CHAPTER III

THEORY

3.1 Introduction of Foaming in Lubricating Oils (Trautman, 1946)

Before the second world war, foaming of lubricating oils did not cause much trouble except occasionally in such equipment as reaching car engines and auto-motive and industrial gears. It was not until early in the war that foaming reached serious proportions in air craft engines, naval diesel engines and military tank engines and gears. One of the principal cause of the foaming was the increased foaming tendency of the oils specified for use in this equipment. the detergent-type, compounded oils meeting the Army-Navy engine oil specification (before foaming limits were applied) in general had greatly increased foaming tendency as compared with the uncompounded base oils. However, foaming difficulties were largely eliminated by the development of anti-foaming agents which reduce foam stability of these compounded, as well as straight mineral oils, to a minimum.

Lubrication oil in automotive differentials and gear boxes of industrial machines frequently foams after prolonged use. When the lubrication oil foams, its volume greatly increases and thus part of the oil is forced out of the gear housing through breather holes and the like. Beside causing a loss of oil, foaming also interrupts the proper lubricating function of the oil and so results in rapid wear in the various components of the gear train.

It has been found that foaming occurs when water has been present for sometime in the lubrication oil in a gear box. Water itself does not cause this foaming as no foaming is observed when lubricating oil is agitated in the present of water deliberately added to the oil. Water in lubrication oil reacts with the steel surface of the gear trains and of other components in gear box to form

ferric-hydroxide. The rate of which such a reaction takes place depends on temperature, and it may take a considerable period of time before ferric-hydroxide is found in any appreciable amount. The ferric-hydroxide formed, being basic, will react with various acidic additives commonly present in lubrication oil. Among such additives, sulfur type and, in particular, phosphorous type additives have been found to react with ferric-hydroxide to form a reaction product, in the presence of which the lubrication oil will foam after the certain amount of agitation. The exact nature of this reaction product is not known, and such reaction product will be generally referred to hereinafter as metallic salts. The amount of water normally present in lubrication oil about 0.05 % of water is sufficient to lead to subsequent foaming.

3.2 Type of Antifoam Agent

3.2.1 Dehydrating agent; (Hesden, 1977)

The foaming of lubricating oils would appear to be caused by reaction of water and/or acidic components of lubricating oils with the metallic surfaces within gear trains and cases to form over a period of time ferric-hydroxide and subsequently iron salts of unknown composition which in tern promoting foaming.
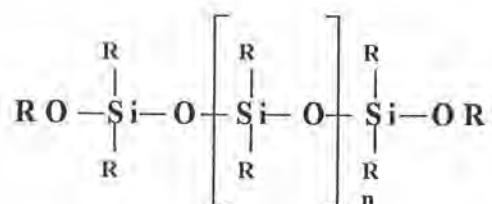
It appears that the addition of certain dehydrating additives to the lubrication oil effectively prevents the formation of these foam-producing iron or other metallic salts, either by reacting with water present in the lubrication oil or by binding the metallic salts in a form not capable of promoting foaming.

The particular additives which have been found suitable for this process are generally characterized as dehydrating agent. Common dehydrating agents such as anhydrous potassium sulfate, anhydrous sodium sulfate, anhydrous calcium chloride, and the like are particularly useful. Being ionic in

character, such inorganic salts do not dissolve in lubricating oil, but they can serve the purpose if their particle size is small enough that they be kept dispersed in the lubrication oil. The dehydrating agent may also be an oil-soluble organic compound, or a mixture of such compounds, including hygroscopic derivatives obtain by reacting alkaline and alkaline earth metal oxides or their salts with fatty acids, saturated or unsaturated dicarboxylic acids, aminocarboxylic acids, sulfonic, sulfinic or sulfamic acids.

3.2.2 Organosilicone; (Colbert, 1981)

These preferred antifoam agents are organosilicone oxide condensation products or condensation products of silanols or organosilicols, including silicones and silicates, having the following structure:

$$R\,O - \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O - \left[\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O \right]_n \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}} - O\,R$$

Where "R" represents similar or dissimilar organic radicals such as alkyl, aryl, alkaryl, aralkyl and heterocyclic groups; the "R's" and "OR's" may be substituted by hydroxyl groups; and "n" is one or more.

A preferred organosilicone antifoam agent is a dimethyl silicone linear polymer chain-stopped with methyl groups, the silicone being mixed with finely divided siliceous material such as silica. A suspension is formed which is relatively inert in contact with known metals and plastics and is relatively nonflammable. If desired, the siliceous material may be omitted. The organosilicone antifoam agents may range in viscosity from 100 to 250,000 cSt. (@ 40 $^{\circ}$C.), higher viscosity compounds, above 900 cSt., being particularly preferred.

Since the silicones have extremely limited solubility in the normal

lubrication oils, a slightly different technique must be used to incorporate the additive than is normally used to add soluble agents. The most common method is to dispersed by homogenization a comparatively large proportion of the silicone into a carrier, usually a part of the same oil or a similar oil. This carrier or concentrate then can be added directly to the final oil by mild agitation in the same manner that soluble compounds are added.

The antifoam agent aids in the reduction of aeration. Obviously, the agent cannot prevent aeration, but it does tend to get rid of the air more rapidly. The agent promotes coalescence and junction between two gas bubbles of moderate size to form a large bubble which escapes more rapidly to the free surface where the antifoam action breaks the bubble. (Trautman, 1946)

3.3 Flow Patterns (Holland and Chapman, 1966)

Agitator are used to produce flow, and subsequently, turbulence in a liquid mass. Each type of agitator causes high velocity liquid to flow through a vessel in a specific path, referred to flow pattern. Flat and curved blade turbine, mixing low or moderate viscosity liquids, produce radial flow patterns when used in a buffle vessel. Radial flow, shown in Figure 3.1, is primarily perpendicular to the vessel wall. The marine type propeller and pitched blade turbine produce axial flow patterns when centered in a buffled vessel containing low or moderate viscosity liquids. Axial flow, shown in Figure 3.2, is primarily flow parallel to tank wall.

If either the marine propeller or any of the impeller agitators are used in an unbuffled vessel containing low viscosity liquid, vortexing develops. The liquid swirls in the direction of the agitator rotating, causing a drop in liquid level around the agitator shaft. Vortexing increases with impeller speed until eventually the vortex passes through the agitator. Gas bubbles will be sucked into the bulk fluid. The mixing efficiency of vortexing systems is usually lower

than for geometrically similar nonvortexing systems. This can be avoided by putting baffles into the vessel. Baffles is fixed perpendicular to the vessel wall.

The basic principles which related fluid velocities and equipment geometry are applicable also to rotating impellers in agitated vessels.

3.4 Impeller Types (Warren, McCabe, Smith and Peter, 1988)

Impeller agitators are divided into two classes: these which generate currents paralleled with the axis of the impeller shaft and those which generate currents in a tangential or radial direction. The first are called axial-flow impellers, the second radial-flow impellers.

The three main types of mixing impellers are turbines, propellers and paddles. Each type contains many variations and subtypes for specific purposes, which will not be considered here.

3.4.1 Turbine Agitator

The type of agitator is used for vigorous mixing where high power inputs are necessary. Materials of construction are designed for acid, neutral or alkaline conditions. General applications are chemical reaction between liquids and solids, reagent mixing, neutralization reactions and mineral surface conditioning. See Figure 3.3

3.4.2 Propeller Agitator

This agitator is similar to the turbine type but for less vigorous mixing and lower horsepower input. General applications are slower chemical reactions, reagent mixing, reaction requiring aeration by the creation of a vortex. See Figure 3.4
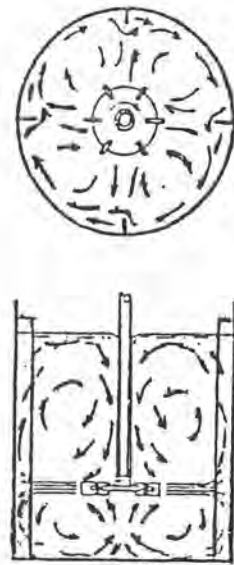
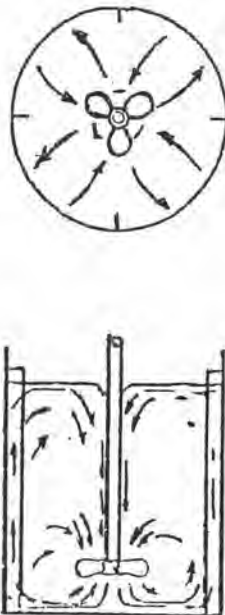Figure 3.1 Radial flow pattern

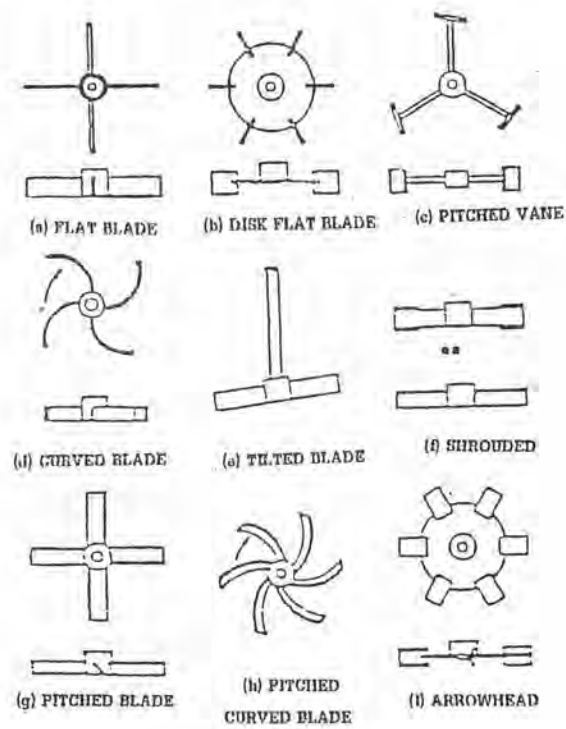

Figure 3.2 Axial flow pattern

Figure 3.3 Turbine impeller designs (Warren, McCabe, Smith and Peter, 1988)
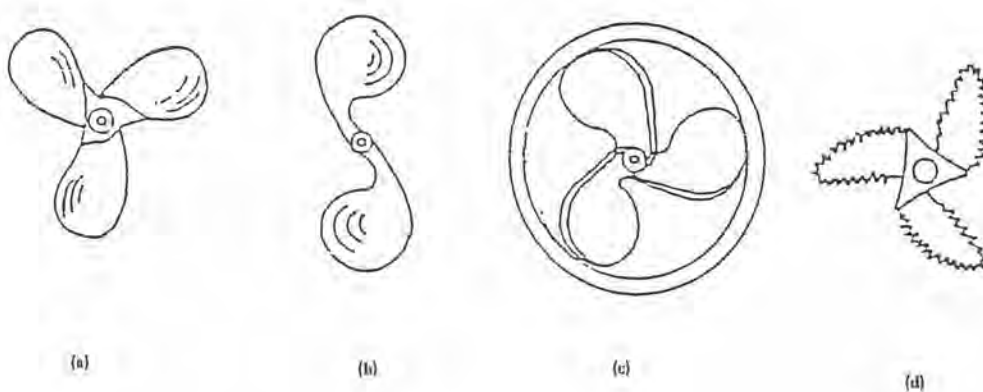

Figure 3.4 Mixing propellers : (a) Standard three-blade

(b) Weedles   (c) Guarded (d) Saw-toothed (Nagata, 1975)

3.4.3 Paddle Agitator

The paddle agitator is essentially a low horsepower input type with the slow paddle speeds to maintain solids in suspension without necessarily maintaining a homogeneous pulp density. The paddle is relatively close to the bottom of the tank which makes this type ideal for pulp or liquid storage. Applications include the storage of solid-liquid suspensions such as lime slurries, flotation concentrates and pulps for intermittent or batch processes. See Figure 3.5
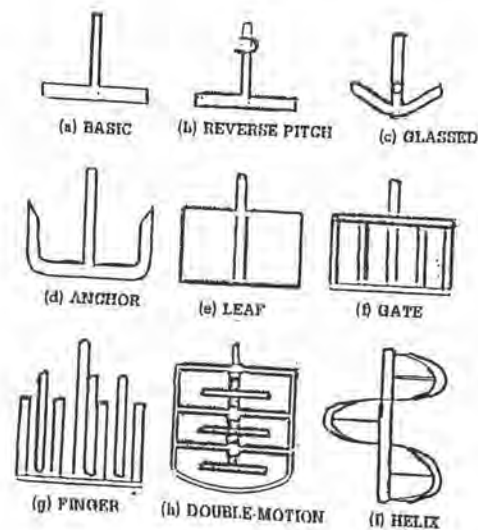

Figure 3.5 Paddle impeller designs (Nagata, 1975)

3.5 Standard Tank Configuration (Oldshue, 1983)

The vessel configuration, shown in Figure 3.6 are known as the standard Tank Configuration. The Standard tank Configuration has the following geometrical relationships:

- The agitator is a standard six-bladed turbine (Figure 3.4)
- Impeller diameter, D_i = 1/3 tank diameter, T.
- Impeller height from the tank bottom, H_i = 1.0 impeller diameter.
- Impeller blade length, L = 1/4 impeller diameter.

- Impeller blade width, W = 1/5 impeller diameter.
- Liquid height, H_l = 1.0 tank diameter.
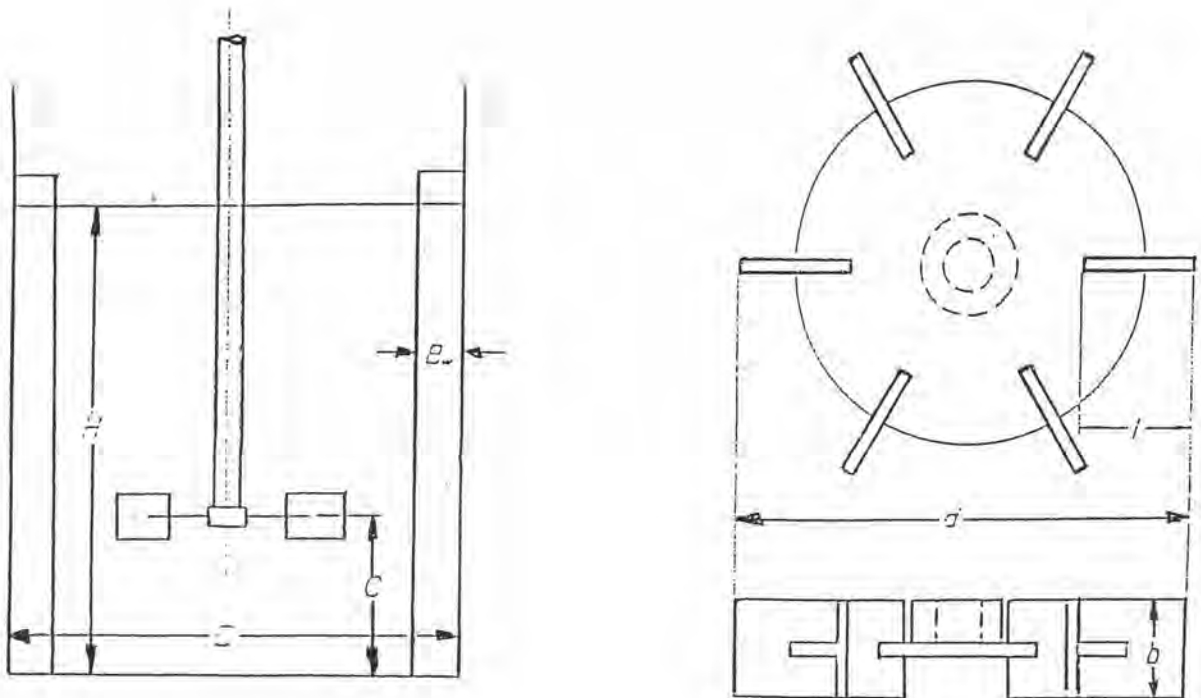

Figure 3.6 Standard Tank Configuration (Nagata, 1975)

3.6 Mixing time correlations (Nagata, 1975)

Required mixing time is one of important parameters in a mixing process. If the time of mixing employed is much longer than the required mixing time, it would waste time and energy. In industry, it means decreasing production capacity and increasing extra expenditure. In many cases excessive agitated can cause segregation of the mixing components. In the other hand, If the time of mixing is insufficient a nonuniform product will be formed.

The dimensionless mixing time, $\tau = t_m(N)$, is influenced by the geometry of the mixing vessel, by the injection methods for the ingredients, and by R_e or P_e which controls the convection flow or diffusion.

In geometrically similar vessels, the state of liquid flow is classified roughly by Reynolds number, $R_e = D_i^2 N/V$ as follows;

1) a low Reynolds range where the impeller speed is not large and the secondary circulation flow due to the centrifugal effect is negligible.

2) a medium Reynolds range where the secondary circulation flow is appreciable (laminar range)

3) a high Reynolds range (a complete turbulent state)

In each individual range, the liquid flow pattern is similar. In a completely turbulent flow range, the turbulent Peclet number (P_{et}) gives a certain constant value, so that dimensionless mixing time $\tau = t_m N$ shows a constant value and t_m is inversely proportional to N.

Blend time, t_m, can be defined as the time from the start of mixing at some unmixed condition until the vessel contents reach a predetermined value of uniformity. Frequently used criteria include the time to reach specified variations in temperature, density, component concentration, etc.

No universally accepted definition exists of what constitutes complete blending. Some process may require as little as 95 % uniformity, while other may require in excess of 99.9 %. Methods of determining uniformity must be considered. The degree of uniformity must be established on the basis of process objectives or decided for each specific case. Since concentration is dependent on location, multiple samples as different locations are required to assure uniformity.

3.7 Product Data Calculations ("Mixing Equipment (Impeller type)," 1987)

3.7.1 Simplified Analysis Batch Operation

Batch mixers are normally evaluated on the basis of the mixing time required to obtain a specified mixture.

Properties of interest are examined as a function of the mixing time, and the required mixing time is the shortest time at which there is satisfactory assurance that the values of properties are within selected limits. Decisions may be based on visual examination of a plot of time of sampling (abscissa and independent variable) versus measured values of the property (ordinate and dependent variable) for many operations. Evaluations may also be made at different operating conditions (for example, mixer speeds) and the effect of important operating variables determined by examining the required mixing time as a function of the operating variables.

AIChE Equipment Testing Procedure recommended the selection of the mixing time of the curing-rate additive as the time required to achieve concentration of mixture within acceptable limit as shown in Figure 3.7 or to reach composition equilibrium by statistical analyzing as shown in Figure 3.8

Kramer et al. (1953) selected required mixing time as the time for concentration variations to become less than 0.1 % of the average KCl concentration as shown in Figure 3.9.

Noi et al. (1973) selected required mixing time as the time to achieve variation of concentration of radioactive material (count rate) at both detectors less than 1 time of standard deviation as shown in Figure 3.10 (a) and Figure 3.10(b).

Pipop T. (1992) selected required mixing time as the time to achieve variation of concentration of radioactive (count rate) at both detectors less than 3 times of standard deviation as shown in Figure 3.11.
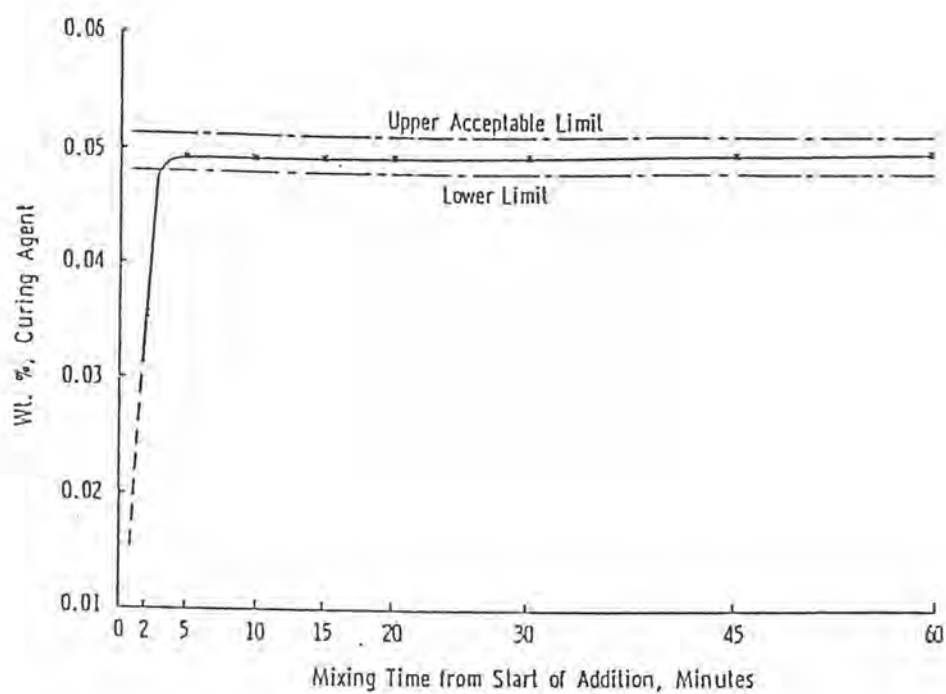
Figure 3.7 Composition & mixing time in 150 gal. dough mixer

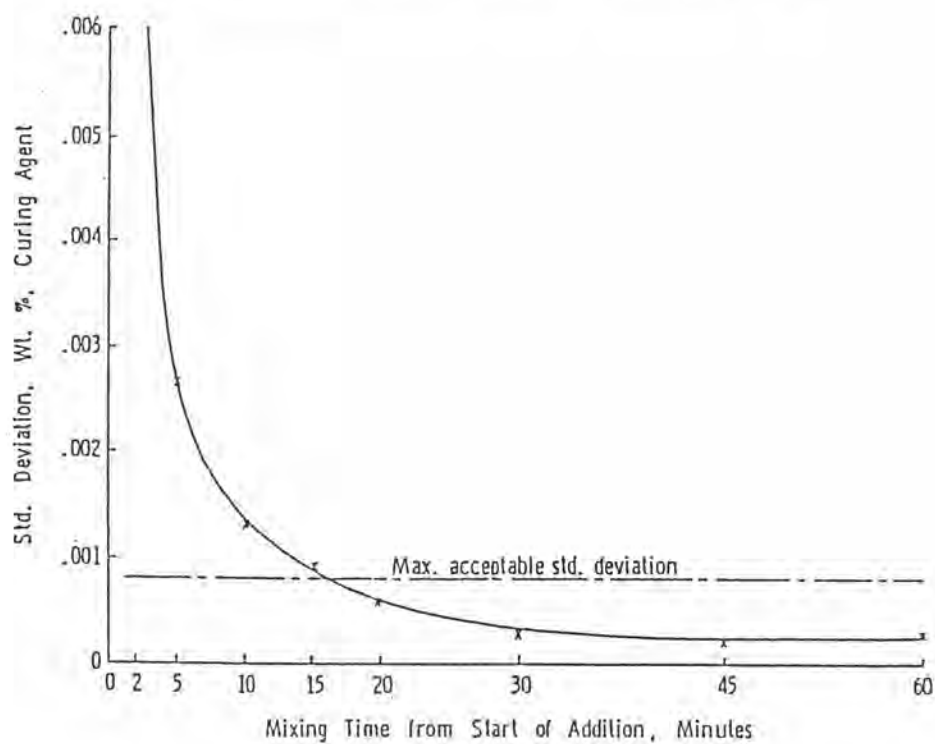(AIChE Equipment Testing Procedure, 1979)

Figure 3.8 Standard variation & mixing time in 150 gal. dough mixer
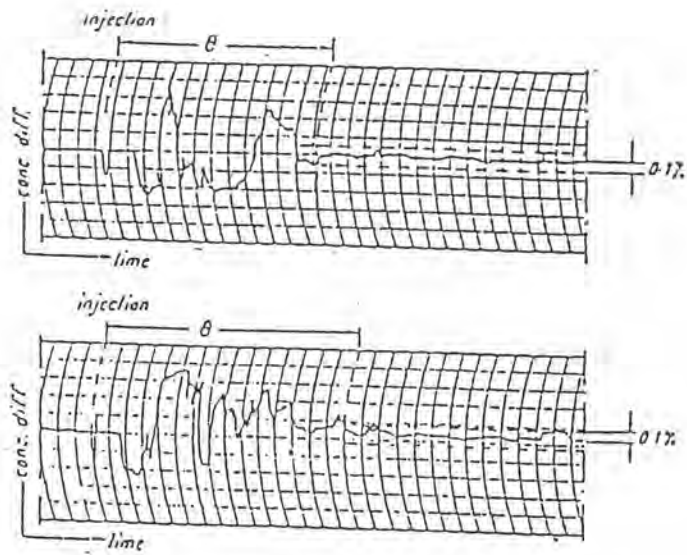
(AIChE Equipment Testing Procedure, 1979)

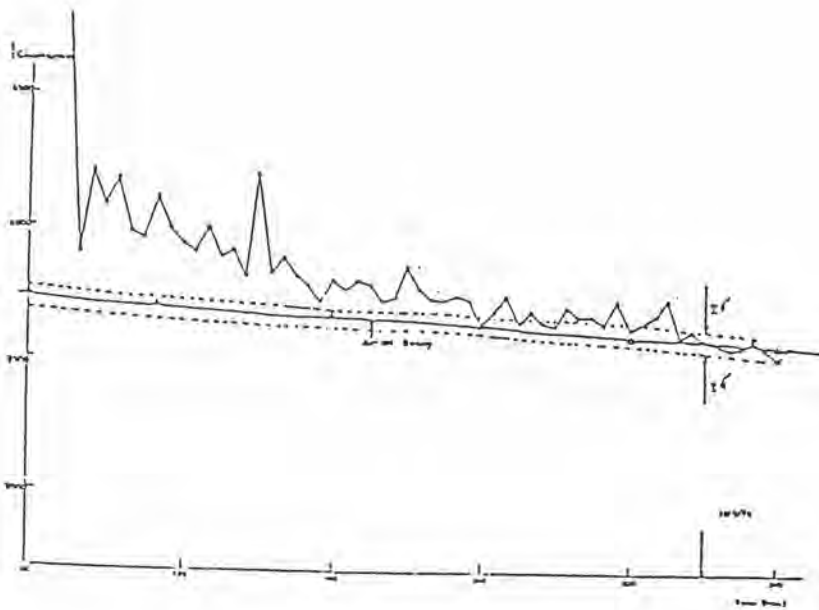Figure 3.9 Method of determining mixing time (Kramers et al., 1953)

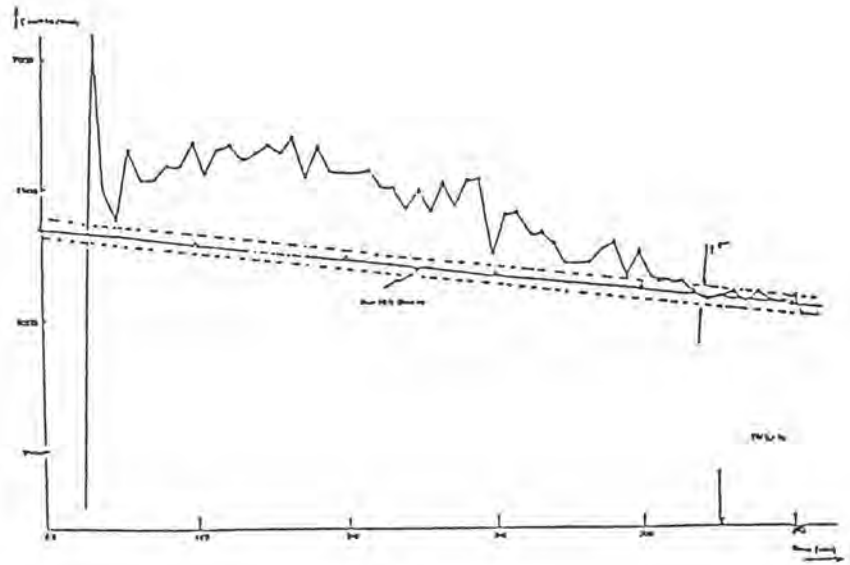Figure 3.10 (a) Scalar counts from detector No. 1 (Noi et al, 1973)

26

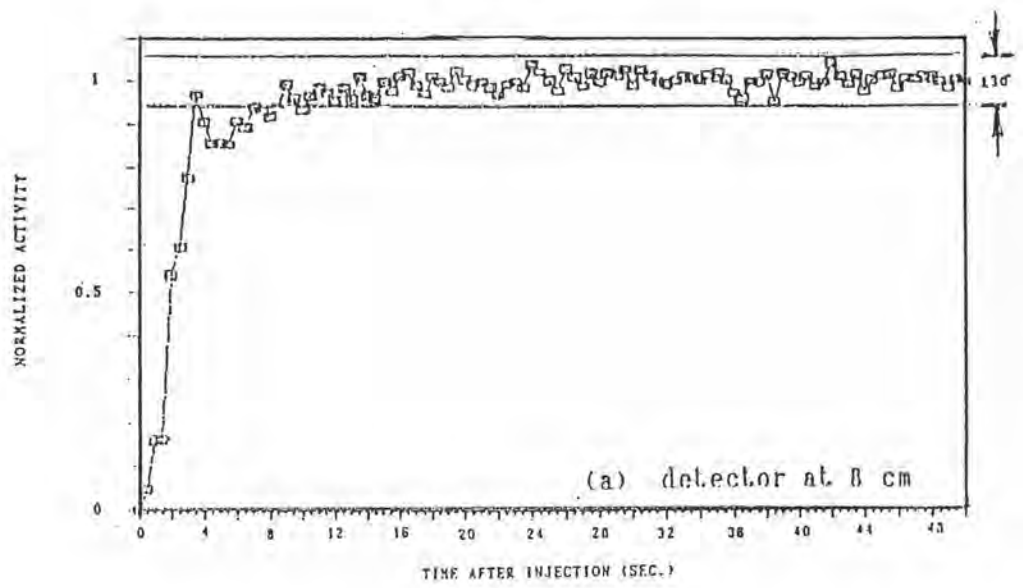Figure 3.10 (b) Scalar counts from detector No. 2 (Noi et al, 1973)

Figure 3.11 Tracer respond curve using radioactive technique. (Pipop, 1992)

3.7.2 Effect of operating conditions

The effect of important operating variables determined by examining the required mixing time as a function of the operating variables.

Kramer et al (1953) studied the mixing time of weak and concentrated KCl solutions using the propellers and turbines. Two size of vessels were used (10.5 in. and 21. in. diameter tank). Kramer used electrical conductivity cell for measuring fluctuations of solutions. The data which Kramer obtained on experiments shown that the mixing time, t_m, was found to be inversely proportional to the agitator rotation speed, N, as shown in Figure 3.12. The line shown has a slope of

Marr (1963) made experimental measurements of batch mixing time using a phenolphthalein indicator, NaOH and HCl solution. First, NaOH and indicator were added to the vessel with the agitator in motion. Then, HCl solution was added adjacent to the impeller and the time for the red color to disappear was measured. A 11.5 in. diameter tank with three 1.5 in. wide, vertical baffles was used. It was found that t_m was proportional to $1/N$. The results of these tests are shown in Figure 3.13.

A plot of apparent viscosity versus shear rate on log-log coordinates gives a straight line of negative slope as shown in Figure 3.14

Metzer and Otto (1957) were the first investigators to propose a useful procedure for prediction of power consumption in non-newtonian fluids using fundermental viscometric data. It found that the fluid motion in the vicinity of the impeller could be characterized by relating shear rate to impeller speed as follow:-

Shear rate α N

This equation is a useful design equation since it can be used to calculate the apparent viscosity of a non-Newtonian liquid in an agitated vessel at any agitator speed.
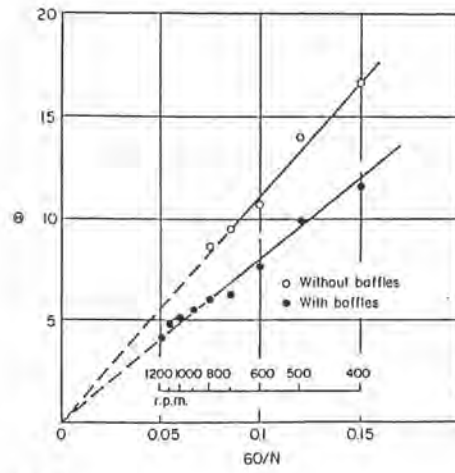
Figure 3.12 Relationship between mixing time and rotation speed (Kramers,1953)
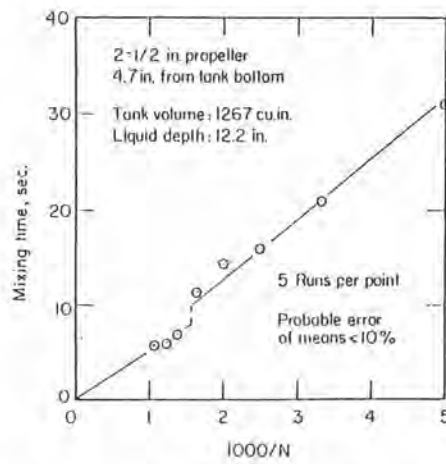

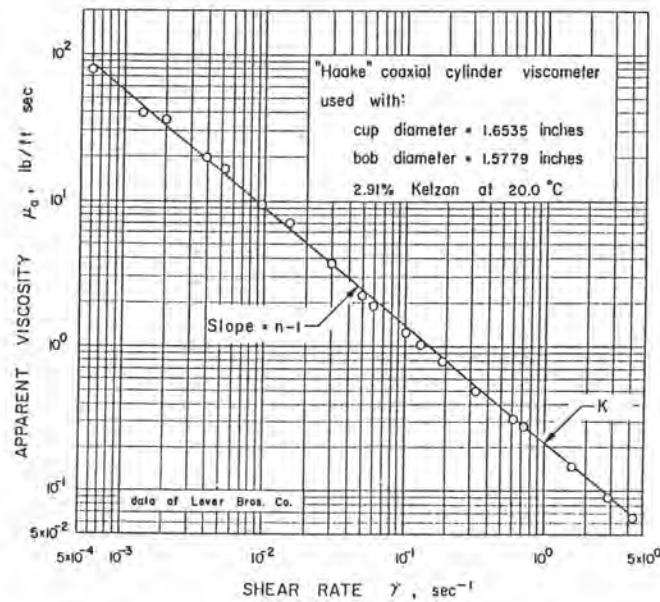Figure 3.12 Relationship between mixing time and rotation speed (Marr, 1963)

Figure 3.14 Apparent viscosity versus shear rate (Vincent and Joseph, 1966)

3.8 Dimensional analysis (Vincent and Joseph, 1966)

3.8.1 General equation

The general dimensionless equation for agitator power was derived by the early investigators using dimensional analysis. They considered that impeller power should be a function of geometry of the impeller and the tank, the properties of fluid (viscosity and density), the rotational speed of impeller, and gravitational force. The Buckingham pi theorem gives the following general dimensionless equation for the relationship of the variables:

$$f\,[\,D_i^2 N\rho/\mu\,,\,D_i N^2/g,\,P_g/\rho N^3 D_i^5,\,D_i/T,\,D_i/Z,\,D_i/C,\,D_i/w,\,D_i/l,\,n_2/n_1] = 0 \qquad (3.1)$$

where

D_i = impeller diameter

T = tank diameter

Z = liquid depth

C = clearance of impeller off vessel bottom

w = blade width

p = pith of blades

n = number of blades

l = blade length

ρ = density

μ = viscosity

P = power

N = impeller rotational speed

g = gravitational acceleration

g_c = Newton's law conversion factor

3.8.2 Similarity

Equality of all groups in Eq. (3.1) assures similarity between systems of different size. The types of similarity of interest here are geometric, kinematic, and dynamic.

A. Geometric similarity. The last seven terms in Eq. (3.1) represent the condition of geometric similarity which requires that all corresponding dimensions in systems of different size bear the same ratio to each other. The reference dimension used is the impeller diameter. The last term in Eq.(3.1) is not a linear dimension relationship but is required to account for change in number of impeller blades-the handling assumes use of reference to some standard condition.

Equation (3.1) assumes a single impeller centered on the axis of a vertical cylindrical flat bottom tank. To be fully inclusive, the equation would have to be expanded to include:

 a. off-center impeller positions

 b. multiple impellers

 c. baffle width and number of baffles

 d. tank shape

B. Dynamic and kinematic similarity. Given geometric similarity, two systems are dynamically similar when the ratios of all corresponding forces are equal, Kinematic similarity requires that velocities at corresponding points be in the same ratio. These two similarity criteria are presented together since they are interrelated in a fluid system.

Confining the discussion to geometrically similar systems, Eq. (1) may be stated as

$$f\{D_i^2 N\rho/\mu \,,\, D_i N^2/g \,,\, Pg_c / D_i^5 N^3 \rho \} = 0 \qquad (3.2)$$

Equality of the groups in this expression insures dynamic and kinematic similarity. This relationship was derived by dimensional analysis, but the same dimensionless groups may also be obtained from the Navier-Stokes equation of motion. A complete discussion of the derivation and application of the Navier-Stoles equation is given in standard references such as Bird et al. and Schlicting and will not be presented here. For the complex, three-dimensional flow in a mixing system an analytical solution to the Navier-Stokes equations cannot be obtained. However, the equations may be stated in dimensionless form as follows:

$$f\{\rho \upsilon L/\mu, \upsilon^2/Lg, \Delta P/\upsilon^2 \rho\} = 0 \tag{3.3}$$

where

υ = velocity

L = a characteristic length

ΔP = pressure difference

The groups in this equation are the time as those of Eq. 3.2, as will be demonstrated below, and a definite physical significance may be attributed to each group.

3.8.3 Physical significance of dimensionless groups

a. Reynolds number, N_{Re}. The first group in Eq. 3.3 is the Reynolds number and represents the ratio of inertial forces to viscous forces. Since this ratio determines whether the flow is laminar or turbulent, Reynolds number is a critical group in correlating power. In similar systems, any convenient velocity and length may be used in the Reynolds number. For agitation, the following are the ones generally employed :

$L = D_i$ and $\upsilon = ND_i$ substitution gives

$$N_{Re} = (\rho)(ND_i)(D_i)/\mu = D_i^2 N\rho/\mu \tag{3.4}$$

Which is identical to the group derived by dimensional analysis.

b. Froude number, $\mathbf{N_{Fr}}$, the group is known as the Froude number and represents the ratio of inertial to gravitational forces. Substituting Eq. 3.4 into this group gives for an agitator :

$$N_{Fr} = (ND_i)^2 / (D_i g) = D_i N^2 / g \qquad (3.5)$$

In many fluid flow problems, gravitational effects are unimportant and the Froude number is not a significant variable. The reason it is included here is that most agitation operations are carried out with a free liquid surface in the tank. The shape of surface and, therefore, the flow pattern in the vessel, are affected by gravitational field. This is particularly noticeable in unbaffed tanks where vortexing occurs; the shape of vortex represents a balancing of gravitational and inertial forces.

c. Power number, Np, is the pressure coefficient in Eq. 3.3, and represents the ratio of pressure differences producing flow to inertial forces. In practice, the pressure distribution is not known, but in dynamically similar systems it can be shown that ΔP and power are related by :

$$k \, P/ND_i3 = \Delta P \qquad (3.6)$$

Making this substitution into the pressure coefficient together with the reference velocity $\mathbf{U} = \mathbf{ND_i}$ gives

$$N_p = Pg / (\rho N^3 D_i^5) \qquad (3.7)$$

The power number derived from dimensional analysis is the same.

An understanding of the physical significance of the power number is enhanced by considering it as a drag coefficient or friction factor. The drag coefficient of a solid body immersed in a flowing stream is usually defined as

$$C_D = F_D g_c / (\rho \upsilon^2/2)A \qquad (3.8)$$

where $\quad C_D \;=\;$ drag coefficient

$\qquad\qquad F_D \;=\;$ drag force on the body

$\qquad\qquad \upsilon \;=\;$ velocity of flowing stream

$\qquad\qquad A \;=\;$ cross-sectional area of the body

For a mixing impeller, N_p can be show to be analogous to C_D from the following arguments:

$$\upsilon \propto ND_i$$

$$A \propto D_i^2 \qquad \text{(geometrically similar impellers)}$$

$$P \propto NF_D D_i$$

Introduction of these relationships into Eq. (3.8) gives

$$C_D \propto [(P/ND_i)g_c]/\rho(ND_i)^2 D_i^2 \qquad (3.9)$$

simplifying

$$C_D \propto [Pg_c]/\rho N^3 D_i^5 \qquad (3.10)$$

or

$$C_D \propto N_p \qquad (3.11)$$

The analogy of C_D to N_p is a useful observation since correlations of drag coefficients and power number bear many relationships to each other; some of these will be noted below. For pressure drop in pipes, the use of friction factor is analogous to N_p for impellers and C_D for immersed bodies.

3.9 Scale-up

3.9.1 Geometric similarity (McDonough, 1992)

Scale-up is difficult at best when it come to duplicating at a large scale mixing and process results observed at a small scale.

Experiments performed relative to scale-up determine the effects on mixing parameters as the size of system changes. Geometric similarity means that all pertinent dimensions are similar and have ratios constant for scale-up. Kinematic similarity is maintained when all viscosities have a common constant ratio. Dynamic similarity occurs when all forces ratio are constant. The four forces readily used for analysis and evaluation of scale-up criteria are : input force from the mixer, which is a function of impeller speed and diameter, and three opposing forces-viscosity, gravity, and surface tension. Dynamic similarity is predicted on the ratios of all four of this forces being equal for scale-up. However, the reality remains that for the same fluid, having the same density and viscosity (i.e., operating at similar temperature in both scales), only two of the four forces can be equal.

Geometric and dynamic similarity require the analysis and evaluation of dimensionless group for scale-up. The ratio of inertia to viscouse force is expressed as the Reynolds number, the ratio of inertia to gravity force is the Froude number, and the ratio of inertia force to surface tension is the Weber number. These dimensionless numbers are useful considerations for scale-up.

For heat transfer scale-up, correlations are required. A process dimensionless ratio depicts the measured process result divided by the relative difficulty of carrying out the process.

In blending applications and scale-up scenarios, blend time relative to either the impeller speed or circulation time is used.

3.9.2 Criteria for mixing (Vincent and Joseph, 1966)

Imagine the mixing process as a breakdown of the larger eddies to smaller, and finally to the smallest eddies, at which point the mixing scale becomes small enough for turbulent no longer to act. Eddies become so small that viscouse shear forces prevent turbulent motion, and molecular diffusion becomes the controlling factor. Molecular diffusion is essential to provide the final mixing between two liquids. In reality, the two processes of breakdown and diffusion must occure at the same time. However, the simple step-by-step process will aid in the discuss to follow. If the fluids to be mixed are gases, the molecular diffusion is very high and diffusion time extreamly small. But if the fluids are liquids, the molecular diffusion is slow, and the diffusion part of the process becomes very important. The slow diffustion time, in case of liquids, required the knowledge of the turbulent, so that and estimate of the size of the smallest eddy and the time for molecular diffusion can be made.