ADVANCES IN CHEMICAL ENGINEERING

VOLUME 17

ADVANCES IN
CHEMICAL ENGINEERING

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PREFACE

The Frontier or Amundson Report of the National Research Council divided chemical engineering problems into three scales: the microscale of molecular dimensions, the mesoscale of equipment dimensions, and the macroscale of entire engineering systems. Electronics and optoelectronics engineers also classify their problems in three levels of organization: materials, devices, and systems/networks. Mesoscale activities such as unit operations and reaction engineering have been strongholds for chemical engineering from the beginning. In recent years, however, studies in the other two scales have been increasing in creativity and effectiveness.

Volume 17 of *Advances in Chemical Engineering* has two extensive chapters on the mesoscale, returning to this theme of historic and continuing importance. The chapter by Shah contains a comprehensive review of the subject of mechanical agitated reactors, which are important in a very large range of industries from large scale chemical manufacturing to small scale biotechnology. The chapter by Kwauk is an overview of particulate fluidization, which draws a great deal from the pioneering work of the author. These two chapters will provide the starting point for any chemical engineer who is seriously concerned with understanding or utilizing these two technologies.

James Wei

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DESIGN PARAMETERS FOR MECHANICALLY AGITATED REACTORS

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I. Introduction

A chemical reactor is a vessel in which reactants are converted to products through chemical reactions. This vessel takes many shapes and sizes depending upon the nature of the chemical reaction. The choice of a suitable laboratory reactor depends upon the nature of the reaction system (fluid–solid catalytic, fluid–solid noncatalytic, fluid–fluid, etc.), the nature of the required kinetic or thermodynamic data, or the feasibility of operation. The important parameters for a successful reactor design are the following:

(1) construction difficulty and cost;
(2) reliable sampling and analysis of products;
(3) isothermality;
(4) start-up and shut-down upsets;
(5) accurate residence-contact time measurements;
(6) roles of interphase mass and heat transfer, as well as intraparticle mass and heat transfer for fluid–solid systems;
(7) selectivity time-averaging disguise; and
(8) safety.

It is important to note that there is no global optimum reactor design that fits all purposes. There are always some trade-offs, and they should be evaluated on a case-by-case basis. Novel reactor designs have been constantly introduced to satisfy specific needs, some of which are outlined here.

One of the most widely used reactors is the mechanically agitated reactor. In this monograph, we examine the design parameters of various types of mechanically agitated reactors. These types of reactors are very popular because they offer the most flexibility in operation. They can be operated in

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batch, semi-batch, or continuous modes. In multiphase systems, they provide the most flexibility in the mixing conditions in each phase. They can be conveniently used to measure intrinsic kinetics of catalytic and noncatalytic reactions. Compared to fixed-bed operation, they provide a higher space–time yield, because of smaller transport resistances under comparable conditions. They provide isothermal conditions, good temperature stability, simple heat recovery, and protection against the formation of hot spots in the reaction volume. They also provide the possibility of continuous catalyst regeneration without any interruption of production.

The mechanically agitated reactors, however, also require high energy consumption and stagewise operation to get a high degree of conversion and/or selectivity in continuous operation. They can also cause unwanted particle attrition and undesired homogeneous side reactions in catalytic operations. Stirring devices are subject to mechanical and sealing difficulties (mainly in pressurized operations) and may have high maintenance costs. In order to prevent gas leakage, the stirrer is often introduced at the bottom of the high-pressure mechanically agitated reactors.

We examine here various types of mechanically agitated reactors used in chemical, biochemical, polymer, and other industries. Both conventional and novel reactors are discussed. The reactors are divided in sections covering gas–liquid reactors, slurry reactors, catalytic (gas–solid or gas–liquid–solid) reactors other than slurry reactors, liquid–liquid reactors, and novel reactor applications in biological, polymer, electrochemical, photochemical, and chemical vapor deposition industries. Finally, experimental methods for design parameter estimations are evaluated. The major aim of the monograph is to evaluate the design parameters of various types of conventional and novel mechanically agitated reactors currently in use. Wherever necessary, strategies and the descriptions on the use of novel agitated reactors are also briefly outlined.

Finally, it should be noted here that the major purpose of mechanical agitation in a chemical reactor is to provide mixing. In recent years, attempts have been made to minimize mixing energy cost by replacing or supplementing traditional mechanical agitation with pneumatic (compressors) and hydrodynamic (pumps) energy inputs (Faust and Sittig, 1980). Some examples of the latter two types of reactor are air-lift loop reactors, pressure-cycle reactors, bubble-column pumped circuits, jet-propelled loop reactors, etc. These and other similar reactors carry a common feature of a recycle loop (most often external, but sometimes internal). While the recycling provides additional mixing just like mechanical agitation, it has some additional important effects (such as increased residence time, increased reactor phase holdup of recycling fluid, etc.) on the reactor performance. As such, the recycle

reactors form a different class of reactors, and they will not be evaluated in this monograph.

A. Conventional Agitated Vessels and Internals

Although, as shown in this monograph, mechanical agitation is provided in a number of different ways, the most common method is by a stirrer in a standard vessel. In many mechanically agitated reactors, the vessel contains internals such as baffles (particularly for low-viscosity fluids), feed and drain pipes, heat transfer coils, and probes (e.g., thermometers or thermocouples, pressure transducers, level indicators). The degree of mixing and power requirement depend on the nature of the internals present in the vessel.

For an axially positioned stirrer in a vessel without internals, agitation causes rotational motion of the liquid and the formation of a vortex. At some critical stirrer speed, the vortex can reach the stirrer and cause gas entrainment in the liquid. This is generally undesirable because it results in a very high mechanical stress on the stirrer shaft, bearings, and seal. For a two-phase system with different phase densities, the centrifugal force produced in the vortex opposes the stirring motion, resulting in inefficient mixing.

For low-viscosity liquids, bulk rotation of the liquid can be reduced with the use of vessels having a rectangular cross-section, with the lateral insertion of the stirrer into the vessel, and with the use of baffles. When the stirring is weak, bulk rotation in cylindrical vessel can also be prevented by installing the stirrer off-center and/or at an angle to the axis, configurations resulting in an uneven mechanical stress on the stirrer shaft.

In cylindrical vessels, the bulk rotation of the liquid is generally prevented by the installation of baffles, which are usually attached to the vessel wall by means of welded brackets (see Fig. 1a). When this is not possible, they are either attached to the cover (e.g., in enamel-coated vessels) or are made in the form of a basket with pressure-fitted rings, as shown in Fig. 1b (e.g., glass vessels, wooden vats, etc.). Generally, fully effective baffling in a cylindrical vessel is achieved with four vertical baffles of width $d_T/10$. However, in recent years novel approaches (e.g., horizontal baffles) have been investigated. The dead volume behind the baffles is reduced by using baffles of width $d_T/12$ at a small clearance of $d_T/50$ from the wall.

The heat transfer (cooling or heating) in a stirred vessel is achieved in a number of different ways. The most conventional method is the use of a coil heat exchanger. The nature and positioning of the coil depends on the nature of the flow pattern created by the stirrer. For an axial flow stirrer, a spiral coil (see Fig. 2a) is effective because it provides good liquid circulation between the coil and the wall. For radial flow stirrers, spiral coils deflect the liquid

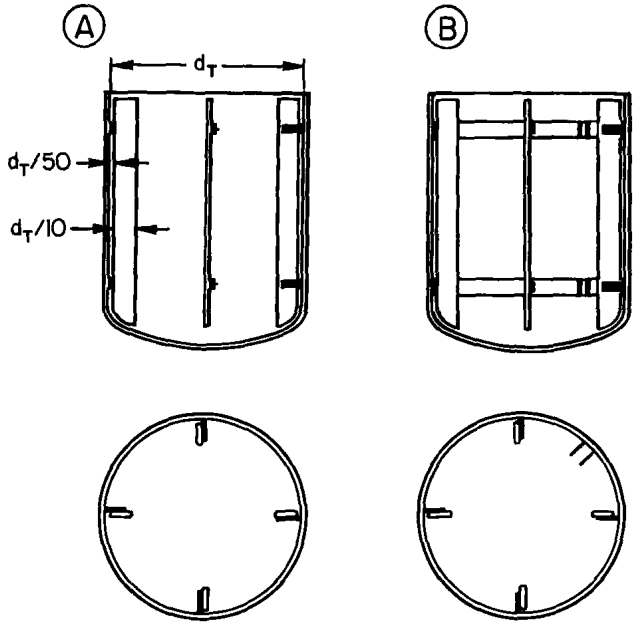

FIG. 1. Baffle designs. (a) Normal design; (b) design for glass and coated vessels (baffle basket with pressure-fitted ring). (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

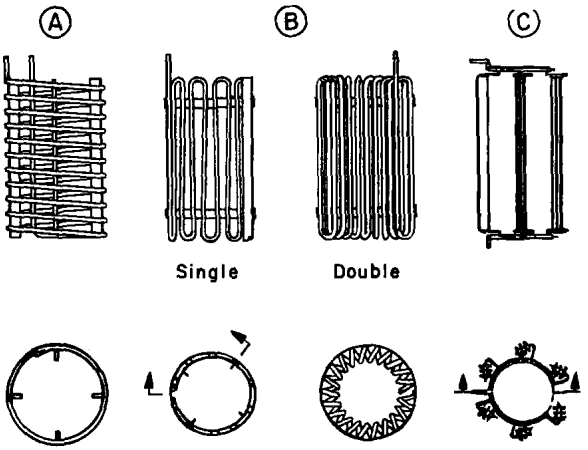

FIG. 2. Tube coil designs. (a) Spiral coil; (b) meander coils (cooling basket); (c) tube bundles. (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

circulation, resulting in insufficient flow between the coil and wall. For this flow pattern, meander coil (see Fig. 2b) is more suitable since this arrangement does not deflect the radial flow pattern, but prevents bulk rotation of the liquid. The heat exchanger tubes can also be arranged into bundles and installed in place of baffles, as shown in Fig. 2c.

B. Types of Stirrers

The mixing is provided by a wide variety of stirrers, the choice of which depends on a specific mixing operation and given material sytem. The following discussion is limited to those stirrer types that are most widely used in the chemical industry, and for which established design guidelines exists (Zlokarnik and Judat, 1988). Various stirrers are illustrated in Fig. 3 according to the predominant flow pattern they produce, as well as the range of viscosities over which they can be effectively used. Typical flow patterns generated by stirrers are axial, radial, and sometimes tangential. The flow patterns and their influence on the design parameters are further evaluated in subsequent sections.

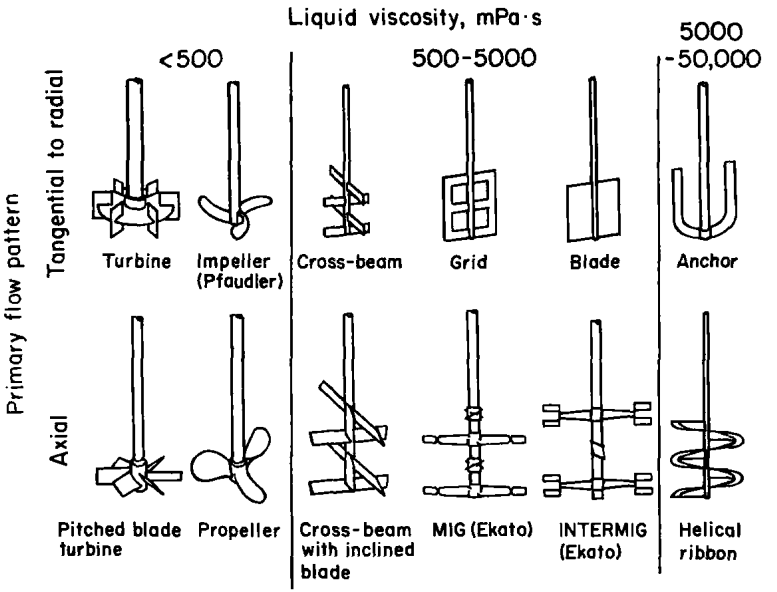

FIG. 3. Common stirrer types. (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

1. *Radial Motion Stirrers*

a. Turbine Stirrer

The most common type is the Rushton turbine with six blades on a disk. It is the only high-speed stirrer that sets the fluids in radial motion—or, at higher viscosities, in tangential motion. This type is only effective with low-viscosity liquids and baffled vessels. In recent years, turbine stirrers with eight or 12 blades have also been employed. Generally, the stirrer diameter is such that the d_T/d_I ratio ranges from 3 to 5. During rotation, the turbine stirrer causes high levels of shear and is well suited for the dispersion processes.

b. Impeller Stirrer

This type of stirrer was developed for use in enamel-coated vessels and thus has rounded stirring arms. The stirrer can be used in vessels with or without baffles. It is generally placed with a small clearance from the bottom, and its diameter is such that $d_T/d_I = 1.5$. It can operate in a vessel with strongly fluctuating liquid levels because it mixes even a small amount of liquids very well.

c. Cross-Beam, Grid, and Blade Stirrers

These are low-speed stirrers and generally have diameters in the range $d_T/d_I = 1.5-2$. For low-viscosity fluids, stirrers are used with baffles, and for high-viscosity fluids, they can be used without baffles. These stirrers are especially suited for liquid homogenization.

d. Anchor Stirrer

This low-speed stirrer is normally used for viscous fluids commonly encountered in biological and polymeric reactors. They are well suited for enchancing the heat transfer rate in viscous fluids. The stirrer is generally placed in a vessel with small clearances from the wall (d_T/d_I-1.05).

2. *Axial Motion Stirrers*

a. Paddle and Propeller Stirrers

Pitch-blade turbine (paddle stirrer with pitched blades) and propeller stirrers provide high mixing with an axial flow pattern. Both of these stirrers are normally used for low-viscosity liquids and in vessels with baffles. They are well suited for providing liquid homogenization and suspension of solids in slurry reactors. The stirrers can also be used in viscous fluids and for vessels with $H/d_T > 1$, which are generally encountered in fermentation processes. For these situations, axial flow is increased with the use of multistage stirrers with pitched stirring surfaces.

b. Cross-Beam Stirrer with Pitched Beams and MIG and INTERMIG Stirrers

The latter two types of stirrers are produced by Ekato Company, Schopfheim, Germany. These are low-speed stirrers with a d_T/d_I ratio of 1.5 in the presence of baffles and 1.1 in the absence of baffles. The stirrers are versatile and are used for liquid homogenization, gas–liquid or liquid–liquid dispersion, and solids suspension in slurry reactors.

c. Helical Ribbon Stirrer

This very low-speed stirrer is normally used for very viscous fluids. It is normally placed in a vessel with small wall clearance ($d_T/d_I \approx 1.05$) and operates in such a way that it drives the liquid downward along the wall. The stirrer is best suited for improving homogenization and heat transfer in very viscous fluids.

3. *Novel Stirrers*

In addition to the radial and axial flow stirrers described above, a large number of special designs exist. Of these, three need to be mentioned (Zlokarnik and Judat, 1988).

a. Rotor–Stator Stirrers

When a high degree of shear on small liquid volume is desired, a rotor–stator stirrer is used (see Fig. 4). This stirrer consists of a blade or paddle stirrer enclosed by a ring of baffles. This type of stirrer thus alleviates the need for separate baffles in the vessel. This stirrer is not useful for biological reactors, but finds special use in polymeric reactors containing non-Newtonian liquids.

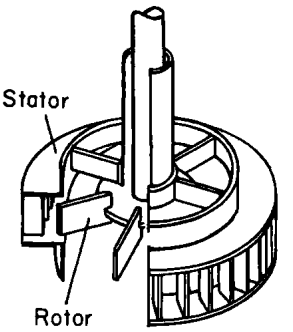

FIG. 4. A rotor–stator stirrer. (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

b. Sawtooth-Disk Stirrer

This type of stirrer also provides high shear without a stator ring or baffles. A schematic of this stirrer is shown in Fig. 5. High shear rate is provided by liquid acceleration in a radial direction in a thin ring away from the center followed by quick deceleration. Both sawtooth-disk and rotor–stator stirrers are particularly suited for emulsification and dispersion over a wide range of viscosities, e.g., production of paint pigments, and polymerization, where the viscosity of the liquid changes significantly during the reaction process.

c. Hollow Stirrers

In this type of stirrer, the stirrer head is hollow and is connected through a hollow shaft to the gas-filled space above the liquid surface. The suction generated behind the stirrer edges during rotation can thus be used to supply a gas to the liquid. The stirrer thus provided internal recirculation of gas, which is needed for "dead-end" systems such as those used in biological waste treatment processes. As a single unit combining both stirrer and gas supply, hollow stirrers are well suited for enhancing mass transfer in gas–liquid systems. Various designs of hollow stirrers are available, and they are described in subsequent sections. The simplest design is the *tube stirrer*, which is schematically illustrated in Fig. 6. Other designs are described in Section 2. Hollow stirrers are not effective for very viscous systems. All hollow stirrers operate at high speeds and are used in baffled vessels with $d_T/d_I = 3-5$. Hollow stirrers are useful for gas–liquid–solid reactors for hydrogenation and oxidation processes.

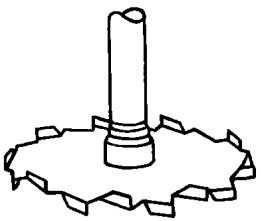

FIG. 5. Disperser disk. (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

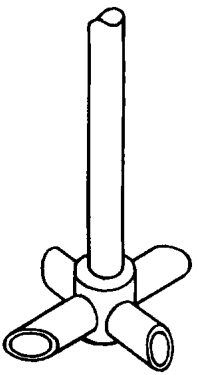

FIG. 6. Hollow stirrer (tube type). (Reprinted with permission from the publisher, VCH Publishers, Inc., after Zlokarnik and Judat, 1988.)

C. Other Forms of Mechanical Agitation

In the previous two sections, we illustrated mechanical agitation by the use of various types of stirrers. This monograph also considers reactors wherein mechanical agitation is provided by means other than a stirrer. In several processes (e.g., the gas–liquid–solid catalytic reactor, the bubble column for viscous fluids, and reactors for latex formation), the agitation is provided by the rotation of the entire vessel. Mixing in such vessels, as well as in centrifugal film or pump reactors, is created by the centrifugal forces. In vibrating bed reactors, microreactors, or reciprocating sieve plate columns, mixing is provided by a vibrating motion of the whole reactor or a part of the reactor. Mixing can also be provided by a rotating belt or a plate such as in a rotary vertical batch reactor for chemical vapor deposition or reactions involving viscous, granular material. Finally, a high degree of mixing is also provided by rotating blades or screws, such as in the wiper blade catalytic reactor and thin film or double screw polymeric reactors. This monograph considers all of these reactors.

D. Design Parameters

The monograph evaluates design parameters for a variety of conventional and novel mechanically agitated reactors. Brief descriptions of the reactors and their operations are also outlined. The important design parameters examined in the monograph are the hydrodynamics (flow regime), phase holdups, macro- and micromixing, gas–liquid and liquid–solid mass transfer, fluid–wall or fluid–coil heat transfer, solids distribution, and power input by the stirrer. Various experimental methods for design parameter estimations are also examined. For those reactors used for intrinsic kinetic measurements, design conditions that allow such measurements are briefly evaluated.

It is important to note that the *issue of design* is much broader than the considerations of design parameters outlined here. The proper design strategies consider the nature of the reaction system. In a biological reactor, aseptic conditions and their implications for the reactor design are important. The nature of by-products and associated separation requirements are important in the detailed design of the mechanically agitated reactor. The use of a high-tech (automated) operation changes design requirements. Automated operation is desirable, when a high degree of selectivity is required or when high-purity products are needed. Automated operation is also justified when the unit price of the product is high. Safety, reliable performance, and cost are also important design considerations. When a reactor is scaled up, the power requirement is generally designed to be higher than the ones estimated

from the design correlations, but not so high that the power efficiency is reduced. Special considerations are given if a variable power instead of a constant power is required. For a large-scale system, safety plays an important role in the decision of how large a reactor system should be built, particularly for reactions involving high temperature and pressure. For large systems, mechanical considerations such as wear and tear of the agitation system also play important roles. For polymerization reactions, product quality significantly depends upon micromixing and effective heat transfer; the effects of scale-up on these parameters are, therefore, extremely important. For biological reactors, foaming is an important design issue.

Some of the above-mentioned design considerations are handled through the design of novel reactors. Few such novel reactors are discussed in this monograph.

II. Gas–Liquid Reactors

Mechanically agitated gas–liquid reactors are widely used because of their versatility. The liquid residence time in such reactors can be varied over a wide range, and semibatch operation can be adopted for systems that require long residence time. For gases, the unit can be designed to be a "dead-end" type, so that the amount of gas introduced into the reactor balances that consumed. It is used for a variety of reactions such as oxidation, hydrogenation, chlorination, carbonation, ozonation, etc.; some specific practical examples are outlined in Table I. In this section, we examine the design parameters for mechanically agitated gas–liquid reactors that are normally used in chemical and petrochemical industries. Discussions on slurry reactors, as well as those gas–liquid reactors for biological (including waste treatment) and polymeric systems, are outlined in subsequent sections.

A. Conventional Reactors

Conventional mechanically agitated gas–liquid reactors, wherein gas and liquid make contact in batch, semibatch, or continuous mode, are widely used in processes involving chlorination, sulfonation, hydrogenation, selective absorptions in amine solutions, etc. (Doraiswamy and Sharma, 1984). These reactors are popular for laboratory studies because of their simplicity in construction and low cost. As a rule of thumb with noncorrosive liquids, the mechanically agitated reactor is most economical when the overall reaction rate is five times greater than the mass transfer rate in a bubble column. If a

TABLE I

TYPICAL GAS–LIQUID REACTIONS[a]

1. Liquid-phase processes such as oxidation, hydrogenation, sulfonation, nitration, halogenation, hydrohalogenation, alkylation, sulfonation, polycondensation, polymerization, etc.	
Examples:	oxidation of acetaldehyde to acetic acid
	oxidation of ethylene to acetaldehyde
	oxidation of paraffins to acids
	chlorination of dodecane
	hydrogenation of olefins
2. Biochemical processes	
Examples:	aerobic fermentation
	oxidation of sludges
	manufacture of single cell proteins from hydrocarbons and other raw materials
3. Gas scrubbing operations	
Examples:	absorption of SO_3 in dilute sulfuric acid
	absorption of NO_2 in dilute nitric acid
	absorptions of CO_2, H_2S, CO, SO_2, NO, N_xO_y, HF, NH_4, phosgene, etc.
4. Manufacture of pure products	
Examples:	manufacture of H_2SO_4, $BaCO_3$, $BaCl_2$, adipic acid, phosphates, etc.
5. Various processes in petroleum refining and recovery of nuclear materials.	

[a] Some of the examples contain three phases (biological or polymerization reactions).

large fraction of gas needs to be absorbed, stirred-tank reactors are not recommended. Over the years, significant effort has been made to understand the hydrodynamic, mixing, and mass- and heat-transfer characteristics of such reactors. The effectiveness of numerous types of agitators has also been investigated. Table II lists important characteristics of some of the agitators used for gas–liquid reactors.

1. *Hydrodynamics*

Flow patterns in a mechanically agitated reactor with disk turbine, pitched-blade turbine, and propeller types of agitator are schematically illustrated by Joshi *et al.* (1982). The flow pattern in the presence of gas is described later in the section on slurry reactors. In each of these cases, the dimensionless velocity profile with respect to the impeller tip velocity has been found to be independent of the impeller speed and has shown slight dependence on the impeller diameter.

The gas holdup in mechanically agitated reactors is a function of the geometric parameters, fluid properties such as viscosity and surface tension, the electrolyte nature of the solution, and the foaming characteristics of the liquid. The best correlations are those of Hughmark (1980) and Sridhar and