Agitation of Liquid Systems Requiring a High Shear Characteristic

PHILIP L. FONDY and ROBERT L. BATES

Chemineer, Incorporated, Dayton, Ohio

The systematic study of agitation, as a chemical engineering operation, has been undertaken in most of the categories possible, but certainly not in the high shear section of the technology. Even the usual very empirical studies are lacking. The reasons typically offered for neglecting this area are lack of adequate theoretical background, limited scope of application, plethora of variables involved, and extreme diversity of equipment types available. The state of the art has improved little since Scoville (*12*), in 1895, reported that "five minutes of very rapid trituration will accomplish more in emulsifying an oil or balsam than an hour of slow trituration."

High shear agitation as discussed here refers to the classes of application known as *emulsification, dispersion, homogenization*, etc. It is the processing area that lies between the agitation intensity produced by conventional impellers operated at high power per unit volume and the shear forces generated by homogenizers or colloid mills. It is a relatively narrow range, at present served by a variety of high speed impellers, most of them being modified disks or cones or the rotor-stator type.

The term *high shear* may be defined in several ways. First to be considered should naturally be a theoretical one. Discussions of the fundamental hydrodynamics such as those by Calderbank (*3*) and Hinze (*7*) do much to help understand the forces controlling dispersion processes. But the mechanism of shear involved in fluid agitation has not yet been satisfactorily established in terms that can be applied to practice. Although theories in favor of cavitation, velocity change, direction change, and mechanical forces have been offered, none has been verified.

A better understanding of the process is obtained from consideration of the impeller action. The shear/flow characteristics of various standard mixing impellers in the conventional range of use have been evaluated by a number of investigators (*1, 10*), and the general concept of shear is established as a function of impeller geometry, system geometry, and power-speed relationships. It is mathematically improper to say, as is often done, that a high shear impeller invests the majority of the total energy via shear and a minority in flow. But it can be stated that performance and power are adjusted to maximize the head term (N^2D^2) and reduce the flow ($N D^3$), and that is done by means of a relatively small D/T ratio, a high speed, and a small opposed blade area.

Specific literature on high shear agitation of liquid systems is predominately qualitative in nature. Case history publications have been universally testimonial in nature and reflect the proprietary designs involved. Patents abound but add nothing of technical value. A good general treatment of the subject is found in the book by Clayton (*5*). Several investigators (*6, 9*) reported quantitative agitation data on emulsification problems, and the papers by Brothman (*2*) and Miller and Rushton (*8*) discuss possible factors controlling shear. All of these sources recognize the importance of peripheral velocity of the impeller and at the same time note the influence of impeller design, but all failed to distinguish between the separate effects on performance.

This investigation of the mechanism of high shear was restricted to the effects of impeller design and operation in order to develop a realistic understanding of the basic agitation variables. Analysis of specific problems and eventual development of a general theory must involve such factors as viscosity, surface tension, and relative concentration. But for this study all such variables were eliminated or controlled. This approach can be justified solely by the need for establishing the basis for scale-up concepts. No apology is offered for the omission of a corollary theoretical treatment; much more empirical work will be required before the background is sufficiently comprehensive.

The system used for this study was selected as the most convenient for this class of problem. Dispersion of a sodium-potassium alloy in mineral oil was used. The nearly equivalent densities, low viscosity, high immiscibility, and low tendency to coalesce are all favorable characteristics. And it has the added value of commercial applicability. The fact that this system allowed use of the photomicrograph technique of recording dispersion data was a major factor in its selection, since this provides a reasonably precise and very consistent method of correlating data. The arithmetic mean particle diameter of a given dispersion provides a convenient qualitative measure of the effects of impeller design and operation.

EQUIPMENT

All experimental runs were made in a 2 gal. capacity vertical cylindrical vessel. The vessel was 8-in. diam. dished bottom, flat top, and had four vertical sidewall baffles. The dished bottom contained a drain fitting and sampling valve. The flat top was fitted with a filling plug and a connection for nitrogen blanket. The vessel was coiled externally for water cooling. The sodium-potassium storage and transfer system was designed to permit direct injection of a measured quantity of alloy into the vessel without exposure to air. Mineral oil was stored in a 55-gal. drum and transferred by hand to the vessel. Agitator drive was a ½ hp. 0 to 16,000 rev./min., universal motor with variable voltage transformer for speed variation.

Temperature control was manual with single dial thermometer in vessel and control valve in cooling water line. Shaft speeds were measured with an accurate hand tachometer. A separate dynamometer assembly, of the type described by Bates (*1*), was used for accurate measurement

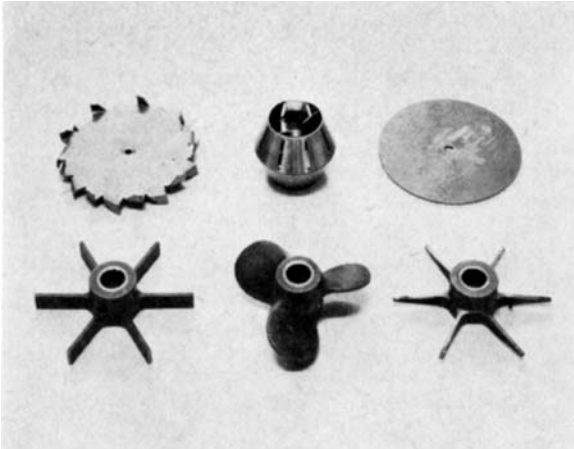

Fig. 1. Test impellers. a. Modified disk. b. Flat-blade turbine. c. Modified cone. d. Propeller. e. Simple disk. f. Modified turbine.

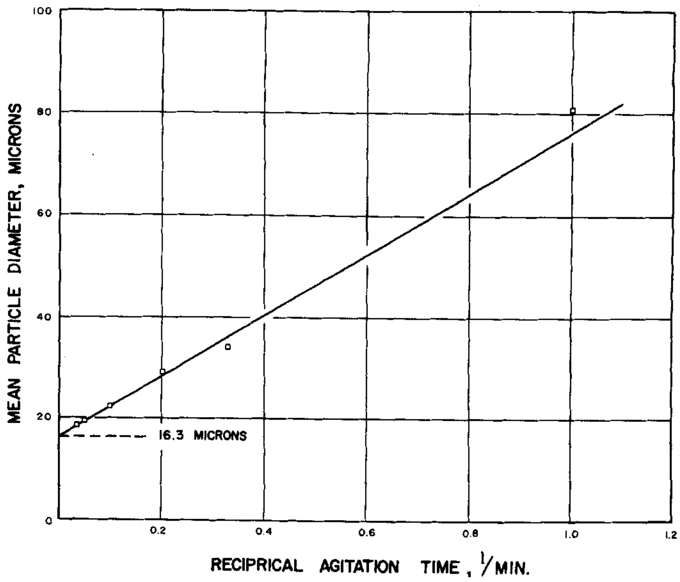

Fig. 3. Particle diameter vs. reciprocal agitation time, 1½ in. modified disk at 1,850 ft./min. tip speed.

of power consumption at operating conditions. Samples were photographed with a simple photomicrograph assembly.

The types of impellers tested are shown in Figure 1. From upper left is shown conventional modified disk, modified cone, simple disk, conventional flat blade turbine, square pitch marine propeller, and finally the modified turbine.

The molten metal used was a standard commercial grade sodium-potassium alloy. The mineral oil was USP 190 pure white oil.

EXPERIMENTAL TECHNIQUE

Every effort was made to exclude water from the system to avoid reaction with the sodium-potassium mixture. All runs were conducted under a protective nitrogen blanket. All runs were made with a 2 gal. working batch consisting of a measured 20 cc. of sodium potassium and the remainder, mineral oil.

Two types of runs were made. The first series consisted of agitating at a given speed with samples being taken at regular intervals. The second series of runs consisted of operating at a selected speed for 20 min., then sampling. The procedure was repeated at various shaft speeds with each impeller. Temperature was held constant at 75°F. over the agitating period to eliminate viscosity as a variable.

Samples were taken in 10-cc. vials, and three or four photomicrographs were generally taken of each sample. Magnifications were accurately determined by photographing a micrometer slide. Sample photomicrographs are shown in Figure 2. The arithmetic mean particle diameter was determined by hand measurement with a standard millimeter scale. Some 200 to 500 particles were counted before a reliable arithmetic mean could be obtained.

Net shaft power consumptions for all impellers at various speeds were measured with a separate dynamometer assembly. Care was taken to duplicate actual run conditions in power tests. The test vessel was actually transferred to the dynamometer to accomplish this.

VARIABLE TIME RUNS

As stated, the first series of runs consisted of operating each impeller at a given speed and sampling at regular intervals. The operating speed was selected such that all impellers were operated at essentially identical peripheral speeds of 1,850 ft./min. The data for all impellers shows that an ultimate particle size is rapidly approached. A plot of particle diameter vs. agitation time shows the measured size approaching an ultimate value asymptotically as time approaches infinity. Figure 3 is a representative plot of particle size vs. reciprocal agitation time for a 1½ in. modified disk at constant speed. The intercept at 16.3 μ is the ultimate diameter at 1,850 ft./min. tip speed.

Plotting data on other impellers, taken at the same tip speed, similar to to Figure 3 results in curves rather than straight lines. To better correlate the data it was reasoned that all impellers would have the same ultimate size as the 1½ in. modified disk. A

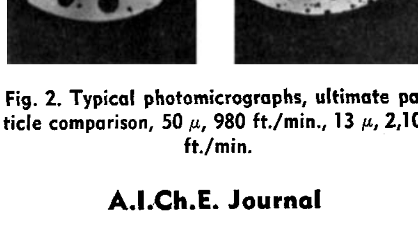

Fig. 2. Typical photomicrographs, ultimate particle comparison, 50 μ, 980 ft./min., 13 μ, 2,100 ft./min.

logarithmic plot of (μ_t − 16.3) against agitation time for these impellers is shown in Figure 4. The linear curves indicate the validity of the assumption. It is therefore apparent that the ultimate particle diameter is a function of impeller tip speed and completely independent of impeller geometry or power investment. Data taken with a 2½ in. plain disk, not shown, also approached the same ultimate diameter, although size reduction proceeds much more slowly than with the other impellers. It is also apparent from Figure 4 that the relative difference between particle size at any time and the ultimate size controls the process rate.

Figure 4 shows that the 2, 2½, and 3 in. modified disks are correlated with the same curve. This suggests that above a given point the shear zone is flooded, and particle diameter vs. agitation time is independent of circulating capacity. It was then theorized that modification of a conventional turbine to lower circulating capacity should not affect the ultimate size or rate of approach. To test this theory a conventional 2½ in. diam., six blade turbine with 5/16 in. blade width was modified as shown in Figure 1 by tapering the blades. Two separate designs were tested. The first modified turbine (style A) measured 5/16 in. width at the hub and ⅛ in. width at the tip. The second (style B) measured ¼ in. width at the hub and 1/16 in. width at the tip. Data taken with each impeller revealed that both produced results identical with the conventional turbine, but at considerably less power consumption. Data points for the style B, which required least power, are shown in Figure 4. Circulating capacity

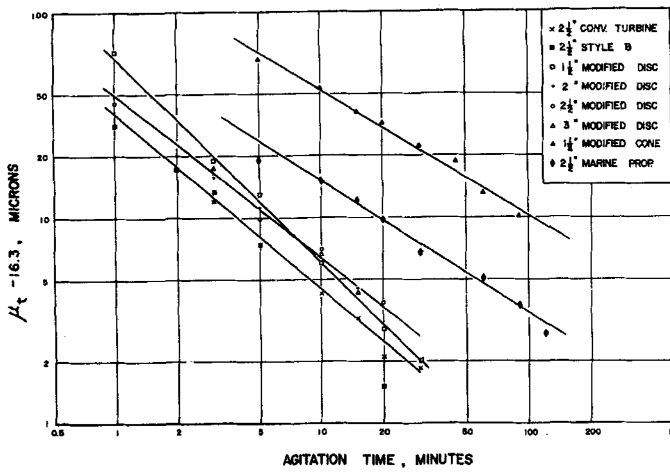

Fig. 4. Correlation of particle diameter with agitation time for various impellers, 1,850 ft./min.

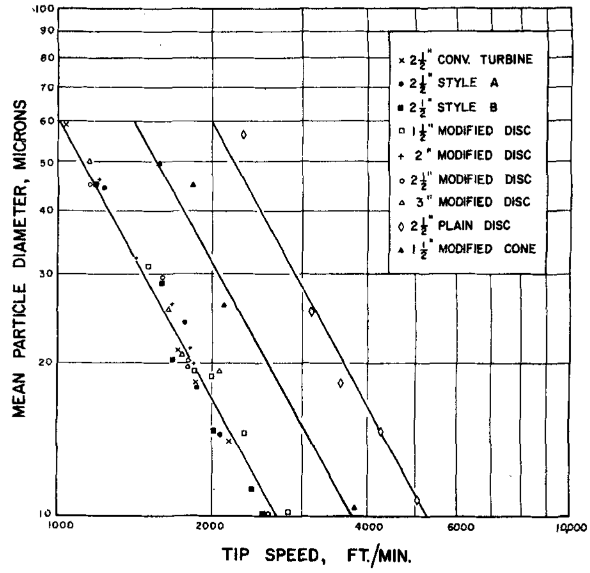

Fig. 5. Mean particle diameter as a function of tip speed for various impellers. Agitation time 20 min.

and power investment are seen therefore to be of secondary importance in this ideal high shear system.

The curve for the 1½ in. modified disk has a marked difference in slope compared with the other modified disks. It is felt that circulating capacity has been limited to the point where it does control the dispersion rate. In fact the slope of −1 indicates that size reduction is directly proportional to agitation time and therefore to circulation rate.

CONSTANT TIME RUNS

The variable time runs were made at only a single tip speed. Data is therefore required to determine the effect of changes in tip speed on particle size. Runs with the various impellers were made at random speeds, each of 20 min. duration. The 20 min. running time is also a reasonable selection for comparing performance. Data are correlated as particle diameter vs. tip speed in Figure 5. All curves show that particle size is inversely proportional to tip speed raised to the 1.8 power. The data for all modified disk impellers, the conventional turbine, and the modified turbines are correlated with the same curve. This again verifies that particle size is a function of tip speed and independent of power consumption. The less efficient plain disk and modified cone of course do not correlate on the same curve. Considerably longer running times are required for these impellers.

POWER

The dynamometer power data is shown in Figure 6. Power data for several impellers are seen to coincide. The data are quite accurate and completely cover the range in which dispersion data was taken. All measurements were made in the impeller Reynolds number range of 2,000 to 4,000 and power is essentially a function of $N^3 D^5$ for each impeller geometry. In Figure 7 the 20 min. runs of Figure 5 are combined with power data of Figure 6 to show the comparative performance of the various impellers. It is seen that the 1½ in. modified disk is more efficient, in terms of power, than a 1½ in. modified cone. This can probably be assumed true for any other equal diameter. The 2½ in. modified disk and 2½ in modified turbine are more efficient than the conventional turbine and plain disk of the same diameter. The turbine wastes power in circulation, and the simple disk has a very low effective circulating capacity. Curves for the four modified disks show the necessity of reducing impeller diameter to minimize power consumption. For best results in low viscosities D/T ratios of 0.15 to 0.20 appear optimum.

GENERAL CORRELATION

Figure 4 indicates that particle diameter at any time for a given tip speed is related to the ultimate size by

$$\mu_t = \Delta\mu + \mu_\infty = kt^{-a} + \mu_\infty$$

The constants (k) and (a) for each impeller can be easily obtained from the curves in Figure 4. The effect of peripheral speed is evident from Figure 5, and the following rate equations for the two gallon batch size result:

$$t = \left(\frac{\omega}{1{,}000}\right)^{-1.8} (125t^{-0.80} + 48) \quad \text{(2, 2½, 3 in. modified disk)}$$

$$t = \left(\frac{\omega}{1{,}000}\right)^{-1.8} (170t^{-1.0} + 48) \quad \text{(1½ in. modified disk)}$$

$$t = \left(\frac{\omega}{1{,}000}\right)^{-1.8} (100t^{-0.85} + 48) \quad \text{(2½ in. conv. turbine and 2½ in modified turbine)}$$

$$t = \left(\frac{\omega}{1{,}000}\right)^{-1.8} (200t^{-0.84} + 48) \quad \text{(2½ in. marine propeller)}$$

$$t = \left(\frac{\omega}{1{,}000}\right)^{-1.8} (530t^{-0.61} + 48) \quad \text{(1½ in modified cone)}$$

From these equations the average particle size at any time, or ultimate size, can be evaluated at any tip speed for a given impeller in a 2-gal. batch. A check against the actual data of 20 min. runs shows very good agreement. Analyses of these equations and curves of Figure 7 show that for equal diameters and power investment over a 20 min. running period the comparative performance of the various impeller types is: (1) modified turbine, (2) modified disk, (3) marine propeller, (4) conventional turbine, (5) modified cone.

The marine propeller is apparently more efficient than a conventional turbine for this type of dispersion operation, if one assumes equal diameters and power investment. This results from a considerably higher operating speed, and thus tip speed, for equal power investment.

Direct comparison of results with previous published works such as (*4, 11, 13*) is not feasible. Other investigations have not considered agitation time and impeller geometry as system variables. Also previous correlations have included numerous fluid property variables, and the effects of agitator variables are obscured.

SCALE UP

It is important that laboratory data be translatable to larger volumes. The ideal result is a general rate equation such as those given above but including batch size and impeller diameter as variables. This would be a complex problem as, for the modified disks, the identical equation resulted for three impeller diameters in a single batch size. It is also generally not economically feasible to vary batch size sufficiently to establish the scale-up curve experimentally.

Scale up however for batch high shear systems such as sodium potassium-mineral oil is rather unique. It has been shown that a single batch size can be used to determine the relationship of particle size with impeller tip speed and also a comparison of various D/T ratios and impeller types. This allows selection of the required tip speed to produce the desired dispersion. Minimizing D/T ratio and selection of best impeller type aid in reducing power requirements and agitation time. An experienced designer could therefore provide a successful scale up from single batch data.

It can easily be shown that holding D/T and power per unit volume constant the impeller tip speed increases with increasing batch size. For example in scaling from 2 to 100 gal. the tip speed of the larger unit would be 1.54 times that of the lab unit, and the ultimate obtainable particle size would be better than the lab unit. Obviously constant power per unit volume scale up is a conservative method of design for batch high shear systems. Scale up at equal tip speed would yield the same ultimate size at lower power investment but might lead to poor overall control of the batch. This would require the judgment of an experienced designer.

It is important in any scale up of agitation data that dimensional similarity of impellers be maintained. In high shear work it is also desirable that impeller geometry be flexible to permit adjustment of circulating capacity as required for example with systems of high viscosity. Neither condition is well satisfied by the conventional high shear impellers, but modification of a conventional turbine meets both requirements.

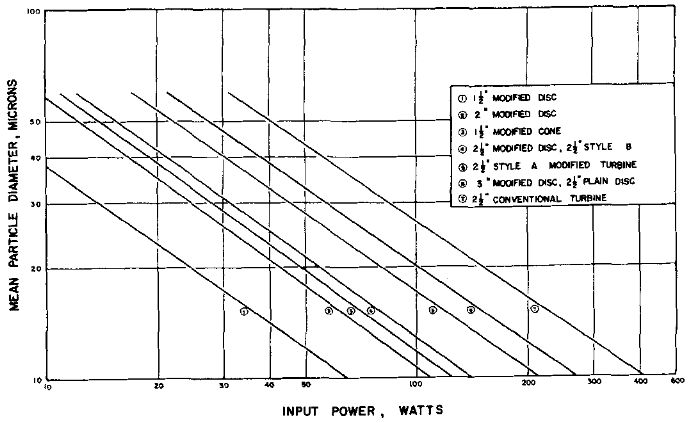

Fig. 7. Comparative power performance for various impellers. *Agitation time 20 min.*

CONCLUSIONS

The results of the experimental work can be summarized as follows.

The system sodium potassium and mineral oil is quite suitable for studying agitation variables at high shear rates. Photomicrograph technique provides direct and accurate means of determining average particle diameter of the dispersions.

The measured process result, arithmetic mean particle diameter, is a function of the impeller tip speed and rapidly approaches an ultimate value. The particle diameter was found to vary inversely with the tip speed raised to the 1.8 power, for all impellers tested.

The general rate equations for all impellers tested indicate that the rate of approach to ultimate size is controlled by $(\mu_t - \mu_\infty)$ or $(\Delta\mu)$.

At low D/T ratios the approach to ultimate size of a well-designed impeller is linear with agitation time. This is attributed to dependence upon circulating capacity of the impeller. At higher D/T ratios (above 0.20 to 0.25) the approach to ultimate size is essentially independent of circulating capacity. This indicates wasted power investment.

For minimizing power consumption smaller impellers at high tip speeds are desirable. For best results the impeller diameter should be about 15 to 20% of the tank diameter for low viscosity applications.

Analysis of the experimental data show that for equal diameters and power investment over a 20 min. running period the order of comparative performance of the various impeller types is: (1) modified turbine, (2) modified disk, (3) marine propeller, (4) conventional turbine, (5) modified cone.

A modified turbine gives the same process result as a conventional turbine but at considerably less required power, since excess circulating capacity is minimized while shear rate is unchanged. Dimensional similarity is easily maintained, and basic design provides simple adjustment of circulating capacity when desired.

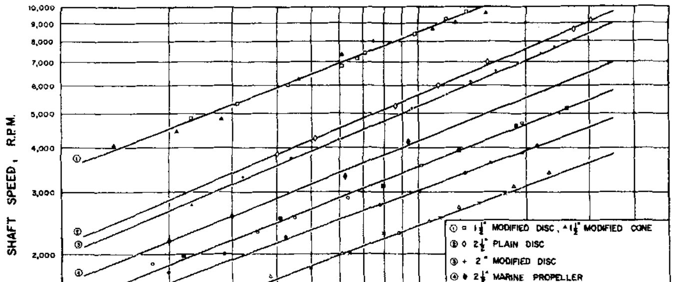

Fig. 6. Dynamometer power data for various impellers.

ACKNOWLEDGMENT

The authors wish to thank Mr. G. O. Charrier, of The Procter and Gamble Company, for technical assistance and particularly for suggestion of the sodium-potassium-mineral oil system. Mr. Charrier's

unpublished report of April, 1958, which the authors were privileged to review, served as a basis for this study.

NOTATION

a, k = empirical constants
D = impeller diameter, in.
N = shaft speed, rev./min.
t = agitation time, min.
T = tank diameter, in.
ω = peripheral speed, ft./min.
μ_t = arithmetic mean particle diameter at time t, μ
μ_∞ = ultimate particle diameter, μ
$\Delta\mu$ = deviation from ultimate particle diameter, μ

LITERATURE CITED

1. Bates, R. L., *Ind. Eng. Chem.*, **51**, 1256-8 (1959).
2. Brothman, A., *Chem. and Met.*, **46**, No. 5, p. 263-5 (1939).
3. Calderbank, P. H., *Brit. Chem. Eng.*, **1**, 206-9, (August, 1956).
4. ———, *Trans. Inst. Chem. Engrs. (London)*, **36**, 443-63 (1958).
5. Clayton, W., "The Theory of Emulsions and Their Technical Treatment," 5 ed., The Blakiston Co., New York (1954).
6. Herschel, W. H., "Technologic Papers of the Bureau of Standards," Vol. 86, pp. 1-37 (1917).
7. Hinze, J. O., *A.I.Ch.E. Journal*, **1**, No. 3, p. 289-95 (1955).
8. Miller, F. D., and J. H. Rushton, *Ind. Eng. Chem.*, **36**, 499-503 (1944).
9. Morton, A. A., and L. M. Redman, *ibid.*, **40**, 1190-3 (1949).
10. Oldshue, J. Y., "Biological Treatment of Sewage And Industrial Wastes," Vol. 1, p. 233, J. McCabe and W. W. Eckenfelder, Reinhold, New York (1955).
11. Rodger, W. A., V. G. Trice, Jr., and J. H. Rushton, *Chem. Eng. Progr.*, **52**, 515-20 (1956).
12. Scoville, W. L., "The Art Of Compounding," The Blakiston Co., New York (1895).
13. Vermeulen, Theodore, G. M. Williams, and G. E. Langlois, *Chem. Eng. Progr.*, **51**, 85F-94F (1955).

Manuscript received May 8, 1961; revision received August 20, 1962; paper accepted August 22, 1962. Paper presented at A.I.Ch.E. Cleveland meeting.

Flow and Diffusion Characteristics of Alumina Catalyst Pellets

J. L. ROBERTSON and J. M. SMITH

Northwestern University, Evanston, Illinois

Steady state constant pressure diffusion measurements were made on a series of alumina pellets using the nitrogen-helium system at 1 atm. and 80°F. The pellets were prepared from the same alumina powder but compressed to different densities. Pore size distribution data indicate that all the pellets had approximately the same micropore sizes and volume, but different macropore volumes. Flow measurements with nitrogen were also carried out for the same pellets over a pressure range, up to 1 atm. The data show that the pellet density, or macropore volume, has a pronounced effect.

On the basis of a simplified model of the pellet, path lengths were evaluated from the flow data. On the assumption that the diffusion path length is the same, a method is presented for predicting diffusion rates. The results so computed are independent of the path tortuosity. The method correctly evaluates the effect of pellet density on diffusion, but measured rates are 40 to 80% of the calculated values.

FLOW AND DIFFUSION CHARACTERISTICS OF ALUMINA CATALYST PELLETS

In the recent literature attention has been given to calculation of effectiveness factors for reactions in porous catalysts (*1, 2, 10, 14*). The parameters used in these calculations contain the transport coefficients for heat and mass transfer. It is therefore important to know the magnitude of these coefficients in order to calculate the effectiveness of a particular catalyst system. Data for experimentally determined diffusivities have been published by Weisz (*13*), Hoogschagen (*7*), and Wicke and Kallenbach (*15*), among others. Henry, Chennakesavan, and Smith (*5*) have presented data for diffusion of nitrogen, helium, and carbon dioxide through a porous alumina pellet. From the ratio of the diffusion rates observed it was concluded that Knudsen flow controlled the process. However it has since been shown (*12*) that this is not a satisfactory criterion for determining the mechanism of diffusion. Masamune and Smith (*9*) have presented data for diffusion of helium and nitrogen through porous silver catalysts. The results indicated that diffusion was primarily through the relatively large macropores.

This paper presents diffusion and flow data through alumina pellets of widely different pore size distributions with the objective of evaluating the effect of geometry of the porous pellet on its mass transfer characteristics. The flow measurements were made at atmospheric pressure, or below, with nitrogen, while diffusion was studied at atmospheric pressure with the nitrogen-helium system. From a model of the pellet a method is developed for predicting the diffusion rate from flow measurements.

PELLET PROPERTIES

Cylindrical pellets were made by compressing alumina monohydrate (Boehmite) powder into pellets of different densities. The average size (with respect to weight) of the particles of the powder used for pellets 1 to 6 was about 85 μ. For pellet 7 the average size is estimated to be 700 μ. The pellets were all 2 cm. in diameter and about 1 cm. in length. Pellets made with the same amount of powder exhibited about 1 to 2% deviation in density.

Figure 1 gives the cumulative pore volume, as measured by nitrogen desorption (for pores smaller than 500 Å.) and mercury porosimeter (for pores whose openings are greater than 500 Å.).* Pellets 1 to 6 were made with the same powder by compressing different quantities to the same size pellet. The least-dense pellet, which had a total pore volume of 1.64 cc./g., was compressed at about 2,000 lb./sq. in. This was the minimum compression pressure necessary to make a pellet of sufficient strength for handling. The most dense pellet was compressed at a pressure of about 50,000 lb./sq.

J. L. Robertson is with the Esso Research and Engineering Company, Linden, New Jersey. J. M. Smith is with the University of California, Davis, California.

* Mr. M. F. L. Johnson, Sinclair Research Laboratories, Harvey, Illinois, determined the pore volume data and also calculated the distribution results, shown in Figure 2, from these data.