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Experimental method to determine the pore structure and pore size distribution of gamma alumina (γ-Al_2O_3) material

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Abstract

Gamma Alumina (γ-Al_2O_3) is a material with many good properties such as small pore size, high specific surface area, highly hygroscopic, and low melting temperature. These characteristics are very suitable for making adsorbent and catalyst carriers. Gamma alumina is widely applied in many industries such as petrochemical industry, chemical industry, and pharmaceutical industry. Therefore, the identification of the characteristics of the Gamma Alumina material is very important and helpful. In this research, experiments will be carried out to determine the pore structure, the pore size distribution of γ-Al_2O_3 particles. Modern and appropriate experimental methods are applied. Descriptions of the experimental methods and equipment are given. The first experiment is the pore structure determination of the material by using environmental scanning electron microscopy (ESEM). The second one is the pore size distribution determination with the help of Hg-porosimetry method. Experimental results will be presented and discussed.

Keywords. Pore structure, pore size distribution, gamma alumina.

1. INTRODUCTION

Due to their highly hygroscopic property, γ-Al_2O_3 materials are used in many different industrial processes such as drying, acid removal, steam purification, hydrocarbon adsorption, etc. For example, this material can be used for making adsorbent and catalyst carriers. In chemical industry, gamma alumina is used to separate polycyclic compounds and volatile organic compounds. In environmental technology, this material can be used to extract arsenic and fluorine in water treatment systems. In oil and gas industries, gamma alumina has the application as selective adsorption, applying to separate liquids and gases. Also in petrochemical industry, gamma alumina can be used as a catalyst for a wide variety of reactions, such as steam reforming, and dehydrogenation [1, 11]. With such advantages and widespread applications, research on Al_2O_3 is very important and necessary.

Besides other properties, the pore structure and pore size distribution are the two most important characters. In order to investigate the pore structure, one modern method that is the environmental scanning electron microscopy (ESEM) can be used. The history of electron microscopy began in the 1920s with the development of electron optics [3]. Following this, many investigations have been made to get the SEM today. The main components of a SEM are an electron column which creates a beam of electrons; a sample chamber where the electron beam interacts with the sample; a detector in which monitor of signals and viewing system to construct images from the signals [2]. In order to get the topography of the sample, in the SEM equipment, either low energy secondary electrons which is ejected from the sample surface or higher energy backscatter electrons which reflected from the sample, is used. The signals are collected by a detector requiring high vacuum environment. The ESEM is a development of SEM in which vacuum gradient is used to maintain high vacuum conditions. The ESEM imaging provides useful information about internal structure of materials. The advantage of ESEM is that it can provide detailed three-dimensional and topographical imaging, the versatile garnered from different detectors as well. Consequently, we can get very accurate experimental results from ESEM. ESEM is normally an associated software to make operation user-friendly. The technological advances in ESEM allow the generation of digital data. In addition, SEM and ESEM equipment work fast compared to other materials analysis methods like BET. BET (Brunauer–Emmett–Teller) is an analysis technique for the measurement of the specific surface area of materials. The BET theory is applied to multilayer adsorption systems. BET theory depends on the adsorbate molecule and cross-section, so that this method is only suitable for mezzo-pore materials in which the pore diameters are larger than 20 Å. As for micro pore (with a diameter less than size 20 Å), we need other methods to determine the material properties. We can overcome this problem by using ESEM. Besides advantages, SEM and ESEM methods also have disadvantages. The first disadvantage is the cost. ESEM equipments are expensive. The second one is that these instruments are large and need to put in an area which is free of electric, magnetic or vibration interference. The third is in order to operate ESEM equipment, we need special training. The sample is also required well prepared before being placed in the sample chamber. However, with many outstanding advantages, nowadays SEM and ESEM techniques have wide applications in many industries [5-8]. More information on SEM and ESEM can be found, for example, in the work of Athene [2] or in the work of Bogner et al. [3].

To determine the pore size distribution of porous material, a well know experiment method can be used, it is mercury porosimetry [4]. By using this method, material's porosity can be characterized by applying various levels of pressure to a sample immersed in mercury. The size of the pores inside the sample is inversely proportional to the value of the pressure required to intrude mercury into the sample's pore. The pore size distribution of the sample can be determined by monitoring the pressure and the intruded volume of mercury [15, 17]. In this research, experiments have been carried out to investigate two above characteristics of gamma alumina particles. Explanation of equipment will be shown. Experimental results will be presented and discussed.

2. MATERIALS

The typical properties of the sample as given by Almatis AC, Inc. [19] are presented in tables 1 and 2. Table 1 introduces the major components of the sample. Selected physical properties of a particle are presented in table 2. Note that in this table, based on the original information, properties have been transformed into relevant volume specific quantities with an assumption of 40 % bed porosity for a packing of monodispersed spheres.

Table 1: Chemical properties of γ-Al_2O_3 particle F-200

Components	Weight percentage (%)
Al_2O_3	93.10
SiO_2	0.02
Fe_2O_3	0.02
Na_2O_3	0.03
Loss on ignition	6.83

Table 2: Selected physical properties of γ-Al_2O_3 particle F-200

Properties	Value
Diameter, mm	4.80
Volume specific surface area a_v, $m^2.cm^{-3}$	436.00
Porosity ψ, %	0.64
Density of particle ρ_0, $kg.m^{-3}$	1282.00

3. INVESTIGATION OF THE PORE STRUCTURE BY ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY (ESEM)

3.1. Experimental Equipment

Scanning electron microscopy (SEM) is widely used in micro analyses of materials. This method creates magnified images by using electrons instead of light waves and shows very detailed monochromatic images. The working principle of a SEM instrument is depicted in figure 1. Firstly, the non-metallic samples should be made to conduct electricity (by coating with a very thin layer of gold in a so-called sputter coater) before the experiment takes place (this is because the SEM instrument illuminates the sample with electrons in the microscope's vacuum column and electrical charges must be removed). The sample is then glued firmly into a basket and put into the sample chamber. A beam of high-energy electrons is produced by an electron gun, which uses filament-heating supply, at the top of the microscope. This electron beam flows through the vacuum column of the microscope in the vertical direction. The use of a vacuum is compulsory to avoid burn, ionization or low contrast and obscured details of the image. The electron beam is then condensed by a condenser lens and focused on a very fine spot on the sample by the objective lens. A set of scanning coils near the bottom, which is energized by varying the voltage produced by the scan generator, creates a magnetic field that moves the focused beam back and forth across on the sample. As the electron beam hits the sample, secondary electrons (or backscattered electrons) are emitted from the sample surface. These electrons are then counted by a detector, converted to signals and amplified. The final image corresponding to the topography of the sample is built from these signals. More information on SEM can be found, for example, in the work of Athene [2] or in the work of

Bogner et al. [3].

The environmental SEM (ESEM) is a modified version of SEM that allows the examination of a sample in a gaseous environment. This means that the ESEM can also be used to examine wet samples. When ESEM is used, it is not necessary to coat the sample surface with a thin layer of gold. In an ESEM instrument, the secondary electrons, which are emitted from the sample surface, are attracted to the positively charged detector electrode (figure 2). Because the sample is put in a gaseous environment, collisions between electrons and gas molecules occur during the movement of the electrons. This causes the emission of more electrons and ionization of the gas molecules and leads to an increase in a number of electrons, which effectively amplifies the original secondary electron signal. The positively charged gas ions are attracted to the negatively biased specimen and offset charging effects. The variation of the amplification effect depends on the number of secondary electrons. The larger the number of electrons emitted from a position on the sample, the more intense the signal. The difference in signal intensity from different locations on the sample allows an image to be formed.

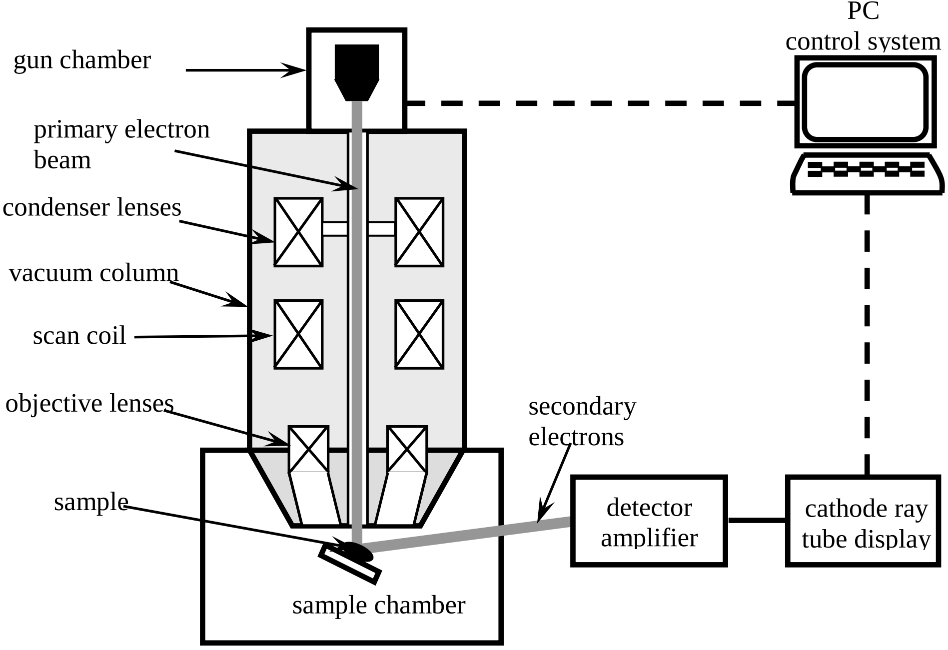

Figure 1: The major components of a SEM

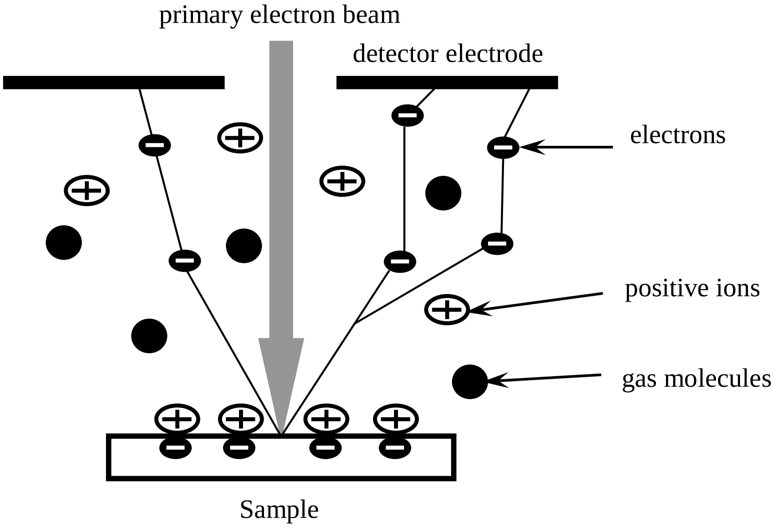

Figure 2: Sample and detector electrode in an ESEM

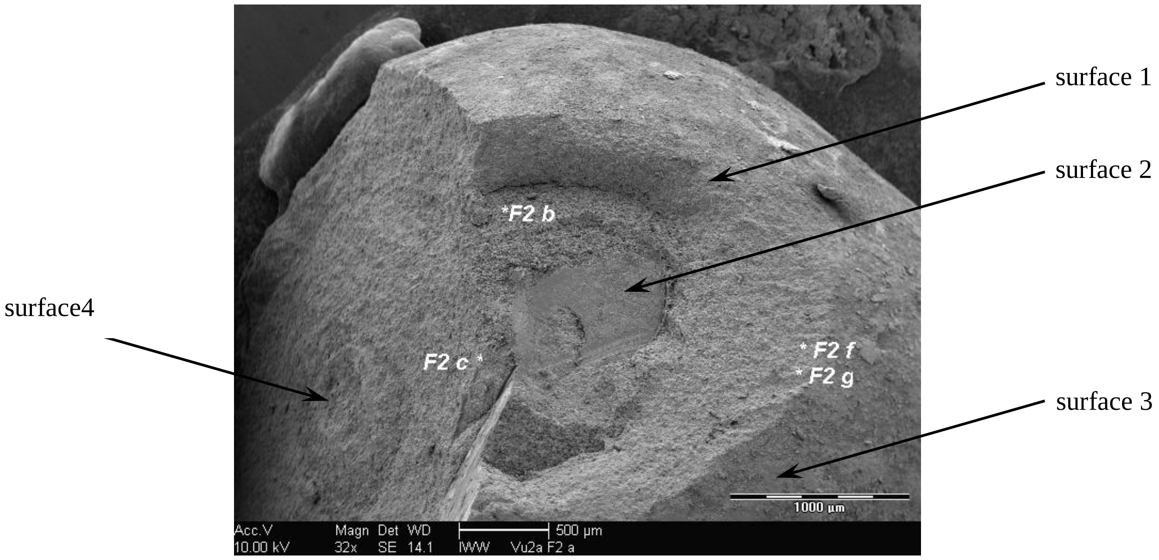

Figure 3: Microphotographs of a γ-Al_2O_3 particle surfaces: macroscopic scale

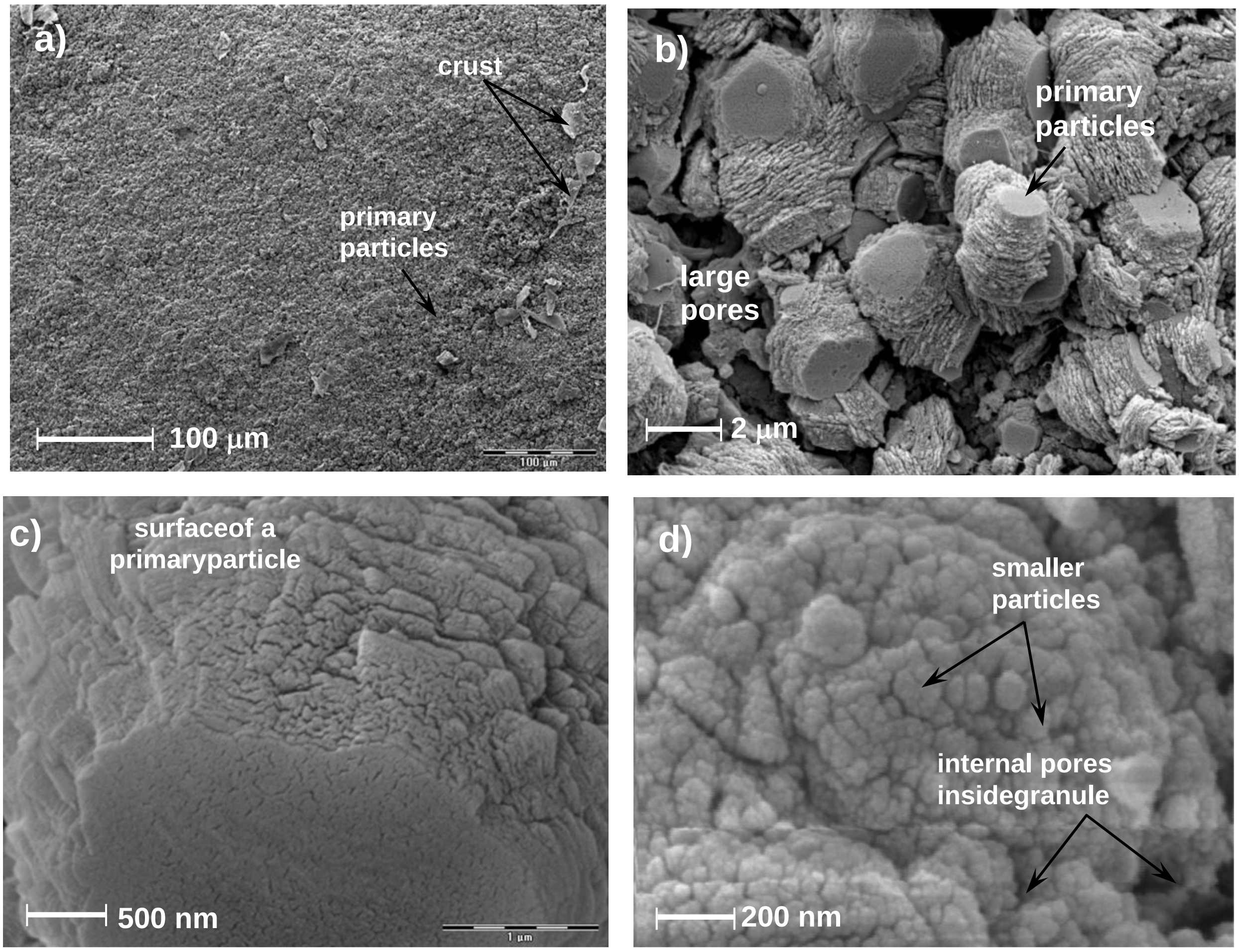

Figure 4: Microphotograph of surface of a γ-Al_2O_3 particle (corresponding to surface 1 in figure 3): microscopic scale

3.2. Experimental Results

Two samples (particles) are analyzed by ESEM. The first sample is a “raw” or original particle that is not subjected to any type of preparation (neither soaked with water nor dried). The second sample is a "product" particle. The "product" particle is obtained by firstly saturating an original particle with water and then drying it at different temperatures. After being dried, the color of the surface of the "product" particle is different from that of the original one. The two particles are then crushed so that the internal structure can be observed by ESEM.

The observation shows that the two particles contain several layers due to the production process. The color inside the "product" particle is the same as the "raw" particle. At the macroscopic scale, the investigation of the structure concerns the particle surface (surface 1), the surface of the inner shell (surface 2), the cross-section between two shells (surface 3) and the cross-section of the particle (surface 4). These surfaces are depicted in figure 3. At the microscopic scale, some selected ESEM microphotographs are shown in figure 4.

4. MEASUREMENT OF PORE SIZE DISTRIBUTION BY Hg POROSIMETRY METHOD

4.1. Experimental Setup

The experimental method of mercury porosimetry for the determination of the pore size distribution of porous material is well known. Mercury (Hg) is used because of its non-wetting property. For the measurement, it is assumed that when mercury is in contact with a porous medium the surface tension σ and contact angle θ of mercury is constant at a given condition. When a pressure P is applied to make mercury intrude into the pores of the porous medium, the higher the pressure P, the smaller the pores being invaded. The relationship between the pressure and the pore radius r is given by the Washburn equation [13, 14]:

$$P = -\ 2\sigma\cos\theta\ /r \qquad (1)$$

By monitoring the pressure P and the intruded volume V, the pore size distribution of the sample can be determined. During one experiment, mercury is first intruded into the pores with increasing pressure and then extruded when the pressure is released. More details on the Hg porosimetry method can be found, for example, in the work of Lowell and Shields [17].

One experiment was carried out at the Laboratory of Institutfür Verfahrenstechnik, University Magdeburg, with Pore sizer 9320 by Micromeritics. In this experiment, 57 "raw" or original particles (not yet subject to any type of preparation such as soaked with water or dried) are packed in a tube and vacuum is applied to assure that the pores are empty. Mercury is then applied to fill the volume between particles. This process continues until the pressure reaches the value of 5.17 bar corresponding to the mean pore radius of 1.360 μm. After that, the pressure is increased up to the maximum pressure of 1720.32 bar in order to obtain the pore size distribution inside the particles. Physical parameters of mercury used in this experiment are shown in table 3. With the assumption that all particles used in the experiment have an average diameter of 5 mm.

Table 3: Physical properties of Hg

Specifications	Value
Contact angle, degrees	130
Surface tension, N.m^{-1}	485.103

4.2. Experimental Results

The experimental results are converted for one particle in table 4.

Table 4: Summary of experimental results by Hg-porosimetry

Specifications	Value
Total intrusion volume V_{in}, cm^3	0.0153
Volume specific pore area a_v, m^2.cm^{-3}	51.19
Density of particle ρ_0, kg.m^{-3}	1288.7
Porosity ψ, %	23.36

Figure 5 illustrates on a logarithmical scale the intrusion volume of mercury versus pore radius. By integrating this curve, the volume of pores within the particles can be obtained. We consider three areas under the curve corresponding to three ranges of pore radius. The first area is the area from point A to point B. In this area, the mean pore radius is in the range of 1.360 to 207.174 μm. It is clear that this area represents the volume between particles with some small contribution from large pores of the particles. In the calculation, this area is ignored because of its small value compared to the remaining areas. The second area (point B to point C) is the main area and this area is used in the calculation of the pore size distribution of the particles. In this area, the mean pore radius varies from 1.360 μm to 3.3 nm which corresponds to the maximum intrusion pressure of 1720.32 bar of the experimental device. Due to this limited maximum pressure of the device, it is physically impossible to detect pores of smaller size (or pores which are separated by "bottle necks" of this size from the outside). The missing part is confirmed by comparing the obtained results with the product data given by table 4. Actually, only around 37% of the pore volume of the particles is measured, the other 63% are missing. One way to overcome this problem could be to vary the missing part of pore size distribution in order to get the best correspondence between experiments, drying data and drying model. Another possibility is the use of other techniques such as Helium adsorption.

The investigation results can be used to calculate some parameters of the continuous model. For example, the relative permeabilities for liquid k_w and for gas k_g phases are calculated from the following relationship

$$k_w = \begin{array}{ll} 0 & X > X_{irr} \\ S_{fw}^{3} & X \leq X_{irr} \end{array} \qquad (2)$$

$$k_g = \begin{array}{ll} 1 & X > X_{irr} \\ 1 + 2S_{fw} - 3S_{fw}^{2} & X \leq X_{irr} \end{array} \qquad (3)$$

where S_{fw} is saturation of free water. X is moisture content and X_{irr} is the irreducible moisture content.

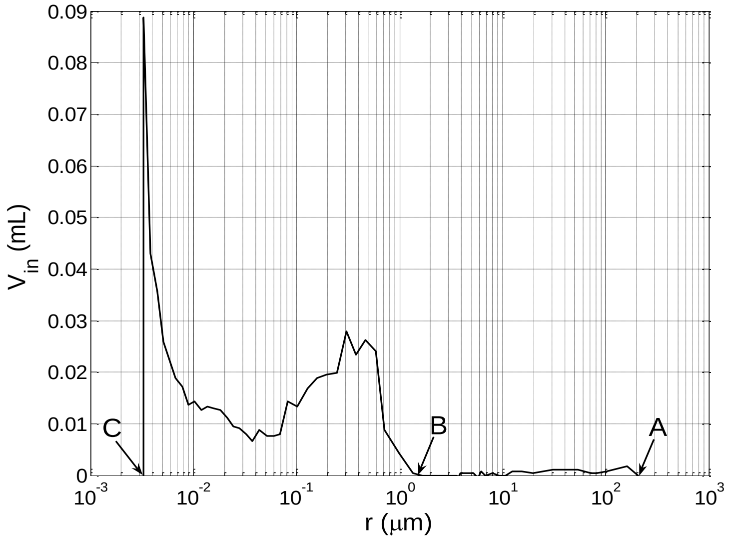

Figure 5: Pore volume distribution - mercury intrusion curve

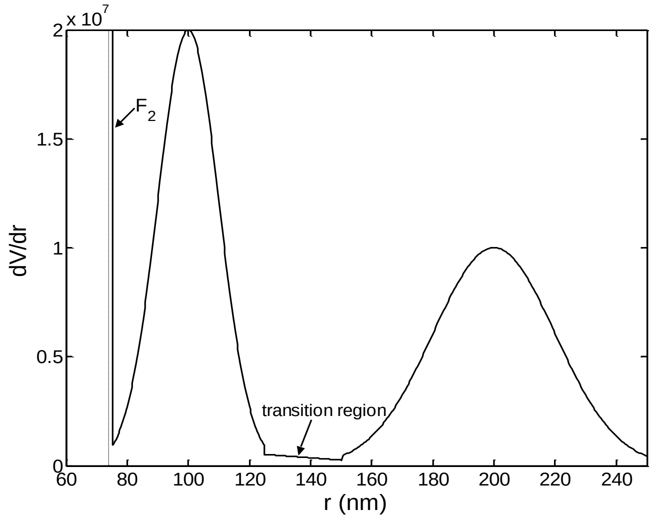

Figure 6: Pore volume distribution - mercury intrusion curve

The effective diffusivity is calculated from

$$D_{eff} = 0.2 \,.\, \delta_{va} \,.\, k_g \qquad (4)$$

with δ_{va} is the binary diffusivity of vapor in air and kg is the relative permeability of gas. These parameters can be treated as bimodal pore size distribution. An example of the bi-modal with $r_1 = 100 \pm 10$ nm; $r_2 = 200 \pm 20$ nm is presented in Figure 6. In this example, r1 is the radius of small pore and r2 is the radius of the big pore.

4. CONCLUSION

To conclude, in this work, the experiments to determine the pore size structure and the pore size distribution of γ-Al_2O_3 particles are presented. By using the environmental scanning electron microscopy (ESEM), it is observed that the samples have a bimodal pore size distribution with large pores (approximately 1.5 μm) and small pores (approximately 15 nm). The pore size distribution of the sample is studied using Hg-porosimetry. However, due to the limitations of the device, not all small pores can be detected. To overcome this problem, it is suggested to vary the missing part of pore size distribution or to use other techniques such as Helium adsorption.

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