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Impact of Shape and Size of Catalysts on the Physical Properties and Pressure Drop in Fixed Bed Catalytic Systems

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Abstract: ***Catalyst shape and size selection is an important aspect of the industrial catalyst design. Shapes of different sizes were made using alumina and characterized using standard methods used in the industry. Tableting machine, extruder and granulating equipment were used for forming different catalytic shapes. The samples were characterized by BET surface area, pore volume (N2 adsorption and water pick-up) and the sphericity & voidage calculations were performed for different alumina shapes. The physical strength and bulk density of the shapes were analyzed using ASTM methods. Spheres exhibited highest pore volume as the forming process exert minimum external force to the material. BET Surface area of all the samples were found comparable. The impact of different shapes and sizes on the pressure drop across the bed was studied for different gas flow rates using a fixed bed reactor set-up. Sphericity & voidage were calculated for different shapes and sizes and a modified Ergun equation was used for theoretical evaluation of the pressure drop. The experimental & theoretical results were compared and the relative error was noted. The study showed how the theoretical and experimental values differ as non-ideality in the flow across the packed bed increases. For special shapes like trilobe extrusions, improved voidage helps to minimise the pressure drop across the bed.***

Keywords: ***Catalyst forming, Catalyst shape, Ergun equation, Pressure drop, Packed bed catalytic system***

I. INTRODUCTION

Catalysts are substances that speeds up chemical reactions by lowering the activation energies. Many researchers conduct experiments around the globe to understand how catalysts work and how to improve the efficiencies. Globally >90% of the chemical reactions use catalysts and impacts 30-40% of the global GDP. As the world moves towards cleaner technologies, heterogeneous catalysis plays a vital role. For an effective catalytic reaction, the catalyst size and shape are very important. The catalyst should have enough geometrical surface area, good permeability for the reactants within the reactor, lower pressure drop and good mechanical strength.

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The catalyst shape and size greatly influence the heat and mass transfer across the reactor and hence the yield [1, 2]. For a high throughput reaction, the packed bed catalyst should offer only optimal pressure drop. In recent years, many catalyst forming technologies were developed and research is focused to improve the catalyst shape and size. Catalyst shape and size are decided based on the type of reaction, mass transfer limitations, thermodynamic and hydrodynamic factors. As a general rule of thumb, lower the catalyst size, higher the activity and higher will be the pressure drop. Optimisation of catalyst shape is a trade of between the catalyst performance and pressure drop. Catalyst forming techniques appear to be a matured research area and some of the commonly used catalyst shapes are spheres, pellets, extrudates (cylindrical, multi-lobed or CDS), hollow cylinders etc. Catalyst forming techniques influence the catalyst porosity, hence the mass transfer and heat transfer throughout the catalyst bed. The intra particle pore of a catalyst decreases with higher compression, which might affect the conversion of a reaction. Catalyst with lower mechanical strength crumbles in the reactor and generates dust & smaller particles which causes higher-pressure drop. The present study focuses on the impact of different forming techniques on the mechanical stability and possible pressure drop across the reactor. Three different types of techniques are used mainly for forming and a short description of these are given below [3, 4, 5]:

Tableting: A forming technique where high compression force is applied in forming the shape. A tableting process involves feed preparation, pre-compression, compression and tablet ejection. Tableting techniques are commonly used for forming bulk solid catalyst, where the entire tablet contains uniform composition. The high-pressure compression generates huge heat and this creates a high interparticle binding, leading to formation of very strong tablets. Tableting often reduces the catalyst pore volume and a catalyst with high crushing strength might result in a lower pore volume.

Sphere making: Sphere shaped catalysts are uniform, better-packed and spherical catalyst beds have better uniformity in transferring heat and mass. Sphere shaped catalysts are mostly supported catalyst, catalyst where the surface concentration of active metals are different from those inside the bulk. Spherical catalyst has good pore volume and ensures uniform packing. The spherical shape offers better attrition resistance over the other shapes. Bulk catalyst are also produced in sphere shape, where channeling is an issue in the reactor. Some of the commonly used equipment for sphere or granule making are pan pelletizer, ribbon blenders and high shear mixers [6].

The properties of the spheres made with different equipment may vary in their properties.

Extrusion: Extrusions are the most commonly used catalyst forming technique. Extrusions are formed by wet mixing the catalyst material or the support material and passing it through a high-pressure barrel to form the required shape as per the die used. Extrusions are used for forming bulk and supported catalyst. The catalyst formed by extrusions are expected to have moderate to high compressive strength and moderate to good pore volume. The present study analyses some of the catalyst shapes & sizes and its impact on the packed bed pressure drop, mechanical strength and geometrical surface area. The studies were done with Alumina (Pseudoboehmite) formed in different shapes and sizes using different forming techniques. Alumina is known to have good binding properties and interesting pore size distributions [5, 7]. The experimental results were compared with the one-dimensional model calculated using modified Ergun equation.

II. MATERIALS AND METHODS

The studies performed in the paper were done following the steps: Forming the material in different shapes and sizes, physical characterization of the formed materials, experiments for the pressure drop across the packed bed and theoretical calculations for the pressure drop across the fixed bed.

A. Forming the material

Alumina powder (Pural SCF) purchased from SASOL was used for the studies. Binders (5 to 10%) were also used for forming the material into different shapes. The binders used are calcium aluminate cements.

Tablets: Tablets were formed in two sizes: (1) 4.8x3mm and (2) 6x6mm. Adept ASR DB26 Tableting machine was used for the tablet formation. Alumina along with 5% binder and 1% lubricant was mixed in helical mixer, granulated and tableted. The tablets were calcined at 550°C for 3 hours in an electrically heated box dryer.

Spheres/ granules: The Spheres were formed using a pan type granulator. Neptune make granulator with 0.5m pan diameter was used for the sphere making. The spheres were formed using the tumbling granulation method, which is a low shear granulation method. Alumina (average particle size less than 10 microns) were used for the sphere making. The spheres (3-4mm dia) formed were calcined at 550°C for 3 hours in an electrically heated box dryer.

Extrudates: Extruder (Precision engineering) with 5HP motor and 2” barrel with single screw was used for producing the extrusions of various sizes. The extrusions were cured for 12 hours and calcined at 550°C prior to the studies. The extrusions were evenly sized with the help of a cutter while extruding itself to maintain the uniform size. The height /diameter ratio 3.0 was maintained for all extrusions [7,8]. Extrusions in 3mm, 2mm and 1.8mm cylindrical and 3.2mm trilobe shapes were made for the study. The extrusions were calcined at 550°C for 3 hours in an electrically heated box dryer.

B. Compression force (Crush Strength)

ASTM D4179 Method was used for the measurement. Mecmesin AFG 500 was the equipment used for measuring the compression force or the crush strength [9].

C. Loss on Attrition (LOA)

The Loss on Attrition measurements were done based on the method ASTM D4058-96 for the catalyst particles [10].

D. Surface area and Pore volume

Specific Surface area and pore volume of the formed tablets were measured by BET method using Micrometrics Tristar 3000. The degasing of the samples were performed at 300°C for 3 h.

The images of the equipment used are given in Fig. 1.

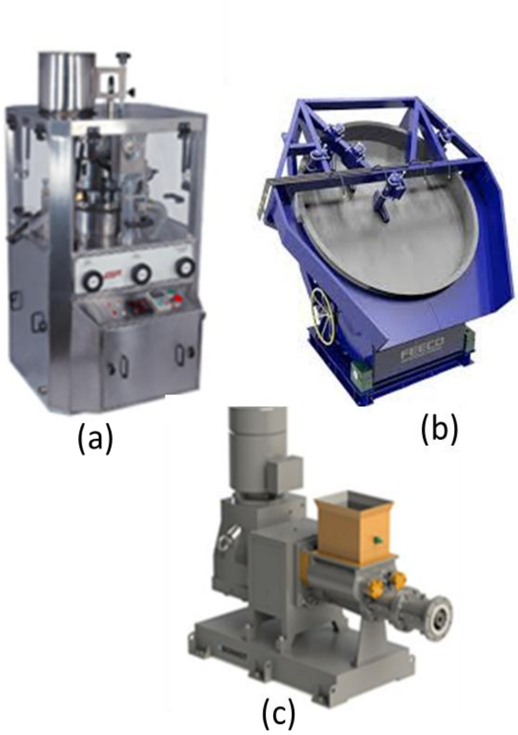

Fig. 1 (a) Tableting Machine (b) Pan granulator (c) Extruder

Fig. 2 Different shapes used for this study

E. Experimental Set up for Pressure drop measurement

The experiments were performed in an SS column reactor, having an internal diameter of 90 mm and height of 900 mm, where the gas was introduced at the top of the column. Alumina sample (2L) was loaded in the tube (maximum number of tapings for effective packing) and connected to the skid. Nitrogen gas was passed through the tube and the flow was varied.

The gas flow rate was controlled and measured by a mass flow controller, which was placed before the inlet of gas into the column. The pressure drop across the catalyst bed was measured using differential pressure transmitters, which were placed at the inlet and outlet of the tube.

The pressure transmitter gave the differential pressure in psi, which was converted to Pascal to compare with the theoretical results [3, 8, 11]. The experiment was repeated for different shapes & sizes and also for different gas flow rates. The experimental set-up and the equipment used are shown in Fig. 3.

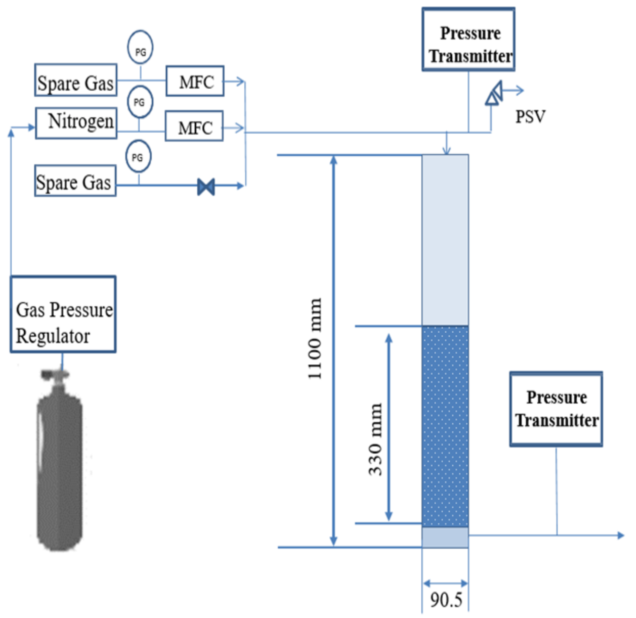

Fig. 3 Equipment used for the pressure drop measurement & the flow diagram of the reactor system.

F. Water Pick-up

Water Pick-up is a common method used to get the total pore volume of a catalyst which is stable in water. The catalyst (pre-weighed) was dipped in a definite volume of water for a few minutes, water was drained and the catalyst was weighed. Density of water being 1.0, volume picked-up can be calculated from the initial and final weights of the material.

Water Pick up = (W2-W1)/ W1 (1)

W1 Initial weight of catalyst before water dipping
W2 Weight of the catalyst after water dipping

G. Voidage

The alumina particles (1L) with different shapes were taken in a measuring cylinder and water was poured slowly to fill the voids in the packing inside the cylinder. Voidage of the packed bed is calculated as the difference between the volume of water used for filling the voids in the packed bed and the water pick up by the particles.

Voidage = Volume of water used to fill 1L sample – Water pick-up (2)

Theoretical calculation of the bed voidage was done using the generalised correlation given in the equation developed by Benyahia and O Neill [12].

$$\in = 0.1504 + \frac{0.2024}{\varnothing_p} + \frac{1.0814}{(d_t/(d_p + 0.1226))^2} \quad (3)$$

d_t *Tube diameter*
d_p *Particle diameter*
$\varnothing_p$ *Sphericity of the particle*

H. Sphericity

The Sphericity of the non-spherical particles were calculated using the equation given by Wadell in 1933 [13].

$$\text{Sphericity, } \varnothing_p = \frac{\text{Surface area of the volume equivalent sphere}}{\text{Surface area of the particle}} \quad (4)$$

I. Modified Ergun Equation for pressure drop calculations

Modified Ergun equations for cylinders and trilobes were used for the calculation of the pressure drop across the bed for the tablets and extrusions, the modified empirical correlations were taken from the literature [14, 15].

$$\frac{\Delta P}{L} = \frac{150\mu(1-\varepsilon)2}{A\varepsilon^2 dp^2} Vs + \frac{1.75(1-\varepsilon)\rho}{B\varepsilon^3 dp} Vs^2 \qquad (5)$$

For cylindrical shapes $A = \varnothing^{3/2}$ $B = \varnothing^{4/3}$

For polylobe shapes $A = \varnothing^{6/5}$ $B = \varnothing^2$

ΔP is the pressure drop, dp is the effective diameter of the particles, L is the height of the bed, *vs* is the superficial velocity of the fluid, ε is the average porosity of the bed, and μ and ρ are the viscosity and the density of the fluid respectively, $\varnothing$ is the sphericity of the particle.

III. RESULTS AND DISCUSSION

The physical properties of the alumina shapes used were analysed and given in Table-I. The bulk density of the tablets were high compared to the other forming techniques, making it evident that the tableting process applies very high compression force [16,17]. The pore volume of the extrusions, plain & trilobe are almost similar showing that these methods apply similar shear force while forming the shape. Spheres exhibit highest pore volume as the forming process does not exert much external force to the material. BET Surface area of all the samples are found comparable.

Crush strength which is a measure of mechanical stability of the product is maximum for the tablets. For the extrusions, it is found dependent on the size & shape of the sample.

Loss on attrition was also found minimum for the tablets (0.8%) whereas for the extrusions and spheres, LOA was found in the range 10-15% and 6% respectively.

Table-I: Physical properties of different alumina shapes

Sample ID	Shape	Size, mm	Crush strength, N	Bulk Density, kg/L	N_2 Pore volume, ml/g	BET Surface Area, m^2/g
T-6/6	Tablet	6X6	120	1.01	0.43	230
T-4.8/3	Tablet	4.8 X3	80	0.98	0.43	236
E-2/6	Extrusion Plain	2 X 6	35	0.85	0.60	227
E-3/9	Extrusion Plain	3 X 9	70	0.83	0.60	227
E-1.8/5	Extrusion Plain	1.8 X 5	25	0.9	0.60	227
E-3.2/10	Extrusion Trilobe	3.2 X 10	65	0.8	0.61	238
S-4	Sphere	4	68	0.9	0.65	234

It can be observed that the catalyst crushing strength decreases as the size decreases. The catalyst with low crushing strength are prone to attrition, hence dust generation and voids-blockage leading to an increase in the pressure drop across the catalytic bed [18].

The experimental pressure drop values are tabulated in Table II. The specific surface area in packed bed is high when smaller diameter particles are used.

The sphericity and voidage data show that the gas dynamics of the packed bed is greatly influenced by the shape and size of the particles. The shape and size of the alumina pellets influence the bed voidage and hence the pressure drop across the bed (Table III). Experimental measurement of the pressure drop per unit length was performed with different alumina pellets at different flow rates. Calculations were performed with the modified Ergun equation to get the theoretical values. A comparison of the pressure drop theoretical *vs* experimental was done for different shapes and sizes. Data clearly indicate the significance of the shape and size in the packed bed.

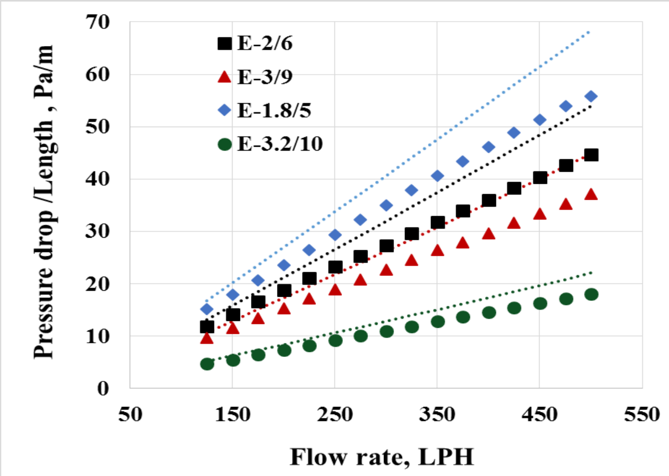

Fig. 4a Pressure drop per bed length for different sizes of alumina extrusions studied. (Dotted line represents the theoretical plot)

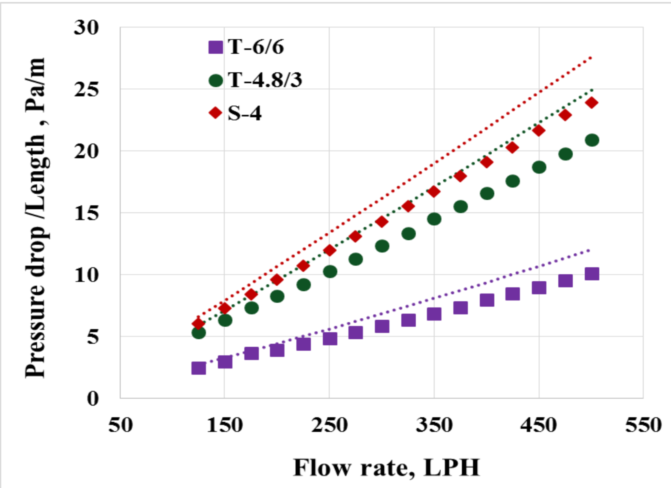

Fig. 4b Pressure drop per bed length for different sizes of alumina tablets and the spheres studied. (Dotted line represents the theoretical plot)

Table II. Experimental pressure drop per unit length (Pa/m) for different samples under different flow rates

Flow, LPH	Experimental pressure drop per unit length (Pa/m)						
	T-6/6	**T-4.8/3**	**E-2/6**	**E-3/9**	**E-1.8/5**	**E-3.2/10**	**S-4**
125	2.46	5.33	11.86	9.71	15.10	4.71	6.07
150	2.96	6.38	14.20	11.57	17.91	5.52	7.30
175	3.67	7.35	16.59	13.37	20.69	6.44	8.39
200	3.94	8.32	18.83	15.26	23.59	7.37	9.58
225	4.44	9.26	21.04	17.15	26.45	8.28	10.76
250	4.87	10.31	23.31	18.94	29.38	9.21	12.00
275	5.34	11.32	25.35	20.78	32.16	10.13	13.13
300	5.84	12.37	27.37	22.72	35.03	11.02	14.32
325	6.34	13.34	29.58	24.56	37.93	11.86	15.55
350	6.84	14.52	31.78	26.51	40.66	12.79	16.72
375	7.39	15.57	34.00	27.82	43.35	13.69	17.96
400	8.01	16.60	36.03	29.59	46.11	14.61	19.09
425	8.47	17.64	38.32	31.60	48.82	15.42	20.32
450	9.01	18.75	40.36	33.36	51.28	16.35	21.66
475	9.57	19.83	42.57	35.27	53.88	17.23	22.95
500	10.13	20.94	44.74	37.10	55.81	18.08	23.91

Table III. Packed bed properties and relative error in pressure drop calculation.

Sample	Sphericity	Voidage, Theoretical	Voidage, Experimental	Calculated pressure drop at 500 LPH Pa/m	Experimental Pressure drop at 500 LPH Pa/m	Specific volume surface area, m^{-1}	Relative error, Theoretical vs Experimental at 25LPH	Relative error, Theoretical vs Experimental at 500 LPH
T-6/6	0.874	0.388	0.41	12.06	10.13	1.00	9	16
T-4.8/3	0.852	0.391	0.415	24.93	20.94	1.50	10	16
E-2/6	0.779	0.412	0.43	53.94	44.74	2.33	10.1	17.1
E-3/9	0.779	0.414	0.42	44.81	37.10	1.56	9.4	17.2
E-1.8/5	0.790	0.408	0.41	68.41	55.81	2.62	10.4	18.5
E-3.2/10	0.588	0.498	0.51	22.05	18.08	2.10	9.4	18
S-4	1	0.355	0.38	20.8	23.91	1.50	7.90	13.50

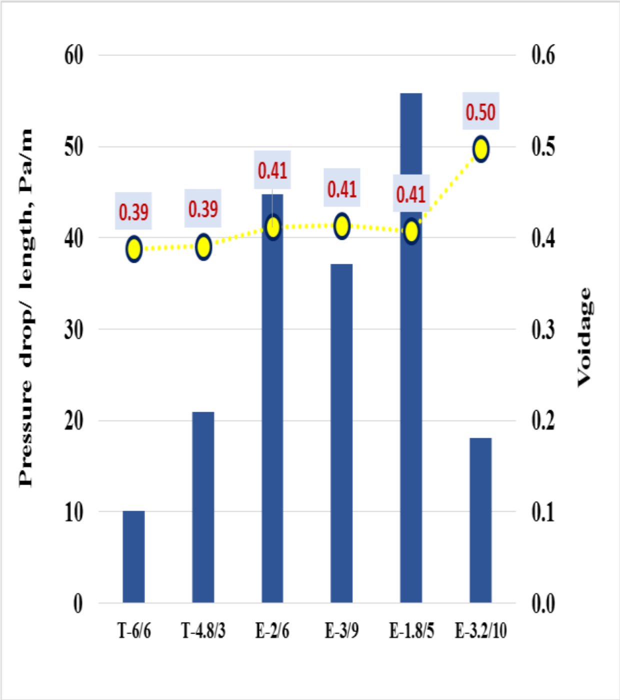

Fig.5 Pressure drop per unit length at max flow and voidage for different Alumina particles.

The relative difference in the theoretical pressure drop calculation and the experimental values were compared and found to increase with increase in flow rate. The results are tabulated in Table III.

Also, data indicate that the pressure drop increases with decreasing particle size. The 1.8 mm extrusions offers the highest specific surface area and the highest-pressure drop. It can be seen that the special structures as tri-lobe offers better specific surface area and has relatively lower pressure drop compared to the regular shape of same size (Fig. 4).

Special shapes like trilobes improve the voidage and hence minimise the pressure drop across the packed bed (Fig. 5). The theoretical model based on the modified Ergun equation works well at low flow rates and particles with higher sphericity, and deviation increases with increasing flow rate. This could be possibly due to the channelling inside the reactor packed bed.

Commercial reactors are often operated at higher operating pressure and higher flow rates. The channelling inside the packed beds are low at higher operating pressure [19].

IV. Conclusion

The catalyst shapes are usually designed balancing the catalytic activity and the pressure drop. The fixed bed with special shapes like trilobe helps improve the voidage in the bed, improves the geometrical surface area and hence lower pressure drop than the regular shape of same diameter. In chemical industry, the catalytic reactors cannot be operated at pressure drops beyond the permissible limits.

Hence higher pressure drop is not desired and is an important criterion for taking the reactor shutdown. The present study gives some insight into the impact of size & shape of particles on pressure drop across the reactor and a possible laboratory method to study the same.

Many other factors like mass transfer limitations and heat transfer rates have to be studied for the actual design of an industrial catalytic reactor [20, 21].

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