Effect of Wood Flour Addition on the Pore Volume and BET Surface Area Properties of the Prepared Gamma Alumina (γ-Al_2O_3) Extrudates Used in Catalyst Carriers

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ABSTRACT

The effect of Wood Flour addition to the gamma alumina powder used in the preparation of gamma alumina (γ-Al_2O_3) catalyst carrier extrudates on the pore volume and BET surface area physical properties was investigated. Two parameters which are size of wood flour particles and its quantity were studied. The sizes of wood flour particles used are 150 µm, 212 µm and 500 µm and the weight percentage added to the gamma alumina powder during the preparation of the extrudates are (1%, 3%, 5% and 10%). The results showed that the addition of wood flour to the gamma alumina powder in order to get gamma alumina extrudates used as catalyst carrier is one of the successful methods to improve the pore volume and BET surface area of the alumina extrudates. The size of wood flour particles and its quantity have main effect on the above texture properties. The smaller the size of wood flour leaded to higher BET surface area, where maximum BET surface area of 127.3 m^2/g was got with addition 10% by weight wood flour of 150µm particle size. BET surface area for the same addition percentage of 10% resulted to 114.5m^2/g and 105.2m^2/g when adding wood flour of 212 µm and 500 µm particle sizes respectively. The weight percentage of wood flour addition has an effect on the BET surface area, where the 3% addition gives maximum BET surface area when the size of the wood flour particles is 500 µm. Regarding the pore volume property for the gamma alumina prepared extrudates, the results showed that the pore volume of the extrudates increased to 0.83 cm^3/g and 1.0 cm^3/g when 10% wood flour of 150 µm and 500 µm particle sizes were added respectively. The maximum BET surface area was reached when 10% wood flour of 150 µm particle size was added, and the maximum pore volume was reached when 10% wood flour of 500 µm particle size was added, the increase percentage for the BET surface area and pore volume is more than 40% and 400% respectively.

Key words: pore volume, BET surface area, texture properties, gamma alumina extrudate.

تأثير إضافة طحين نشارة الخشب على خواص حجم المسام والمساحة السطحية نوع BET لمبثوقات الكاما ألومينا المستخدمة كحامل للعوامل المساعدة

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الخلاصة

تم إجراء هذا البحث لمعرفة تأثير إضافة طحين نشارة الخشب إلى مسحوق ألكاما ألومينا (γ-Al_2O_3) المستخدم في تحضير مبثوقات الحامل للعوامل المساعدة الكاما ألومينا على خاصيه المساحة النوعية (BET) وحجم المسام . تم دراسة تأثير متغيرين وهما الكمية وحجم الدقائق لطحين نشارة الخشب المضافة الى مسحوق الكاما الومينا ، حيث تم استخدام حجوم دقائق طحين النشارة بمقدار 150 µm، 212 µm و500 µm ، بينما النسب الوزنية المضافة الى مسحوق الكاما الومينا المستخدم

في تحضير العجينة لانتاج مبثوقات الكاما ألومينا كانت (1%، 3%،5% و 10%). أظهرت النتائج إن إضافة طحين نشارة الخشب الى مسحوق الكاما الومينا عند تحضير العجينة المستخدمة لانتاج مبثوقات الكاما الومينا من اجل استخدامها كحامل للعوامل المساعدة ومن اجل تحسين خواص حجم المسام والمساحة السطحية نوع BET هي عملية ناجحة في تحسين الخواص النسيجية أعلاه عند تحضير المبثوقات، وإن حجم دقائق طحين النشارة المستخدمة وكميتها لها تأثير أساسي على الخواص النسيجية اعلاه. كلما كان حجم دقائق طحين الخشب أصغر يؤدي إلى مساحة سطحية نوع BET أعظم ، حيث تم الحصول على أعظم مساحة BET بمقدار127.3 م^2/غم عند اضافة 10% وزنا نشارة خشب ذات حجم 150 µm عندما كان حجم دقائق طحين النشارة 150 µm ومساحة نوعيه (BET) بقيم 114.5 م^2/غم و 105.2 م^2/غم عندما كانت حجوم دقائق طحين نشارة الخشب هي 212 µm و 500 µm على التوالي. إن متغير نسبة طحين نشارة الخشب المضافة له تأثير على المساحة السطحية نوع BET ، حيث تم الحصول على مساحة عظمى عند اضافة 3% طحين خشب ذو حجم دقائقµm 500.
فيما يخص خاصية حجم المسام للمبثوقات كاما الومينا المحضرة فقد أظهرت نتائج الدراسة أن حجم المسام ازداد الى 0.83 سم^3/غم و 1.0 سم^3/غم عند إضافة 10% طحين خشب ذو حجم دقائق 150 µm و500 µm على التوالي. أعظم مساحة نوعية (BET) تم التوصل اليها كانت عند اضافة 10%طحين خشب ذو حجم دقائق 150 µm واعظم حجم مسام تم التوصل اليه كان عند اضافة 10% طحين خشب ذو حجم دقائق 500 µm ، أن نسبة الزيادة في المساحة النوعية كانت اكثر من 40% ونسبة الزيادة في حجم المسام كان اكثر من 400%.

الكلمات الرئيسية: حجم المسام، المساحة السطحية نوع BET ، الخواص النسيجية، مبثوقات الكاما ألومينا.

1. INTRODUCTION

Catalytic supports are low activity materials or totally inactive materials for most of the reactions that supported catalysts will be used for it, **Derouane, et al., 2001**.The size and number of pores determine the internal surface area. It is usually advantageous to have high surface area (large number of small pores) to maximize the dispersion of catalytic components. However, if the pore size is too small, diffusional resistance becomes a problem, **Antos, et al., 1995.** Surface area, pore volume and pore volume distribution are important properties among which strongly associated to the adsorption capacity .Large surface area and high pore volume are widely used in chemical and gas separation, medicine and catalyst while total surface area may supports the accessibility of active site relating to the catalytic activity. In addition, value of surface area is proportional to the productivity of the catalyst when adsorbent is used as catalyst support. This is because of the fact that it provides larger area per unit mass of catalyst for the chemical reaction. Micropore volume on the other hand determines adsorptive capacity and the frequency of regeneration of the adsorbent required during adsorption –desorption cycles. Obviously, adsorbents having larger micropore volume and surface area are preferred in purification and bulk separation processes, **Allwar, 2012 and Vyas, 2004.** Chemical reaction speed is frequently enhanced at a surface, particularly when materials like platinum are present. Thus an important use for porous materials is as a substrate and media to promote chemical reactions**..** However small pores are not always easily accessed by some of the organic liquids in which these catalytic reactions ideally take place**, Webber**, **2014**.The textural properties of the alumina carrier play a major role in governing the performance of alumina based heterogeneous catalysts. The regulation of the pore size distribution in the support is of paramount importance in the development of a promising catalyst, **Kumar, et al., 2001.** Alumina (Al_2O_3) is a porous material and is extensively used as an adsorbent and catalyst support, the chemical properties and the structure of alumina play an important role in the catalytic process. These properties can be modified by the addition of impregnate, which has a profound effect on both the reactivity and the selectivity of the surface in the catalytic reactions and that functions as an adsorbent, Qadeer **and Ikram, 2004.** Catalysts are widely used in petroleum refinery processes (such as: catalytic reforming, catalytic hydro isomerization, catalytic hydrotreating and other processes). These processes are usually carried out over bifunctional catalysts which consist mainly of a metal phase (platinum, rhenium, iridium, and tin) dispersed on an acidic support such as chlorinated alumina, sillca, and zeolites. Therefore, many types of modified catalysts are used in industry to improve the process activity, selectivity and catalyst stability, **Adawiya, et al., 2012.** Due to their wide potential applications in catalysis, the preparation of ordered mesoporous alumina with high surface area and large pore volume has attracted much attention, **Baca, et al., 2007.** One of the most important physical properties of a catalyst is its specific surface area. The surface area of a porous catalyst, is almost entirely composed of the surface of pores which are present in each catalyst particle. The diameter of the pores may vary from a few to a few hundred Angstroms. The accessibility of the surface to reactants depends on the relative proportion of pores of different size, **Rasmer and Hill, 1958.** Pore volume is one of the factors affect the amounts of catalyst cursors that can be introduced on the supports, **Nielsen, 2006**. Specific Surface area is the most important physical characteristics in the catalyst, gas adsorption and applying Brunauer-Emmet –Tailer (BET equation), is from the first techniques used in specific surface measurements. This method was introduced since more 60 years and is still used in catalyst characterization till now. The adsorption of the gas is achieved in very modern automatic equipment and can analyze more than one sample at the same time, these equipment can transfer the information to specific surface (BET) and porosity (pore volume and pore volume distribution) measurements, **Antos, et al., 1995.** The steps used in the gamma alumina extrudate manufacturing are; mixing, wetting, the mixture ; granule molding; drying of the extrudate; calcination of the extrudate, **Derouane, et al., 2001.**

1. EXPERIMENTAL WORK

1.1 Materials:

Gamma alumina powder (Yuguang Special Ceramic Material Co., Ltd.) from China with specifications as shown in **Table 1**; wood flour with different particle size (150 µm, 212 µm and 500 µm) ; distilled water, hydrochloric acid HCl (Riedel de Haen).

1.2 Equipment:

The experimental apparatus used in this study consisted of home electric mixer (used for cake making) for stirring the gamma alumina powder and wood flour with water to make the paste for alumina extrudate; stainless steel perforated mold for making the extrudate; Muffle furnace (1200^0C, Gallenkamp, made in England) for the drying and calcination process of the alumina extrudate, Sieve shaker (Endecott sieve shaker); laboratory balance (Sartorius 60 g, 0.01 mg readability).

1.3 Procedure:

1- 30 g of γ-Al_2O_3 powder was taken as a base for all the pastes prepared with different wood flour particle sizes and quantities.
2- Wood flour (fine wood sawdust) was taken from carpenter workshop and then sieved analyzed to sizes of (150 µm, 212 µm and 500 µm).
3- Thirteen samples were prepared from gamma alumina powder with the wood flour particle size and addition percentage as shown in **Table 2**.
4- Distilled water containing 3% HCl (volumetric ratio) as peptizing agent was added to the 13 samples (mixtures of gamma alumina with wood flour in a weight ratio of 1.0-

1.1:1($H_2O:Al_2O_3$) for low wood flour addition percentage and around 2-2.25:1($H_2O:Al_2O_3$) for high wood flour addition percentage.

5- The above acidic water was added gradually during the mixing process with the electrical paste mixer, mixing stay for a period of ten (10) minutes until plastic paste suitable for making the alumina extrudates was obtained.

6- The paste was left for a period of thirty (30) minutes for aging.

7- The paste was rubbed against the apertures of perforated stainless steel plate with thickness of 3 cm in order to get the extrudate of suitable size, **Mukhlyonov, et al., 1976.**

8- The perforated plate with the paste inside it was put in the furnace with temperature of 170 ^{0}C to dry the extrudate and let it easy to be out of the perforated stainless steel plate.

9- The alumina extrudate after be removed from the perforated stainless steel plate was put in the furnace for a period of (1.5 h) to continue its drying while the temperature of the furnace is 170 ^{0}C .

10- All the (13) samples of the dried prepared extrudates were calcined in the furnace for 4 hours and the temperature of calcination was 450 ^{0}C.

11- All the samples were analyzed for pore volume and BET surface area.

12-

1.4 Test Methods:

BET Surface Area & Pore volume: These analysis were done in the Applied Researches Office which belong to the Ministry of Science and Technology using Horiba SA-9600 series of surface analyzers(USA made).

2. RESULTS AND DISCUSSION:

Fig. 1. , shows some photos about the work details for this study. The results for the pore volume and BET surface area for all the gamma alumina extrudates samples to which wood flour was added (12 samples) and the sample of gamma alumina extrudate to which no wood flour was added to it are shown in **Table 3** (Total samples are 13). **Fig.2** shows the relationship between the weight percentages of wood flour added to the gamma alumina powder and the pore volume of the produced gamma alumina extrudates for all the particle sizes of wood flour used. The results show the optimum addition percentage of wood flour of 1%, gives maximum increase (250%) of pore volume when the particle size of wood flour is 150 µm and 212 µm while the size of 500 µm wood flour leads to increase of 200% in pore volume. For the addition percentage of wood flour in range of 1-5%, the smaller size of wood flour of 150 µm has higher pore volume than larger wood flour particles because the number of particles will be higher when the size of wood flour particles are smaller, while for particles added at percentage higher than 6% , the wood flour of higher particle size (500 µm) will have higher pore volume and the increase will be 500% in 10% addition of 500 µm wood flour . **Fig. 3** show the relationship between the weight percentages of wood flour added to the gamma alumina powder and the BET surface area of the produced gamma alumina extrudates for all the particle sizes of wood flour used. When the percentage of addition of wood flour is small (less than 1%), The particle size of wood flour added has almost no difference on the property of BET surface area i.e all of the sizes have almost same rate of increasing BET surface area, the optimum addition is 1% which gives of about 20% increase in BET surface area . For higher percentage of wood flour added the wood flour of 150 µm particle size has higher BET surface area, at 10% addition of 150 µm leads to BET surface area increase of 40% . **Figs. 4-7** show the relationship between the particle size of the wood flour added to the gamma alumina powder and the pore volume of the produced gamma alumina extrudates for all

the particle sizes of wood flour used. **Figs. 8-11** show the relationship between the particle size of the wood flour added to the gamma alumina powder and the BET surface area of the produced gamma alumina extrudates for all the particle sizes of wood flour used. From the above figurs the results show that:

a. The pore volume of the prepared alumina extrudates was increased with addition of wood flour particles to the gamma alumina, and the addition of 10% wood flour with 500 µm particle size leaded to maximum pore volume of 1.0 cm^3/g while the smaller size of the wood flour particles of 150 µm resulted to 0.83 cm^3/g pore volume. For the addition percentages of 3% and 5% the 150 µm wood flour leaded to maximum pore volume of values 0.69 cm^3/g and 0.63 cm^3/g respectively. While the 1% addition of wood flour of 212 µm resulted to maximum pore volume of 0.72 cm^3/g.
b. The BET surface area was almost higher when using 150 µm wood flour with all addition percentages and the maximum reading of BET area (127.3 m^2/g) was produced when the addition percentage to wood flour added to gamma alumina powder is 10%.
c. To get increase in both pore volume and BET surface area properties for the gamma alumina extrudates using wood flour, wood flour size of 150 µm should be added in 10% addition percentage.

4. CONCLUSIONS

- The techniques of adding wood flour particles to the gamma alumina powder during the stage of manufacturing the alumina extrudates is successful technique for improvement of BET Area(Specific surface area) and the pore volume (porosity) of the gamma alumina extrudate which can be used as catalyst carriers .
- One should optimize between the pore volume and the BET surface area required**,** though the general proportional relation between the pore volume and the BET surface area**.**
- The BET surface area in our study was increased from a value of 89.5 m^2/g to a value of 127.3 m^2/g (> 40%) when adding 10% by weight 150 µm particle size wood flour to the gamma alumina powder, and the pore volume was increased from 0.2 cm^3/g to 0.83 cm^3/g for the same wood flour particle size of 150 µm and same addition percentage of 10%, while the addition of 10% of 500 µm particle size wood flour, leaded to 1 cm^3/g pore volume i.e. the increase for pore volume was more than 300% and 400% for adding 10% by weight wood flour of particle size 150 µm and 212 µm respectively .

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Table 1 Properties of the gamma alumina powder.

NO.	Property	Description
1	Name	High purity alumina powder
2	Type	Gamma – Al_2O_3
3	Purity%	99.99
4	Particle size, µm	0.2
5	Loose density, g/cm^3	0.16

Table 2. Details of alumina extrudate samples prepared for this study.

2Nos. of Sample	Particle size for the wood flour used, μm	Weight Percentage(%) of wood flour added
1	150	1
2	150	3
3	150	5
4	150	10
5	212	1
6	212	3
7	212	5
8	212	10
9	500	1
10	500	3
11	500	5
12	500	10
13	No wood flour used	zero

Table 3. Results of the BET surface area and the pore volume for the prepared alumina extrudates.

No. of Sample	Pore Volume, cm^3/g	BET surface area, m^2/g
1	0.71	107.5
2	0.69	104.9
3	0.63	104.4
4	0.83	127.3
5	0.72	105.9
6	0.53	98.9
7	0.6	103.5
8	0.63	114.5
9	0.63	103.2
10	0.62	105.2
11	0.6	102.2
12	1	104
13	0.2	89.5

Figure. 1 Photos shows the details of equipment and work for this study.

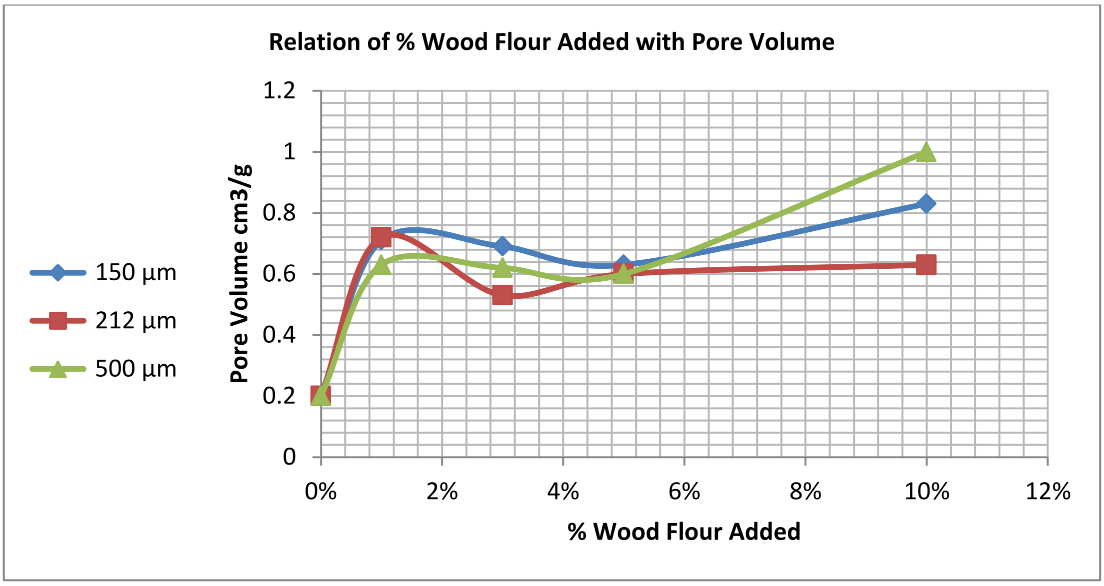

Figure 2. Relation of pore volume of alumina extrudates with % wood flour added.

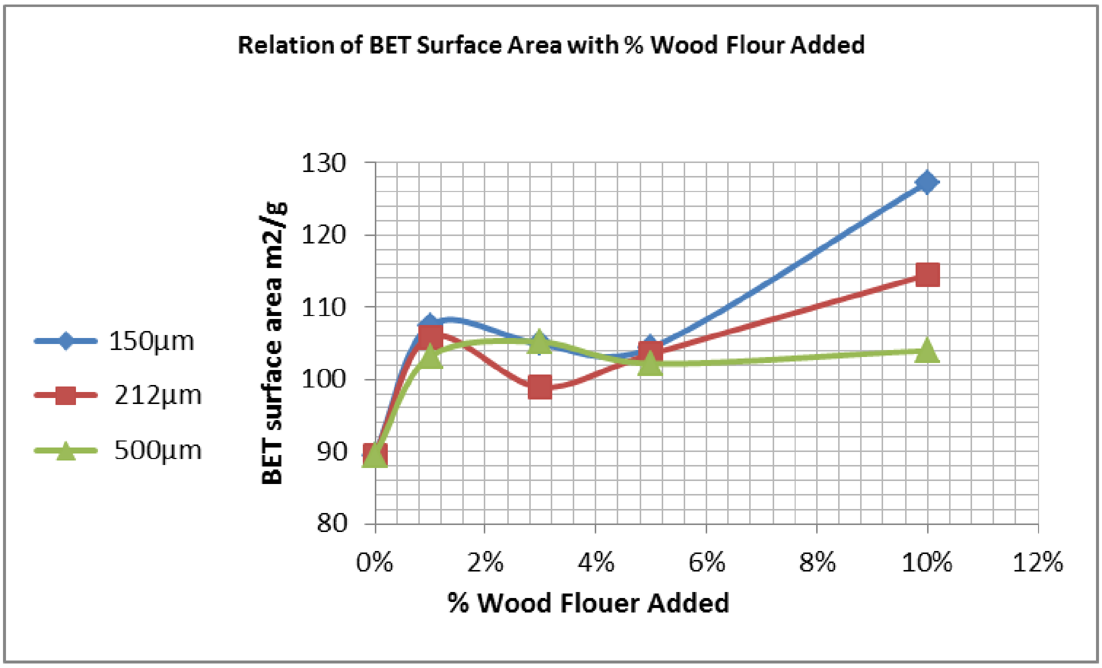

Figure 3. Relation of BET surface area of alumina extrudates with % wood flour added.

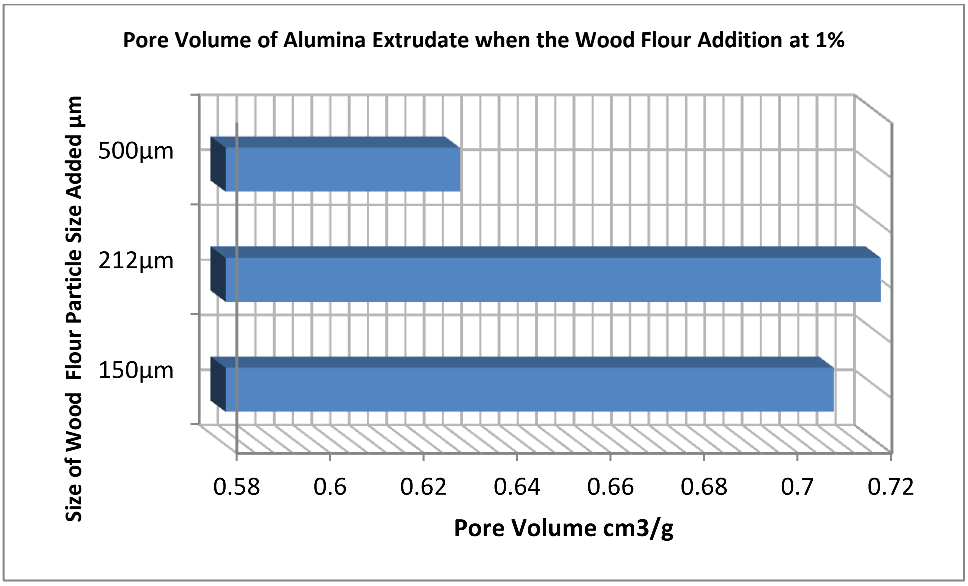

Figure 4. Pore volume of alumina extrudate when the wood flour addition at 1%.

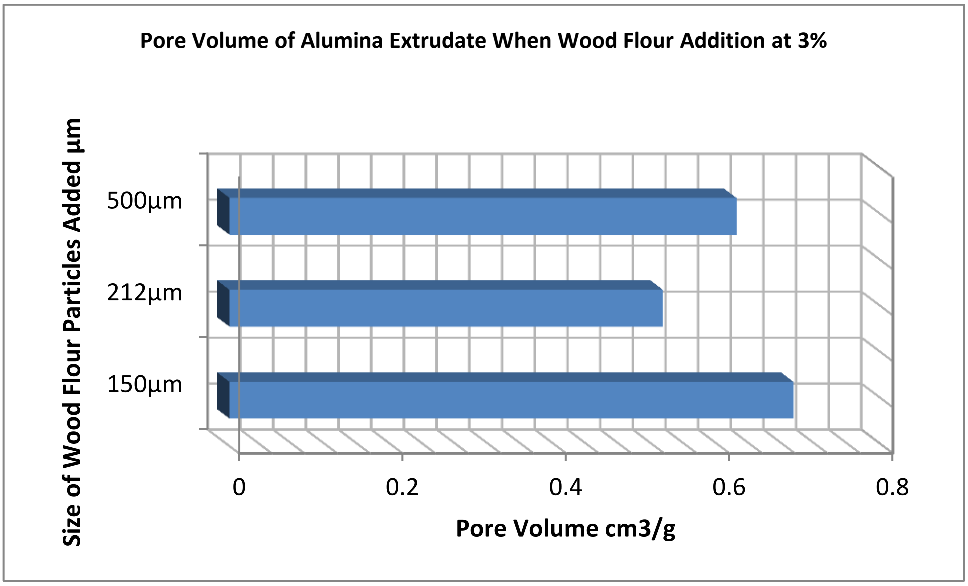

Figure 5. Pore volume of alumina extrudate when the wood flour addition at 3%.

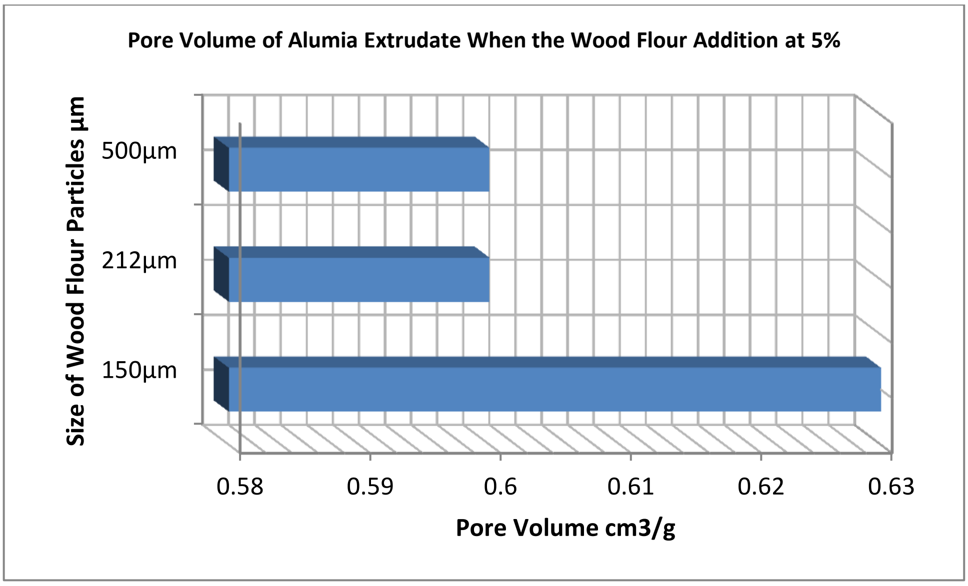

Figure 6. Pore volume of alumina extrudate when the wood flour addition at 5%.

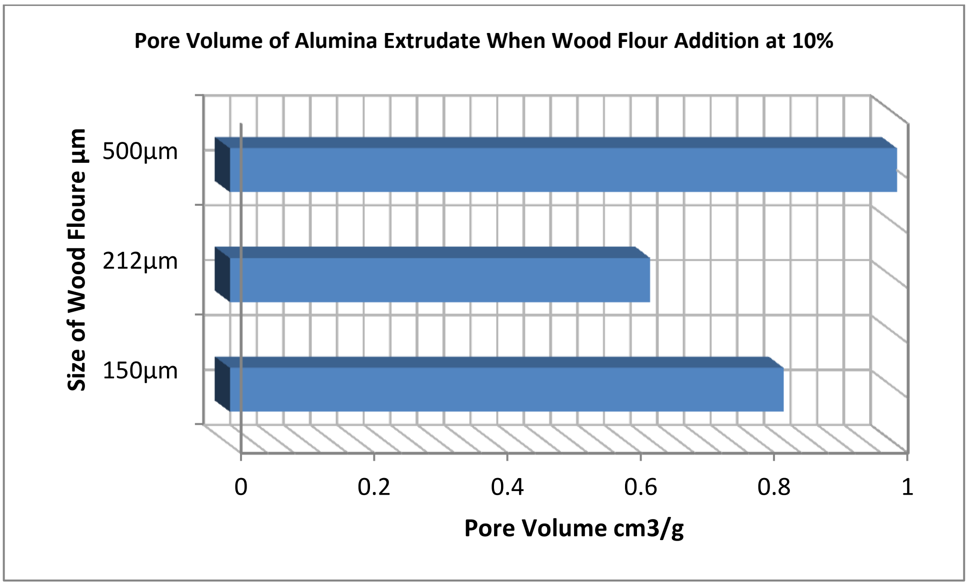

Figure 7. Pore volume of alumina extrudate when the wood flour addition at10%.

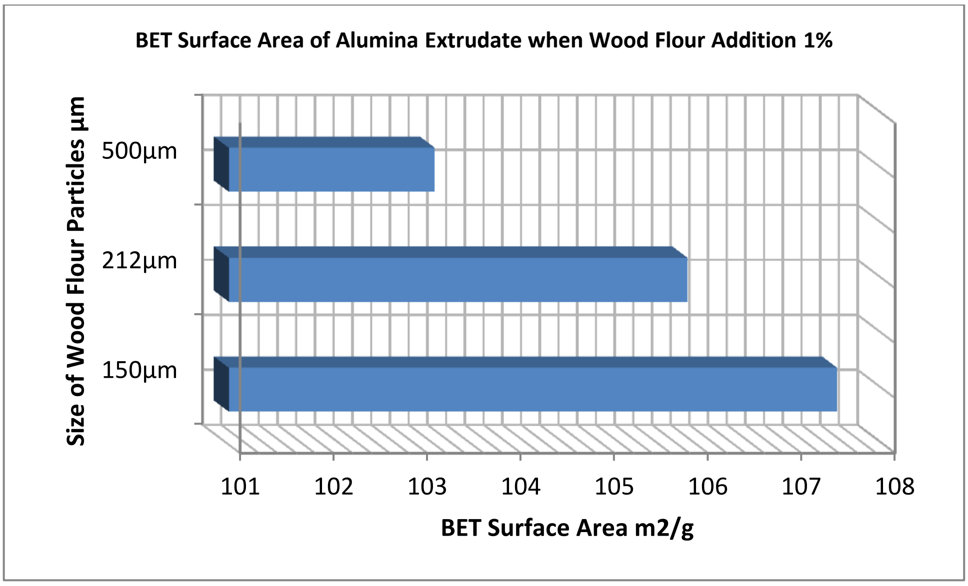

Figure 8. BET surface area of alumina extrudate when the wood flour addition at 1%.

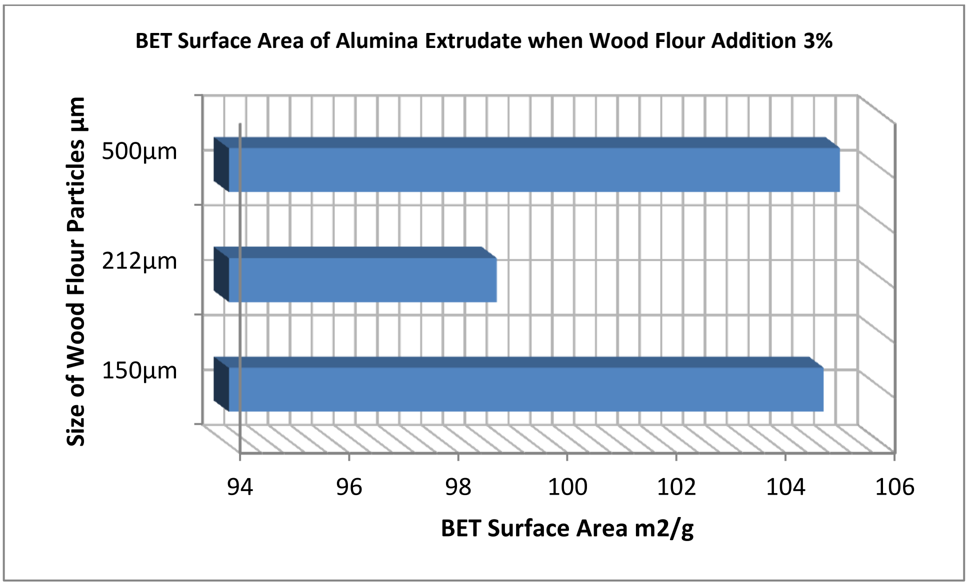

Figure 9. BET surface area of alumina extrudate when the wood flour addition at 3%.

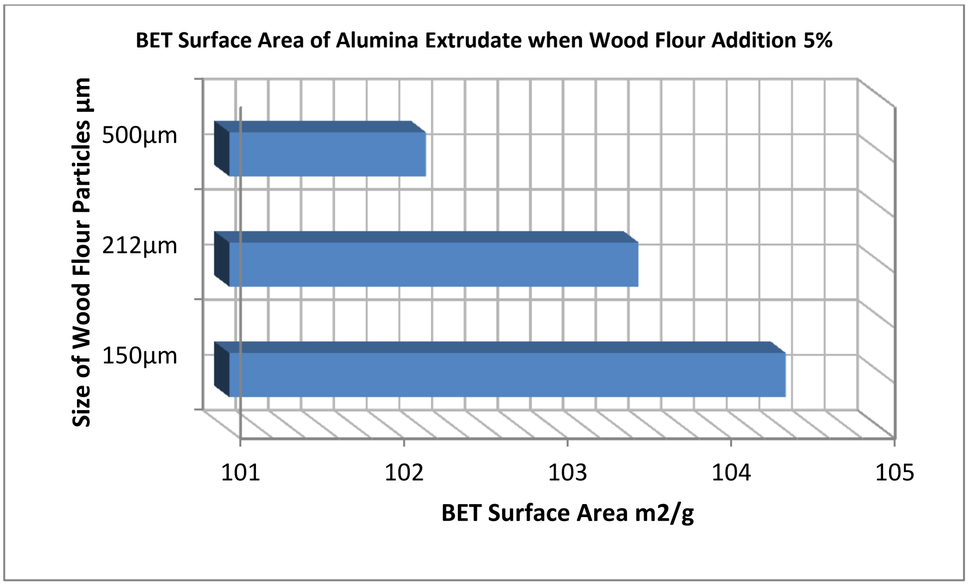

Figure 10. BET surface area of alumina extrudate when the wood flour addition at 5%.

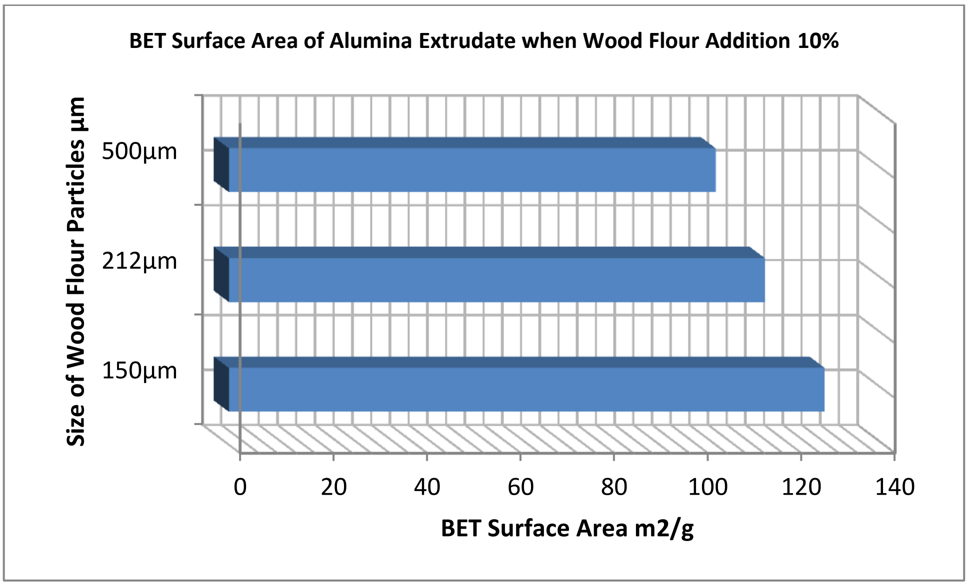

Figure 11. BET surface area of alumina extrudate when the wood flour addition at 10%.