquid. Because of the drying process is actually a supercritical fluid extraction, the high resolving power of supercritical fluid is very important at this point .SCF extraction conventionally high-pressure pump for achieving critical conditions. These conditions are achieved by a system with the extractor and separator. SCF decided to be use a predetermined pressure value sent to the system passed through a heater at this time is transferred to the extractor. Here SCF interacting with sample which desired to be dried gains the components which can be solved. After that the fluid passing through the separator under reduced below critical conditions of temperature and pressure of the drying cycle is completed.

Up to the present the developing polymeric materials which are used for different purposes and different areas, forces scientific world to find other modern and effective solutions.

Among known materials on Earth lightest and lowest density aerogels with presents itself as a solution to humanity at this point. Because of the easily controlled pore structure, carbon aerogels which has features such as huge surface area, low electric resistance, high electrical conductivity, and its thermal and mechanic aspects, are produced by supercritical drying with the help of supercritical fluids. Carbon aerogels (CA) have many features to make our lives easier in many sectors such as textile, health, food, agriculture, medicine, materials.

2. Traditional Drying Process

Among the most commonly used ones of traditional drying methods; air drying, freeze drying, vacuum drying, spray drying, fluidized-bed drying and drum drying. Cost of drying methods is shown in Table 2[3]. Figure 2.1. and Figure 2.2. also clearly shows the relation between costs of drying methods.

Table 2. Cost of drying methods

Drying method	Fixed costs ($/kg)	Manufacturing costs ($/kg)
Air drying	610	17
Fluidized-bed drying	1000	17
Drum drying	1040	23
Spray drying	1360	19
Vacuum drying	5860	49
Freeze drying	1228	95

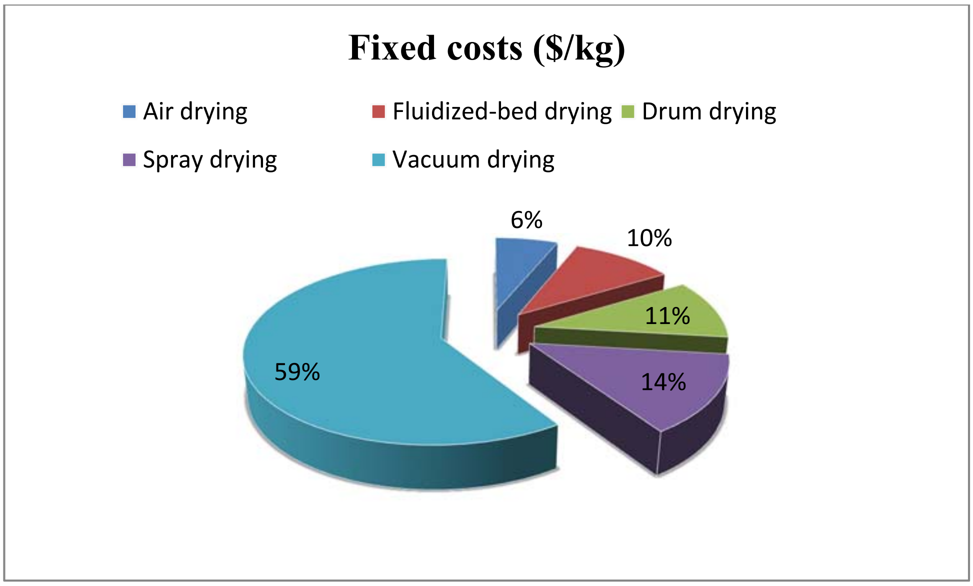

Figure 2.1 Fixed costs of drying methods

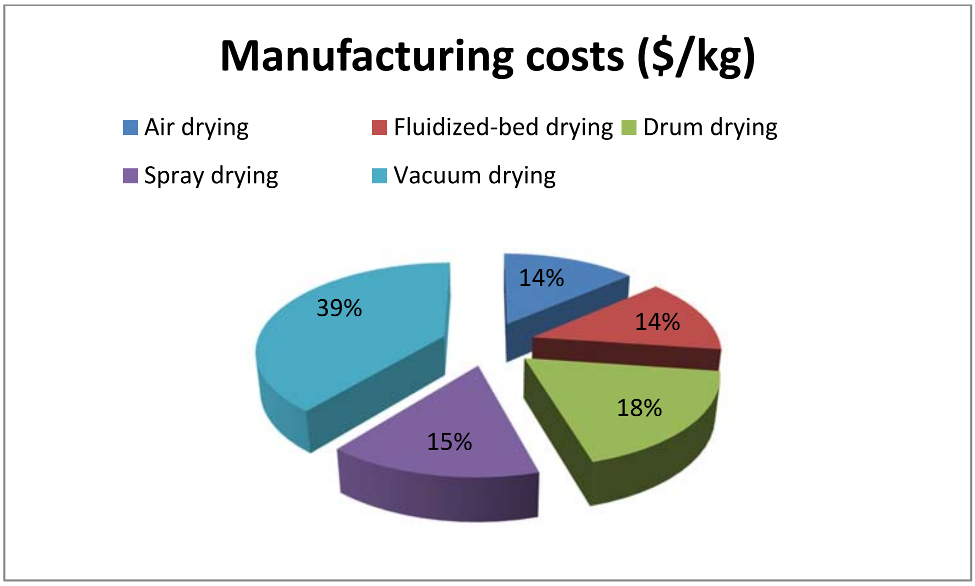

Figure 2.2 Manufacturing costs of drying methods

3. Supercritical Drying

All of substances found in nature have different physical and chemical properties allowing them to be distinguished from other substances. Still in this direction substance has peculiar features like critical temperature and pressure conditions which they reach SC states. So SCD process is carried out from this material owned SC states.

In this study SCD methods were classified due to the usage of SC solvents. So SCD's were investigated in basically five different groups. These are supercritical organic solvent drying (SCOD), supercritical gas drying (SCGD), supercritical mixture solvent drying (SCMD), and supercritical gas extraction-drying (SCGED). Besides the term "supercritical fluid drying" was also used when scientists employed SCFs to assist the spray drying of aqueous solutions[4]. This work introduces therefore, SCF assisted spray-drying/atomization (SASD) process as a special SCD for drying aqueous solution to obtain fine particles[1].

Depending on above classification, Figure 3 shows classic process usages of these SCDs. As it shows, high porosity of products can finally be obtained by using SCOD, SCGD, SCMD, and SCGED[1].

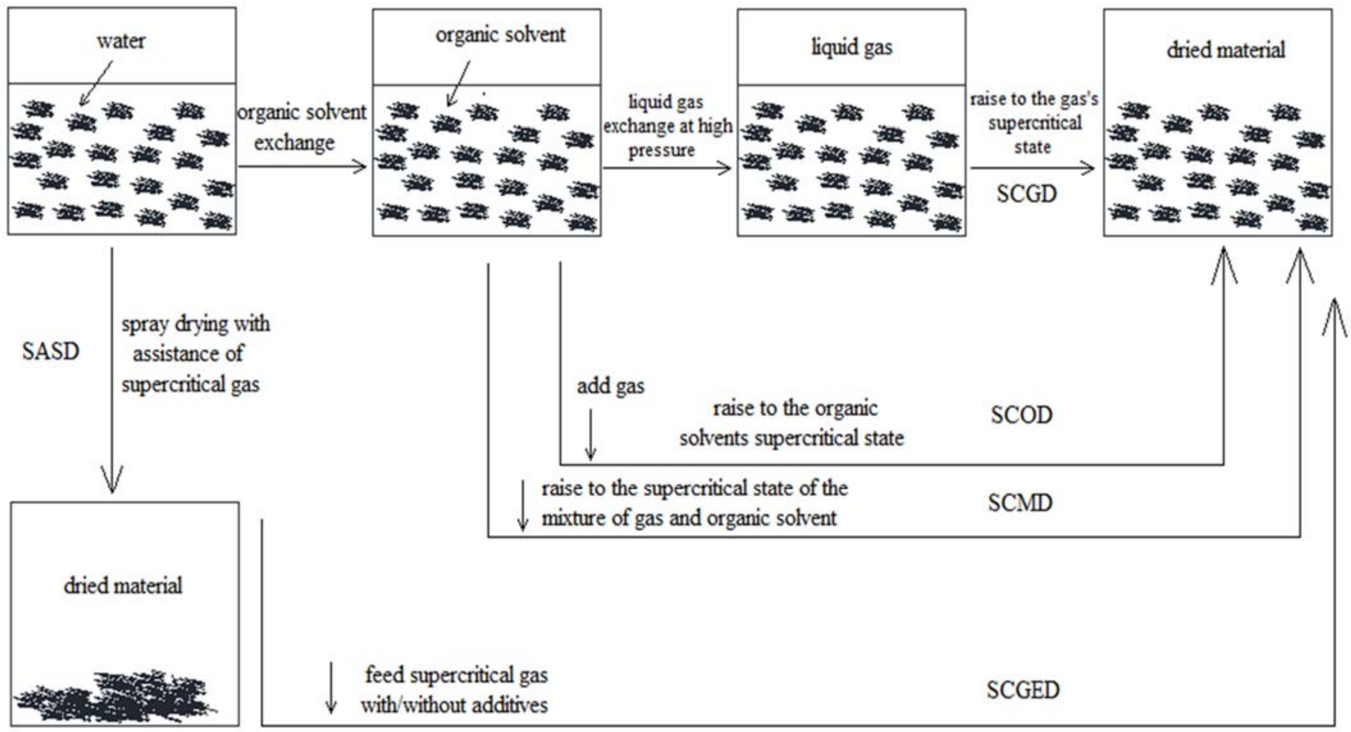

Figure 3. Classic process usages of SCDs

3.1. Supercritical Organic Drying (SCOD)

SCOD is the drying process which an organic material is used as the solvent. Referring to earlier studies, it is seen that as the solvent ethanol is used frequently. For this process to work, it’s quite hard to reach the critical point of the organic solvent, because SCOD needs high operating temperature. On the other hand depending on organic solvent exchange conditions, drying time is longer than the other methods.

3.2. Supercritical Gas Drying (SCGD)

Another method for SCD was suggested where the solvent present in the gel (generally alcohol) prior to drying was exchanged normally by liquid CO_2 with a critical point close to ambient temperature[1]. Liquid CO2 was the best useful material because of its low operating temperature and pressure.

3.3. Supercritical Mixture Solvent Drying (SCMD)

In 1994, van Bommel et al. described a procedure in which the complete alcohol - CO_2 exchange was carried out under supercritical conditions[5][1].

Compared with SCGD, SCMD provides a great advantage by reducing process and apparatus costs, thanks to its low operating temperature. Again, if SCMD compared with SCGD, SCMD decrease drying time, because it does not require relocation process of organic solvent with liquid CO2.This feature has made it much cheaper and effective of large quantity production of silica aerogel.

3.4. Supercritical Gas Extraction-Drying (SCGED)

According to Zheng et al. SCGED cannot guarantee that there will be no crash in the structure of the material[1]. On the other hand, a declaration about this method says the drying process is carried out using supercritical carbon dioxide [6]. And it should be noted that SCGED does not require water replacement step.

3.5. SCF-Assisted Spray-Drying (SASD)

This method also comes into existence the aid of SCF. So it is an effective method for particle formation. However SASD process is classified in only one way, it is concerned with aqueous solutions and suspensions [7,1].

4. Supercritical Reactor

Some criteria's for the realization of the design is determined primarily. Studies have found that the material covering the outer body is the most important parameter for the design of the reactor is analysed. Because of this, the material used in this design is determined as 310 quality stainless chromium steel. Main production objective of this steel is that it provides high resistance to heat. However, it has unique welding ability[8].

Design criteria considered in the selection of the materials used in the design of this study was determined as follows;

- Sample to be processed before drying begins, the aqueous solution may comprise. Therefore, it should have a high resistance to corrosion of the material to be used.
- The drying process does not take place only in SCC(Supercritical conditions), the temperature can reach very high values. So material must be able to maintain its form at high temperatures.
- In manufacturing, in order to avoid problems during installation, the material to be used must have good weld ability.
- The most important of them all is that it has physical properties which provides mechanical advantage.

Table 4 shows us some mechanical properties of 310 quality of stainless steel[9,10].

Table 4. Mechanical properties of 310 quality of stainless steel.

Tensile strength/min (MPa)	Yield strength (MPa)	Extension (%mm)	Hardness	
			Rockwell (HRB max)	Brinell (HB max)
515	205	40	95	217

Considering all of these criteria, a SCR design which capable of SCD was carried out. Drawings, using a three-dimensional design program are shown in Figure 4.1,4.2 and 4.3.

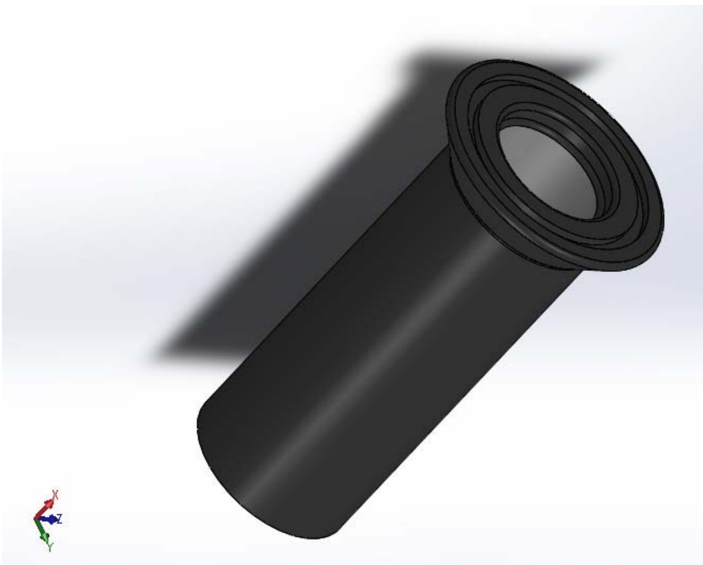

Figure 4.1. Main body of the reactor

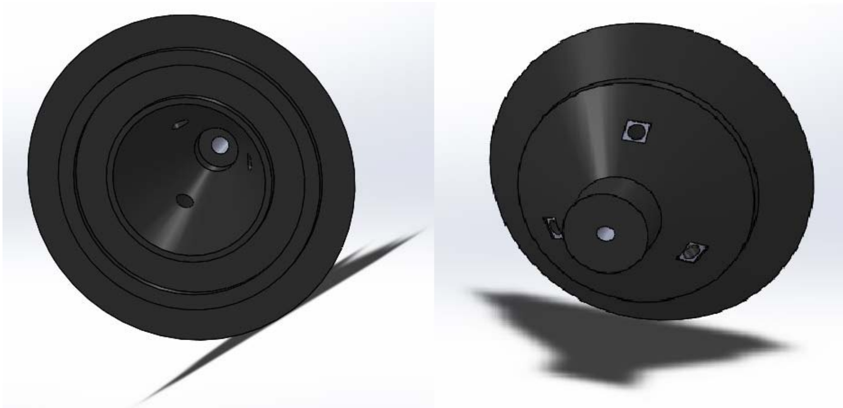

Figure 4.2. Cover of the reactor

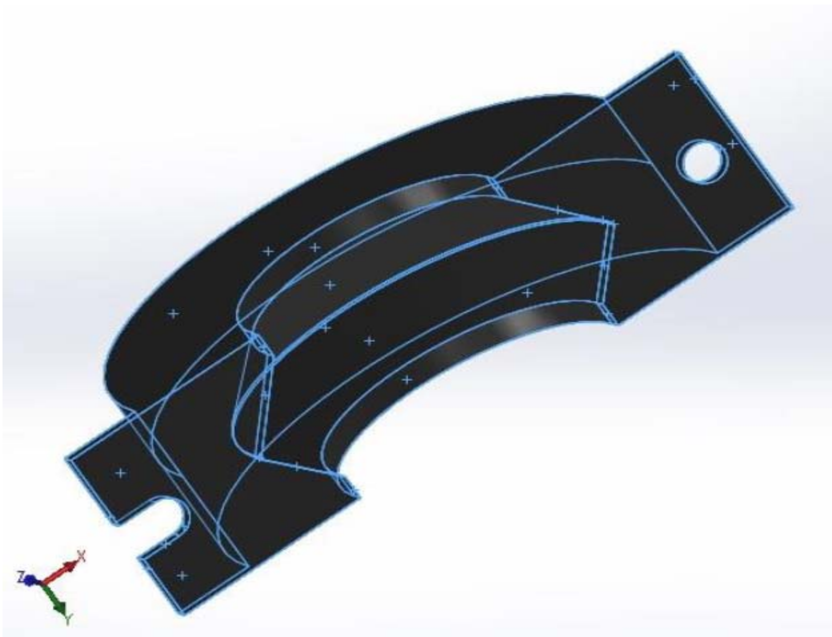

Figure 4.3. Clamp of the reactor

5. Conclusions

In order to determine the strength characteristic of reactor, some criteria's are aranged. While operating temperature is fixed at 304,3K° , working pressure is considered at 7,4 MPa. Figure 5 shows heat dissipation of the main body.

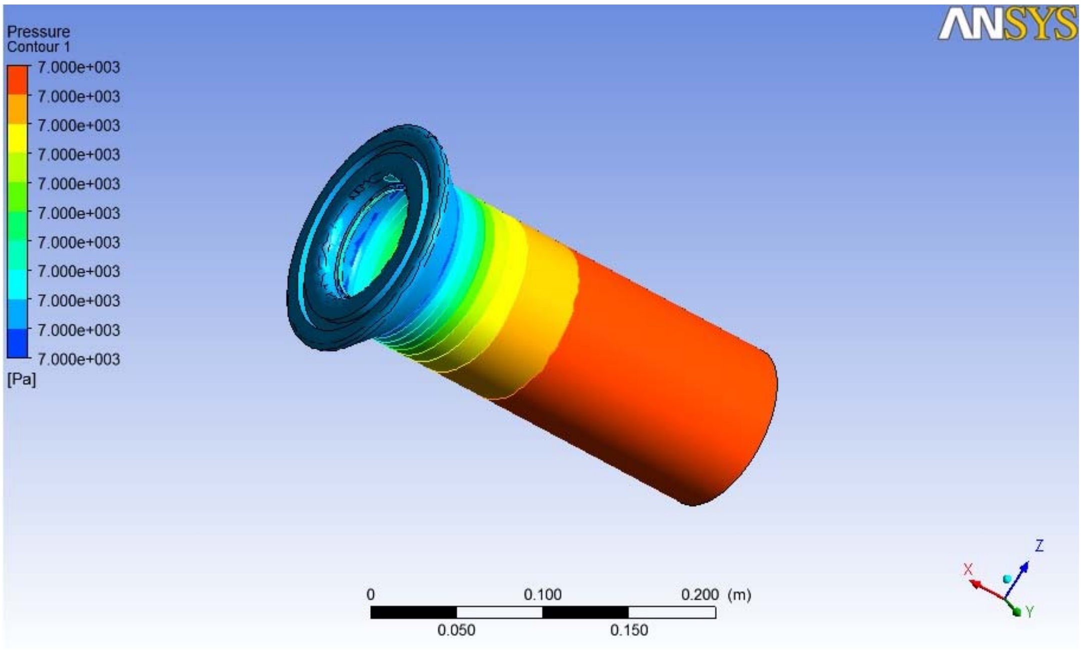

Figure 5. Heat dissipation of the main body.

Considering the supercritical fluids, CO_2 is the most useful fluid among them to reach a certain value which is supplied to SC conditions. Critical temperature and pressure of CO_2 which is used for processing SCD are 304.25 K and 7.39 MPa, respectively. Therefore designing the reactor body and coupling cover, 800K temperature-resistant and 20 MPa pressure-resistant, has found suitable to carry out 310 quality Cr material. According to the analyses performed with a finite element analysis program was found to be appropriate to the design made under these conditions. When the temperature and pressure deployment are analysed, it was observed that there is no risk of any region.

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