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Aerogel Production and Determination of Its Thermophysical and Characteristic Properties

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Abstract
Porous materials are at the forefront of research in terms of providing superior insulation properties and energy efficiency. The most important point that makes porous materials different and unique is the space inside the pore. Aerogel has become the insulation material that stands out as the most interesting alternative in this context. In this study, the production of aerogel insulation materials with high insulation properties, suitable mechanical properties, and different contents was aimed at. Silica aerogels are synthesized using the sol-gel technique with Hydrolysis, Condensation, Aging, Solvent change, and Surface modification, Drying main steps in general. According to the results obtained, it was determined that the densities of the aerogels produced were in the range of 0.66 to 1.053 g/mL, and the thermal conductivity values were in the range of 0.067 to 0.097 W/mK. The results show that many opportunities are available to improve the insulation property of aerogel, which is considered an important insulation material of the future.

1. Introduction

The need for energy, which is the most important indicator of economic and social development, continues to increase today due to population growth and technological developments. In order to ensure the continuity of the existing system, it is of great importance to ensure the maximum benefit from data sources. In this direction, focusing on insulation applications for thermal interactions in systems will contribute more to getting results. The purpose of insulation is to approach the theoretical cycle calculations by keeping the system as far away from the influence of the external environment as possible. This use may be an industrial process cycle, or it may also occur as a requirement for the conditioning of a living space.

Porous materials are at the forefront of research in terms of providing superior insulation properties and energy efficiency. Porous materials are used in many different fields, such as adsorbents, catalysts, and support materials, due to their large surface areas. The presence of nanometer-sized voids in their structure and their controllability have brought porous materials to an important place in terms of science and technology. The most important point that makes porous materials different and unique is the space inside the pore. The pore sizes of porous materials are classified into three different categories according to the international standard IUPAC (International Union of Pure and Applied Chemistry) definition. If their diameter is less than 2 nm, it is called a micropore; if it is between 2 and 50 nm, it is called a mesopore; and if it is larger than 50 nm, it is called a macropore [1].

Aerogel has become the insulation material that stands out as the most interesting alternative in this context. Aerogels are silica-based solid substances obtained by replacing the liquid component in their structure with air. It was first

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produced by Stefan Kistler in early 1931. The surface of aerogels, which consists of very small pores, is reminiscent of a sponge. Since there is 99.8% air in their structure, they are insulating, lightweight, and low-density materials. Aerogels are known as the lightest and lowest-density solids in the world [2]. For this reason, it is used in many different fields, such as isolation, storage and transportation media, sensors, catalysts, and separation processes. Silica-based aerogels are produced by the sol-gel method using silicon sources in an acidic or basic environment. The sources of silica used in the production of silica-based aerogels are usually Tetraethyl orthosilicate (TEOS), Tetramethyl orthosilicate (TMOS), sodium silicate, and water glass. The production cost can be reduced by using various industrial wastes while aerogel is synthesized. Considering this feature, there is a need to develop environmentally friendly methods [3].

There are various types of aerogels, such as carbon, silica, alumina, metal, and nanotube aerogels. It is the most widely used because it is synthesized from natural raw materials and is environmentally friendly; silica is an aerogel. Silica aerogels have superior properties such as high surface area, high porosity, low density, low dielectric constant, and high porosity. Aerogels are synthesized by the sol-gel method, which consists of gel preparation, aging, and drying stages [4].

In their study, Li and his colleagues produced silica aerogel at an atmospheric pressure of 40 ºC using the sol-gel process. In the analyses of the obtained silica aerogels, the bulk density of the silica aerogel was found to be 0.33 g/cm3, its porosity was 87%, the total pore volume was 3.31 cm3/g, the average pore diameter was 26.5 nm, and the specific surface area was 500 m2/g [5], [6]. In a study, it was found that silica aerogel, which was supercritically dried, contained fewer fire hazards and had lower smoke toxicity. However, in general, it has been found that hydrophobic silica aerogel is risky in terms of fire hazards [7]. In another study, Jones and colleagues evaluated the aerogel's low density, high porous structure, and ability to form a thermal barrier. It has been reported that composite materials consisting of silica aerogel and oxide will offer new possibilities for the design of thermoelectric devices and space studies [8].

In this study, different aerogel materials with high thermal resistance, insulation properties, and suitable mechanical properties were produced. In this regard, silica aerogels were synthesized using ethanol and methanol as TMOS and TEOS hydrolysis catalysts and NH4OH and NH4F as condensation catalysts. Then TMOS and TEOS were diluted with different concentrations of ethanol and methanol.

2. Material and Method

Silica aerogels are nanostructured materials that are of great interest due to their effective properties such as low density, transparency, high surface area and high porosity, and low thermal conductivity. Silica aerogels are three-dimensional nanostructured materials containing a cross-linked SiO2 network [9]. The properties of silica aerogels are also indicated in Table 1.

Table 1. General Properties of Silica Aerogels [9, 10].

Property	Value
Intensity	0.003 g/cm^3
Surface area	500-1000 m^2/g
Porosity	% 80-99.8
Pore diameter	20-150 nm
Primary connection diameter	2-5 nm
Thermal conductivity	0.017-0.021 W/mK
Sound speed	100 m/s
Dielectric constant	1.1
Refractive index	1-1.05

Silica aerogels are synthesized using the sol-gel technique with Hydrolysis, Condensation, Aging, Solvent change and Surface modification, Drying main steps in general. Aerogel synthesis begins with the creation of a gel with a porous structure, the pores of which are filled with liquid. Aerogel is obtained by replacing the liquid in the pores with air without changing the network structure of the gel. A two-stage sol-gel method was chosen to control the microstructure of aerogels.

2.1. Content of Silica Aerogel

In the synthesis of Silica Aerogel; Tetramethyl orthosilicate (TMOS-$Si(OCH_3)_4$) and Tetra-ethoxysilane (TEOS-$Si(OC_2H_5)_4$) were used as the source materials of silica; Ammonium Hydroxide (NH_4OH) and Ammonium Fluoride (NH_4F) as base catalysts; and Methanol (CH_3OH) and Ethanol (C_2H_5OH) as structural water removers. Within the scope of the experimental researche, the parameters affecting aerogel synthesis were examined. The properties of the materials used in the production of silica aerogel are given in Table 2.

Table 2. Properties of materials used in making aerogels [9], [10].

Material	Formula	Density kg/m³	Molar mass g/mol	Melting point °C	Boiling point °C
TMOS	$SiC_4H_{12}O_4$	1003	152.22	5	122
TEOS	$SiC_8H_{20}O_4$	940	208.33	-77	168
Ammonium hydroxide	NH_4OH	880	35.04	91.5	24.7
Ammonium fluoride	NH_4F	1001	37.037	100	260
Methanol	CH_3OH	792	32.04	-97.6	64.7
Ethanol	C_2H_5OH	789	46.07	-114.1	78.37

In the catalyst addition steps, the other steps are the same except that the catalysts are changed. The experiment consists of five stages. First of all, TMOS and TEOS were diluted with ethanol and methanol in different concentrations. Then, water and alcohol were added under continuous stirring to initiate hydrolysis. Condensation was initiated by the addition of the base catalyst, and the solution was filled into pre-prepared molds (5 mL).

2.2. Synthesis of TMOS and TEOS Solutions

The experimental procedure for the production of silica aerogel is as follows: Ammonium hydroxide solution is prepared by adding 5.4 mL of concentrated ammonium hydroxide to 1000 mL of water. During the hydrolysis stage, 10 mL of TMOS and 10 mL of methanol are filled into a beaker to form an alkoxide solution and mixed in a magnetic mixer until a homogeneous solution is formed. During the condensation stage, it is mixed with 5 mL of ammonium hydroxide stock solution and 10.0 mL of methanol in another beaker and mixed in a magnetic mixer until a homogeneous solution is formed. This mixture is the catalyst solution. Then, the solution formed by combining the alkoxide solution with the catalyst solution is mixed in a magnetic mixer at 25 °C for 3-5 minutes, and filling is performed into previously prepared molds. The gelling process is completed in an average of 8 to 15 minutes. After the gel hardens, the gel is allowed to age for at least 24 hours with methanol. The aging process is done by replacing the gel with methanol at least four times between a few days and a week. If liquid is observed in the gel, it is decided that it should wait for gelification.

It is the same as the TMOS stages, but the prescription is different. Ammonium fluoride/ammonium hydroxide solution is prepared by adding 1.852 g of NH4F and 22.78 mL of ammonium hydroxide solution to 100 mL of water. In the hydrolysis stage, 5 mL of TEOS and 11 mL of ethanol are filled into a beaker to form an alkoxide solution and mixed on a magnetic stirrer until a homogeneous solution is formed. In the condensation phase, 7.0 mL of distilled water and 11.0 mL of ethanol are mixed in another beaker, and 0.371 mL of ammonium fluoride/ammonium hydroxide stock solution is added. The aging process involves the addition of new monomers to the silica network and an increase in the degree of crosslinking of siloxane. The stiffness and strength value of the aerogel formed during aging increases and gel bonds strengthen. Gels prepared from the same solutions and having the same concentration by weight are placed in different aging solutions at the same time, while the control sample is transferred directly to ethanol or methanol. The contents of the different samples prepared according to the solution changes are given in Table 3. The realization stages of the synthesis of TMOS and TEOS silica aerogels are given in Figure 1.

Table 3. The content of produced Silica Aerogel samples.

No	TMOS g	TEOS g	Ethanol g	Methanol g	Pure water g	NH_4OH g	NH_4F g
1	-	5.26	19.56	-	8.21	0.06	0.006
2	-	5.52	20.54	-	8.63	0.07	0.007
3	11.66	-	-	18.1	5.55	0.027	-
4	12.24	-	-	19.0	5.97	0.029	-
5	10.35	-	8.03	-	5.04	0.025	-

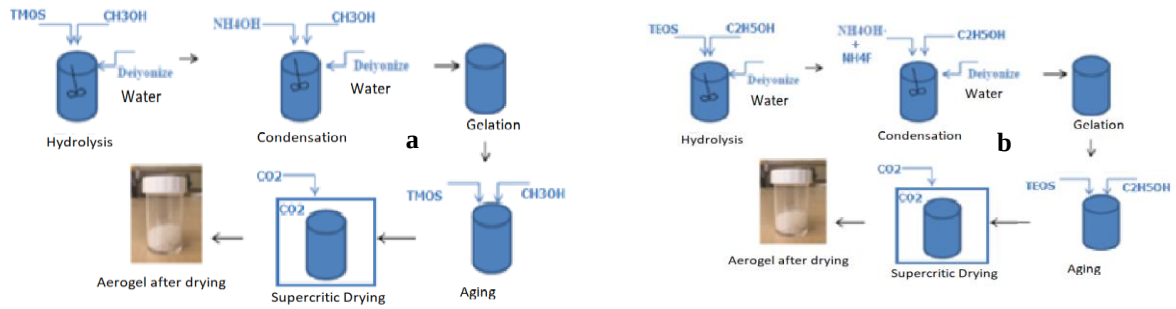


Figure 1. The synthesis of silica aerogels: a) TMOS b) TEOS.

The gelation time changes with the change in TEOS and TMOS concentrations in the solutions. This time may be as short as a few minutes, starting with the addition of the catalyst solution, and sometimes there may not be enough time for the solution to be molded. Since the gel adheres to the test tube after the gelation point is reached, drying was achieved without removing the molds in which gelation took place, thus producing aerogels with a monolithic structure. In addition, the use of round-shaped Teflon molds to reduce the adhesion forces in the gel pores and prevent adhesion has contributed to the formation of a crack-free monolith structure.

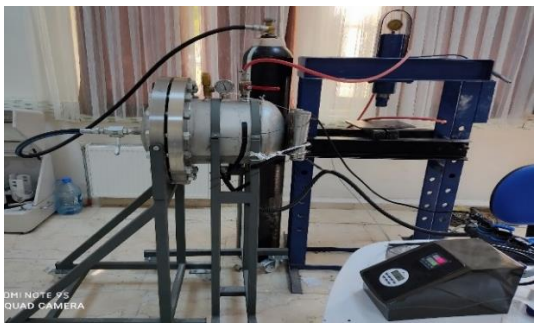


Figure 2. Supercritical drying experimental set.

The entire aerogel production process, including supercritical drying, takes about 3 days (Figure 2). Before the drying process is started, the wet gel-filled molds are placed in the reactor and filled with a sufficient level of alcohol to prevent initial evaporation. Then the lid is closed, and sealing is ensured with nuts and bolts on the reactor. The loading process is started by opening the valve for the liquid carbon dioxide. In order to prevent the pore structures of the gels contained in the reactor from deteriorating, the loading process is performed for 1 hour. Until the reactor reaches full filling, when the pressure inside the reactor is equal to the carbon dioxide tube pressure (55 bar), the reactor inlet valve is closed to ensure tightness control. After the impermeability is achieved, the solvent alcohol in the reactor is expected to be replaced with liquid carbon dioxide for 2 days. In this case, the speed of the drying process is mainly controlled by the diffusion of ethanol through the pores. In the next step, the supercritical drying state is passed.

In the supercritical process, first of all, heating is performed until the pressure inside the reactor reaches 82.7 kPa and the temperature reaches 40 °C. As the reactor is heated, the pressure will rise quite rapidly. The pressure control valve on the reactor switches to unloading if high pressures are reached and ensures that the pressure remains within safety limits. Thus, the pressure was reduced to 73.9 kPa (preferably higher pressure) by using the discharge valve on the reactor, as shown in Figure 3.

Figure 3. CO_2 reaching supercritical state in the reactor.

In this case, the temperature inside the reactor was kept constant at around 31.1 °C, allowing the carbon dioxide gas to reach the critical state. This critical situation has been ensured to last for at least 3 hours. After completely replacing the ethanol contained in the pores of the gel with supercritical carbon dioxide, the carbon dioxide gas was completely discharged from the reactor by reducing the pressure by 7 kPa per hour. The aerogels obtained after the supercritical drying stage were brought to room temperature, and it was ensured that they took their final form. After all the stages of the drying process have been completed, the condition of the gels is given in Figure 4.

Figure 4. TEOS-TMOS aerogels after drying.

2.3. Test Methods Applied to Aerogel Samples

Several test methods applied to aerogel samples were carried out as follows: Thermal, physical, and material characterization tests. The thermal and physical tests consist of density and mass loss determination and thermal conductivity tests, and the characterization consists of porosity, specific surface (bet surface) determination, XRD, and SEM tests.

Sol-gel and Air-gel samples prepared in certain volumes (V) in accordance with the known recipe are weighed with an accuracy of 0.01 grams, and the density values are calculated by taking the average of the three samples.

$$\rho_k = \frac{M_k}{V} \quad (1)$$

The thermal conductivity test was determined by using a Thermtest portable device, as indicated in Figure 5. The Thermtest device uses the Transient line source (TLS) method for thermal conductivity measurement. After the heating period is complete, temperature readings are taken at the same intervals throughout the cooling period. The thermal conductivity is then calculated from this temperature information using the following equation:

$$k = \frac{q}{4\pi a} \quad (2)$$

where k is the thermal conductivity (W/mK), q is the heating power of the needle, and a is the slope of the line for temperature rise over the log of time.

Figure 5. Thermal conductivity tests applied to aerogels.

Scanning electron microscope (JEOL JSM 7001F) device for the acquisition of SEM images for the examination of the surface morphological changes of the produced aerogel materials. The surface area and pore analysis (Micromeritics-TriStar II Plus 3030) device was used for pore characterization, and the X-ray diffractometer (Bruker D8 Advance) device was used for crystal structure analysis.

3. Results and Discussion

In this study, different aerogel samples were produced with the synthesis of TMOS and TEOS alkaline solutions. The thermophysical and microstructure properties of the aerogel samples were determined by applied tests, and the results are shown in Table 4. It was determined from the results that the densities of the produced aerogels were in the range of 0.66 to 1.053 g/mL, and the thermal conductivity values were in the range of 0.067 to 0.097 W/mK.

Table 4. The content of produced Silica Aerogel samples.

No	Density of Sol-gel g/mL	Density of Aero-gel g/mL	Thermal conductivity W/mK
1	0.946	0.589	0.087
2	0.990	0.620	0.091
3	1.002	0.636	0.092
4	1.053	0.670	0.097
5	0.660	0.420	0.067

When the results obtained were examined, it was seen that samples with higher values of density and thermal conductivity were obtained compared to the literature. The expected thermophysical targets have not been fully achieved; however, the thermal conductivity values of the samples are below 0.1 W/mK, which shows that they can be used as an insulating material. In addition, it was determined that an increase in the concentrations of TEOS and TMOS sol-gels during the production phase caused an increasing trend in density and indirectly in thermal conductivity values for those aerogels.

Pore size distribution (BET), surface morphology (SEM), and crystal structure (XRD) analyzes play an important role in the characterization of the produced materials. Thanks to these analyses, the properties of materials produced under different conditions and contents can be compared, and performance evaluations can be performed.

SEM images of silica aerogels at different magnification ratios (x500, x1000) are given in Figure 6. When the morphology of all silica aerogels was investigated, it was generally seen that spherical particles with nanometer sizes form agromel (combined) structures. These combined structures vary in the range of 2-20 μm. Although the surface morphologies of aerogels produced by three different methods are very close to each other, it can be clearly detected from SEM photographs that they exhibit regional differences.

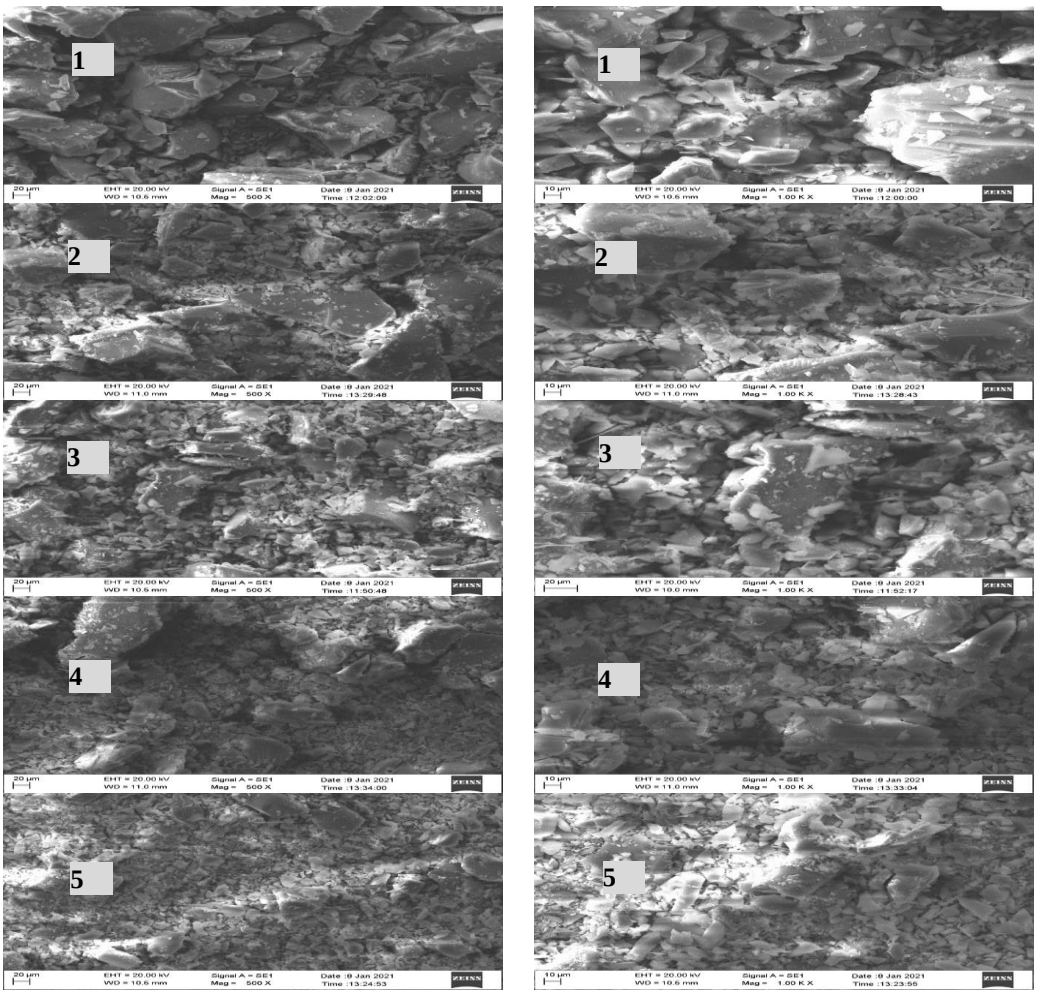


Figure 6. SEM images of synthesized silica aerogels at different magnifications (x500, x1000).

The results obtained from the Sem analysis show that aerogels have advanced micro and primary mesopores. The XRD patterns of the synthesized silica aerogels are shown in Figure 7. The broad bands seen around 2θ=22° in the diffractograms proved that silica materials in an amorphous structure were obtained.

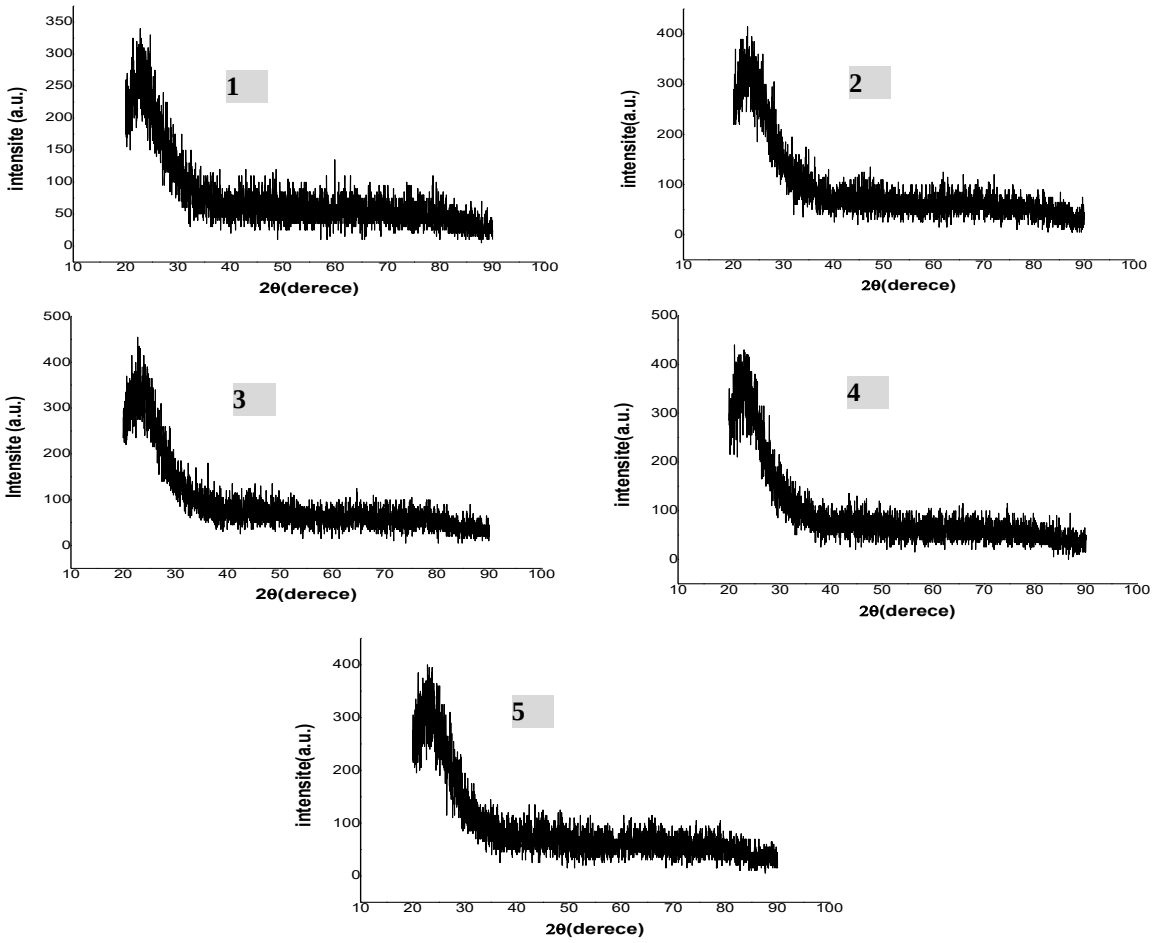


Figure 7. XRD patterns of synthesized silica aerogels.

The surface area (m^2/g), pore size (nm), and porosity (%) of the silica aerogels synthesized in the study are given in Table 5. When the table is examined, it is seen that the highest surface area belongs to TMOS + Ethanol aerogel. In Figure 8, adsorption-desorption isotherm curves in the bet analysis were performed. The fact that the values and changes are very close to each other shows that the materials produced are structurally very close to each other.

Table 5. The porosity values of the silica aerogels.

No	Average pore diameter nm	Porosity %	Specific surface m^2/g
1	2.84	88.85	662.08
2	3.50	86.45	653.15
3	3.41	84.89	646.08
4	3.19	78.76	608.88
5	3.09	96.36	715.53

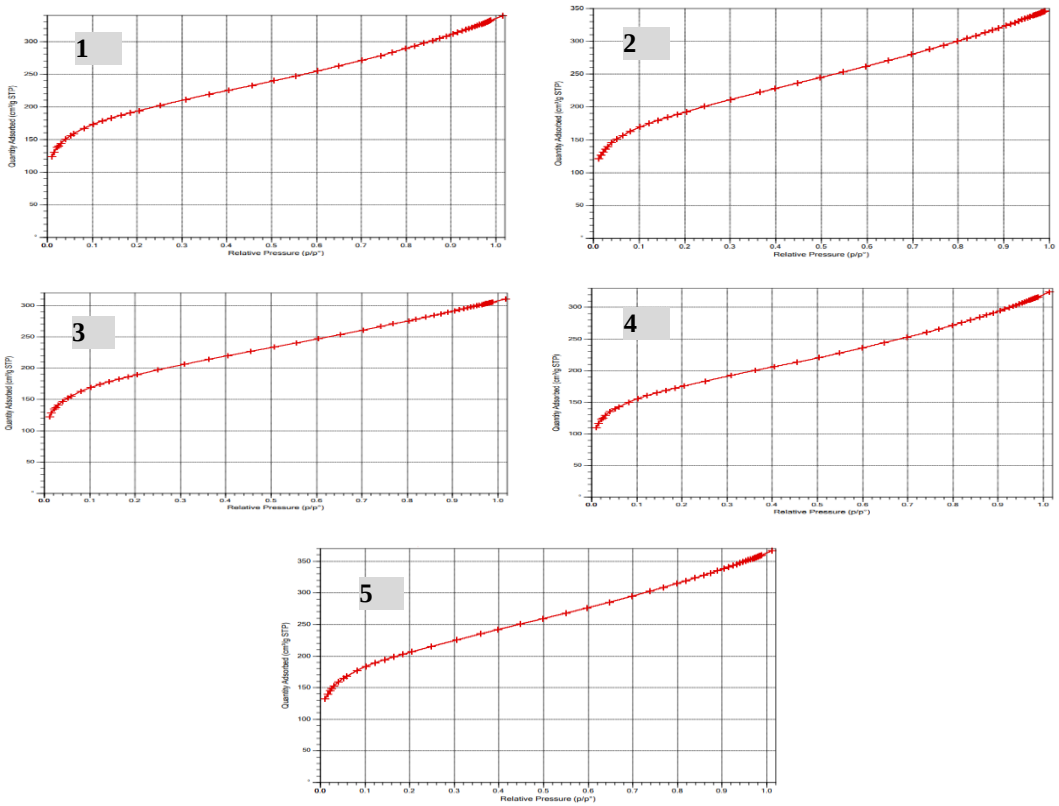
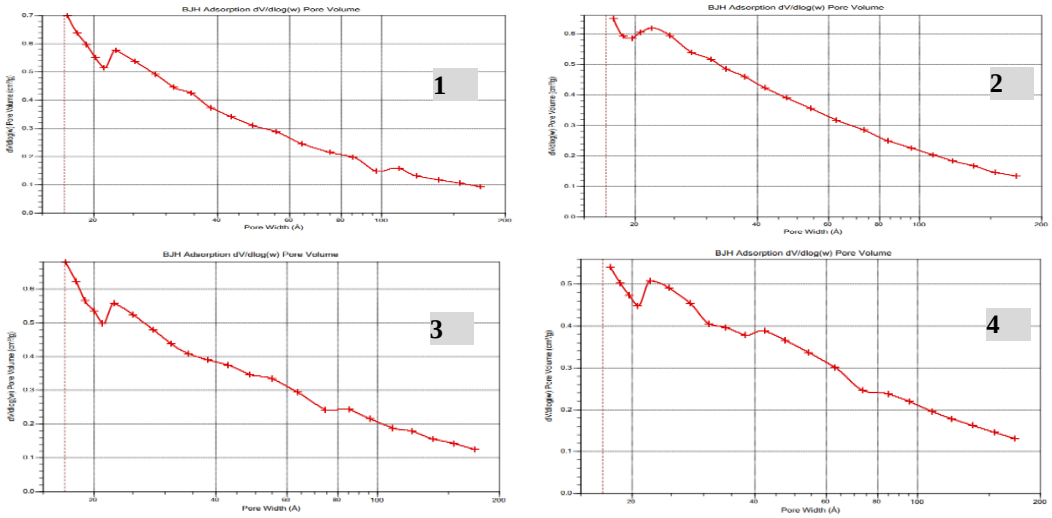


Figure 8. Adsorption-desorption isotherm curves of aerogel samples.

It can be said from Figure 9 that the N_2 adsorption isotherms of the produced aerogels comply with the combination of Type II and Type IV isotherms in the B.D.D.T. (Brunauer, Deming, Deming and Teller) classification defined according to IUPAC (International Union of Pure and Applied Chemistry, 1985). This indicates that aerogels have advanced micro and primary mesopores whose radii are between 2nm and 50 nm.



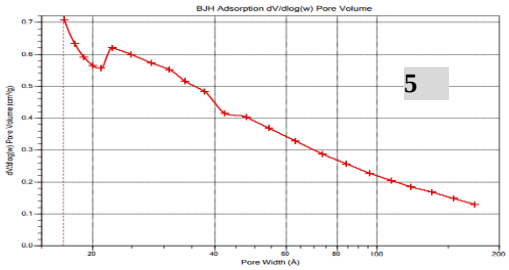


Figure 9. Space distribution curves of synthesized aerogel samples.

4. Conclusion and Suggestions

In this study, five different syntheses were applied for the production of aerogels; the necessary tests were performed, and the determined data were analyzed. According to the results obtained, it was determined that the densities of the aerogels produced were in the range of 0.66 to 1.053 g/mL, and the thermal conductivity values were in the range of 0.067 to 0.097 W/mK. Due to the thermal conductivity values of the samples formed being below 0.1 W/mK, they can be used as an insulating material. In addition, the increase in TEOS and TMOS concentrations during the production phase has led to an increase in the density and thermal conductivity of aerogel samples. To solve the problem, the integration of a carbon dioxide drainage line for solvent removal provided partial improvements. Due to the large internal volume of the reactor and, in particular, the inability to control the temperature stages precisely, the structural effects of different pressure-temperature transition processes have affected the approach to the targeted thermophysical properties. Factors such as the fact that the drying process is carried out under high-pressure conditions such as 100 bar, the long and arduous preparation process, and the high cost of the chemicals used have limited the number of solution trials. As a result of this study conducted with limited facilities, it is thought that if the necessary supports are provided, many opportunities are available to improve the insulation property of aerogel, which is considered an important insulation material of the future.

Contributions of the authors

M.Z. IŞIK and M. KAYIR conceived of the presented idea. H. OKTAY developed the theory and H. SAYĞILI performed the test. M.Z. IŞIK and H. OKTAY verified the analytical methods. M.Z. IŞIK encouraged M. KAYIR to investigate [a specific aspect] and supervised the findings of this work. All authors discussed the results and contributed to the final manuscript.

Conflict of Interest Statement

There is no conflict of interest between the authors.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics

References

[1] A. Enes, "Silika Aerojel Sentezinde Farklı Katalizör Kullanımının Etkisi ve Adsorpsiyon Kapasitesinin Belirlenmesi," Gazi Üniversitesi, Ankara, 2019.

[2] R. Baetens, B. P. Jelle, and A. Gustavsen, "Aerogel insulation for building applications: A state-of-the-art review," *Energy Build.*, vol. 43, no. 4, pp. 761–769, 2011.

[3] N. K. Mermer, "Silika Temelli Aerojellerin Sol-Jel Yöntemi ile Sentezi ve Yapısal Özelliklerin İncelenmesi," Yıldız Teknik Üniversitesi, Istanbul, 2018.

[4] N. Saraç, "Silika esaslı doğal hammadde ve atıklardan aerojel tozu üretimi ve karakterizasyonu," Sakarya Üniversitesi, Sakarya, 2018.

[5] T. Li and T. Wang, "Preparation of silica aerogel from rice hull ash by drying at atmospheric pressure," *Mater. Chem. Phys.*, vol. 112, no. 2, pp. 398–401, 2008.

[6] Y. Yilmaz, "Farklı başlangıç maddeleri kullanılarak sol-jel yöntemiyle monolitik silika aerojel ve silika aerojel sentezi ve karakterizasyonu," Gazi Üniversitesi, Ankara, 2013.

[7] Z. Li, X. Cheng, L. Gong, Q. Liu, and S. Li, "Enhanced flame retardancy of hydrophobic silica aerogels by using sodium silicate as precursor and phosphoric acid as catalyst," *J. Non Cryst. Solids*, vol. 481, pp. 267–275, 2018.

[8] S. M. Jones, "Aerogel: Space exploration applications," *J. Solgel Sci. Technol*., vol. 40, no. 2–3, pp. 351–357, 2006.

[9] N. Siyin, "Yüksek Sıcaklık Isı Yalıtım Uygulamalarına Yönelik Üstün Performanslı Aerojel Şilte Sentezi ve Karakterizasyonu," İstanbul Teknik Üniversitesi, İSTANBUL, 2016.

[10] S.-W. Hwang and S.-H. Hyun, "Capacitance control of carbon aerogel electrodes," *J. Non Cryst. Solids*, vol. 347, no. 1–3, pp. 238–245, 2004.