

Scale-Up in Suspension Polymerization

INTRODUCTION

The subject of scale-up is primarily an engineering discipline and as such is not normally dealt with by applied polymer scientists. However, there is a need for the latter to know how laboratory scale experiments on possibly new formulations in the technique of suspension polymerization will turn out on the production scale.

Scale-up in chemical engineering is the subject of a monograph by Johnstone and Thring.¹ Suspension polymerization is not specifically referred to, and it seems appropriate that the methods therein used be applied to this technique.

DISPERSION THEORY

A quantitative basis for the dispersion of immiscible liquids is provided by the work of Vermeulen, Williams, and Langlois.² In their experiments, two immiscible liquids, water and an organic liquid, were stirred in a cylindrical vessel which was fitted with baffles attached to the sides. A wide range of organic liquids was studied. The organic liquid was dispersed as droplets throughout the continuous phase, the purpose of the investigation being to study the parameters which controlled mean drop size. For geometrically similar mixers and equal volume proportions of the two liquid phases, it was found that the mean drop size is given by

$$\frac{\bar{d}}{L} = K \left(\frac{N^2 L^3 \rho}{\sigma} \right)^{-0.6} \quad (1)$$

Naturally, consistent units must be used in the above equation. Actually, Vermeulen et al. used a weighted mean density, but this is close to the mean density.

A more general equation which takes account of the volume fraction is

$$\frac{\bar{d}}{f(\phi)L} = K \left(\frac{N^2 L^3 \rho}{\sigma} \right)^{-0.6} \quad (2)$$

where $f(\phi)$ is a function of the volume fraction ϕ .

This function is linear, and to a good approximation is given by

$$f(\phi) = 1 + 3.3\phi. \quad (3)$$

The term in brackets, $N^2 L^3 \rho / \sigma$, is a dimensionless group, called the Weber number. Actually it is a modified form of a true Weber number: why a modification is necessary is explained below. The true Weber number, $\rho v^2 d / \sigma$, is the ratio between the inertial force on a single droplet of diameter d and velocity v , proportional to $v^2 d^2$ and the surface tension force, proportional to σd . The inertial force is the force causing a drop to accelerate and is equal to $\frac{1}{3} \pi d^3 \rho dv/dt$. This term is of dimensions $\rho v^2 d^2$. As to the surface tension force, if a spherical drop of diameter d tends to split circumferentially, the force tending to hold the drop together is $\sigma \pi d$. This term is of dimensions σd . The ratio inertial force/surface tension force has dimensions $\rho v^2 d^2 / \sigma d = \rho v^2 d / \sigma$, and this ratio is the true Weber number.

As for the modification of the Weber number referred to above, in order that the mean drop size be expressed as a function of a dimensionless group that does not itself contain the mean drop size as a dependent parameter, d in the Weber number is replaced by L , the impeller diameter, and the velocity v of a droplet is replaced by NL , proportional to the tip speed of the agitator, so that the Weber number now becomes $\rho N^2 L^3 / \sigma$. This number has been found² experimentally to be related to mean drop size as shown in eq. (2), with a mean deviation for various pairs of liquids of 20%. These modifications to the Weber number do not destroy its meaning, because the factors of proportionality between d and L and between v and NL , after being raised to the power n (where $n = -0.6$) can be absorbed into the constant, giving the overall constant K , called the shape factor. The value of K depends on the shape of the mixer, which should be the same for the model and large plant. Large plants are of cylindrical shape, whereas laborato-

ry experiments are often performed in spherical vessels. The laboratory vessels should be scaled-down versions of the large plant, including the stirrer and baffles, if the results obtained from laboratory experiments are to be used for scale-up. The geometrical shape used by Vermeulen et al. was a cylindrical vessel completely filled and fitted with four baffles symmetrically placed and of specific dimensions relative to the cylinder.

The significance of the above correlation between mean drop size and modified Weber number lies in the fact that the viscosities of the dispersed phase and continuous phase are not involved. The continuous phase was water. Now in suspension polymerization, in order to decrease drop coalescence, suspending agents are dissolved in the aqueous phase, and as a result the viscosity of this phase increases considerably. The author has carried out experiments on the dispersion of methyl methacrylate in water containing 1–3% polyacrylamide, and it has been found that there is good correlation of the mean drop size with the modified Weber number as given in eq. (2). It has also been found that for volume fractions below about 0.3, the relationship between $f(\phi)$ and ϕ is approximately linear.³

Since invariably in suspension polymerization the composition of each phase is unchanged as between laboratory and plant scale, eq. (2) for the case of equal drop sizes and equal relative volume fractions becomes

$$L_1(N_1^2L_1^3)^{-0.6} = L_2(N_2^2L_2^3)^{-0.6} \quad (4)$$

where the subscripts 1 and 2 refer to the small and large plants, respectively.

On simplifying, eq. (3) becomes

$$N_1^3L_1^2 = N_2^3L_2^2 \text{ or } N_1 = N_2 \left(\frac{L_2}{L_1} \right)^{2/3} \quad (5)$$

Since in the case of installed plant equipment L_2 and N_2 are known, the main use of this equation is in calculating the rpm required in laboratory apparatus.

Table I compares a 1/2-ton reactor with a small-scale laboratory apparatus. In both, a suspension polymerization on methyl methacrylate was carried out at 85°C, using a 1% solution of polyacrylamide as suspending agent, at equal volume fraction of dispersed phase. The mean drop size from each apparatus was the same. The tip speed of the agitator and the Reynolds number $NL^2\rho/\mu$ are also given. These results show that the scale-up law shown in eq. (5) is obeyed.

TABLE I
Comparison of Two Reactors

Reactor	Impeller diam., in.	rpm	Tip speed, ft/sec	N_{Re}
1/2-Ton	32	80	5.6	8.8×10^3
Laboratory	4	320	11.2	14.08×10^4

These results show that the scale up law shown in equation (5) is obeyed.

The critical N_{Re} for transition between streamline and turbulent flow lying in the range of 10–300, for both reactors the motion is that of fully turbulent flow. Equation (4) does not lead to excessive rpm in the small plant. If it did, there would be the possibility of cavitation.

POWER REQUIREMENTS

From the point of view of an applied polymer scientist, the power requirement is not of great interest, provided that it does not impose limitations, which it generally does not. It is shown in reference 1 that the power requirements are expressible in terms of the Reynolds number and that for baffled mixers, at $N_{Re} > 10^3$,

$$\pi = \frac{C}{g} N^3 L^2 \quad (6)$$

where π = power input per unit volume; C = constant, involving liquid density; and g = accelera-

tion due to gravity. Thus, for homologous mixing systems at equal values of π , the scale equation is

$$N^3 L^2 = \text{constant.} \tag{7}$$

It happens that this is identical with eq. (5).

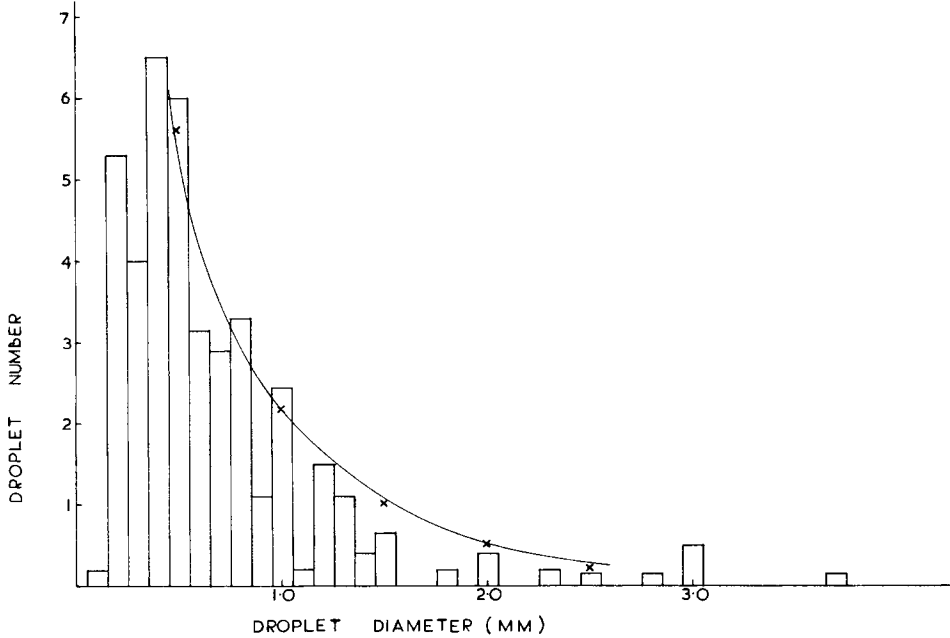


Fig. 1. Size-number distribution for kerosene.

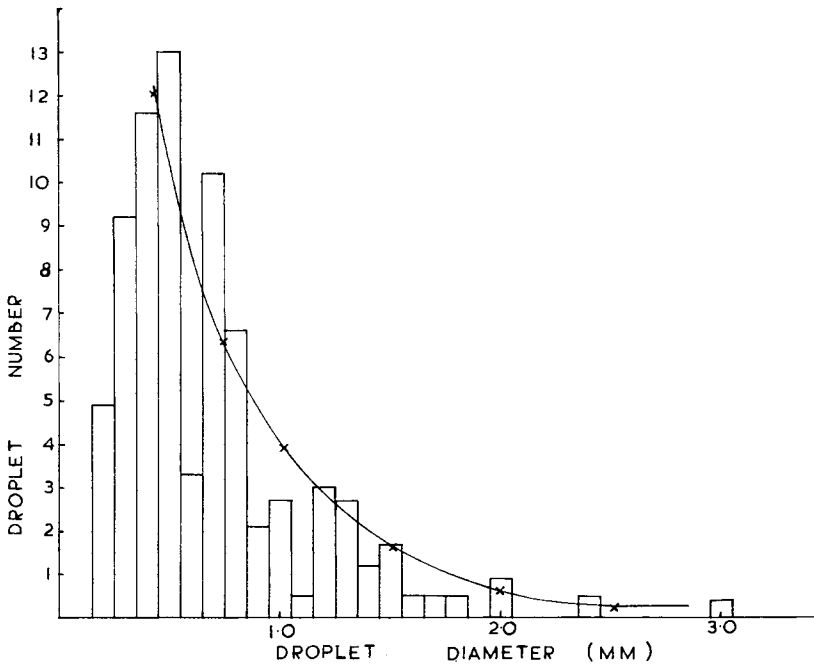


Fig. 2. Size-number distribution for benzene.

COOLING WATER REQUIREMENTS IN AN INDUSTRIAL REACTOR

In order to determine the amount of cooling water required in a large industrial-size reactor, it is best to use directly the equations used in heat transfer theory. The reason for this is that in performing a laboratory scale experiment on a polymerization reaction, it is relatively easy to keep the reaction temperature constant, and it is seldom that detailed studies on heat transfer are required, whereas on a large scale, heat transfer equations must be used in order to ensure proper cooling.

A typical reaction vessel for industrial suspension polymerization is a jacketed cylindrical vessel. In the heating up-stage steam is passed through the jacket, and when the temperature at which the reaction is to be carried out is reached, the steam is replaced by cooling water. The equations that are used for calculating the cooling water requirements are given in standard texts on heat transfer, e.g., reference 4. The scheme of the calculation is as follows. Since the maximum heat of reaction per unit volume of monomer, the volume of monomer, the temperature at

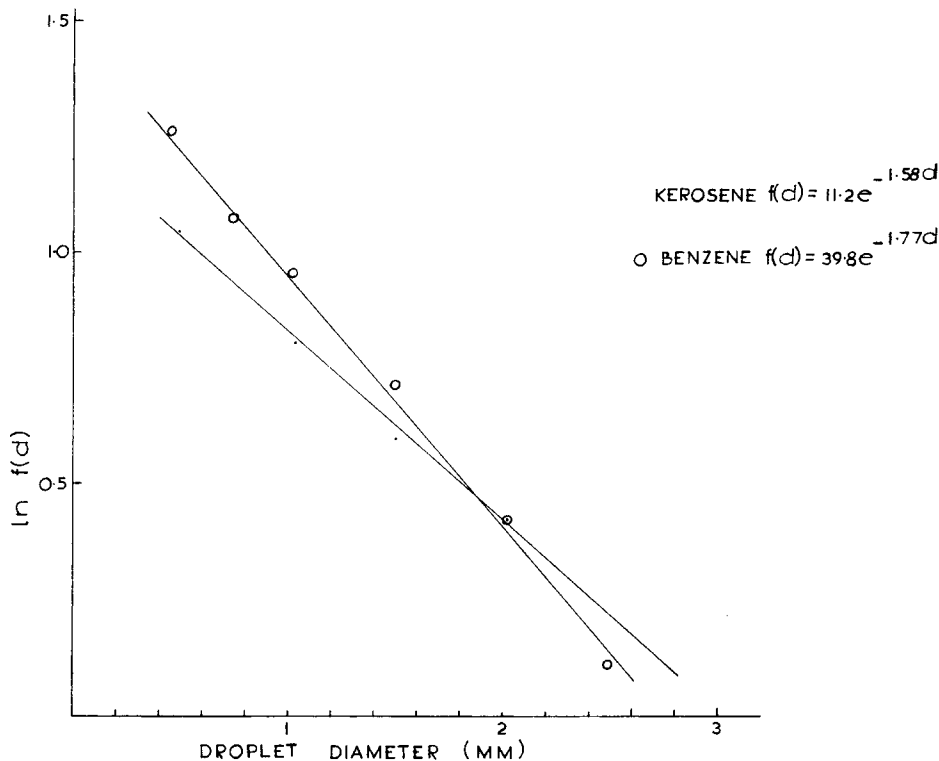


Fig. 3. Size distribution function.

which the reaction is to be carried out, and the inside area of the reactor wall are all known, an overall heat transfer coefficient can be calculated. The overall coefficient must be resolved into its components, in particular, the outside film transfer coefficient, and it is from this latter that the cooling water requirement can be found. It turns out that temperature dependence of the viscosity of the suspension must be known.

Of particular interest is the effect of polymer build-up on the reactor wall. Calculation shows, assuming an average thermal conductivity of polymer of 4×10^{-3} watt/(cm)(s)(°K), that polymer deposits of 2×10^{-2} cm, 5×10^{-2} cm, and 10^{-1} cm, respectively, reduce the overall heat transfer coefficient by 9%, 19%, and 32%. Hence it is easily possible that the degree of cooling required to maintain the reactor temperature could not be attained. This means that reactor walls must be periodically cleaned. Highly polished surfaces of an antiadsorbent nature are clearly desirable.⁵

PARTICLE SIZE DISTRIBUTION

Solid particles obtained by suspension polymerization have a size distribution, but fortunately it is such that the distribution is concentrated in a relatively narrow size range, the standard deviation about the mean being small. Dispersion experiments on a single drop⁶ have shown that the size distribution function $f(d)$ has the form $f(d) = be^{-ad}$, where d is the drop diameter and a and b are constants. Figures 1 and 2 show the size-number distribution for a droplet of kerosene and benzene, respectively, when broken up by a water jet. Figure 3 is a plot of $f(d)$ against d for both liquids. On continued dispersion in the presence of other droplets, the small droplets either dissolve (their total volume is of the order of 1%), or else they coalesce to form larger drops.

Concerning experimental work on the formulation of new products of copolymers, new suspending agents, or even different initiators or chain transfer reagents, the parameters ρ and σ must both be known. Of these, σ is the more difficult to measure, for it must be measured at the temperature of the polymerization reaction and in the presence of the suspending agent, including inorganic salts.

CONCLUSIONS

The relationship between mean drop size and volume fraction has been given as linear, the volume fraction function $f(\phi)$ being of the form

$$f(\phi) = 1 + C\phi. \quad (8)$$

Linearity holds for values of ϕ up to about 0.3. As ϕ increases, it is likely that a quadratic term will appear. Furthermore, the constant C will vary with amount and nature of suspending agent and salts added to modify the suspending agent. This, of course, does not affect the scale-up law.

As for the bulk viscosity of the reacting mixture, further work is required to obtain quantitative information as to the effect of droplets and particles on the dynamic viscosity of the suspending agent solution.

Nomenclature

\bar{d}	volume-to-surface mean diameter (Sauter diameter) of droplets
d	diameter of a drop (as in Weber number)
K	shape factor
L	diameter of agitator
N	agitator rpm
π	power input per unit volume
ρ	mean density of phases; density of a drop
σ	interfacial tension
ϕ	volume fraction of dispersed phase
μ	bulk dynamic viscosity

References

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