Fundamental Principles of Laboratory Fixed Bed Reactor Design

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Abstract

A few important, foundational principles enable more effective discovery and development of heterogeneous catalysts. Numerous experts have documented and illustrated these principles over the past several decades, but many current practitioners fail to heed their sage advice. We revisit the concepts, which we categorize as the bed-scale phenomena of isothermality, contacting pattern ideality, isobaricity, and wetting efficiency, and the particle-scale phenomena of internal and external temperature and concentration gradients. In addition, we introduce a new public domain, web-based tool for quickly estimating the magnitude of the effects of these phenomena. Our objective is to motivate and equip our colleagues to teach these principles and to apply sound reaction engineering practices in their laboratory work.

Keywords

Fixed bed; packed bed; reactor; heterogeneous catalyst; reaction engineering; reactor design; mass transfer; heat transfer

Introduction

“Those who cannot remember the past are condemned to repeat it” [1]. This article intentionally deviates from the review of current advances to emphasize our current opinion, undergirded by foundational work that has accumulated over the past five decades. We feel this topic is perennially relevant. Just as each generation must teach the next generation the fundamentals of reading, so each generation of reaction engineering and catalysis practitioners must teach the next generation the fundamentals of our discipline.

In particular, this article targets an audience that lives at the interface of two disciplines, chemical reaction engineering and heterogeneous catalysis. Our objective is to provide a service to that community by highlighting the fundamental principles that must govern the experimental evaluation of heterogeneous catalyst systems at the laboratory scale. In our experience, researchers often ignore these fundamental principles. We hope that, by drawing attention to this admittedly mature knowledge base, we will remind those who have forgotten, equip those who want to collaborate in our effort to educate the next generation, and teach those who never learned these foundational principles. We begin with brief comments addressing the historical context.

Historical Context

The field of heterogeneous catalysis can trace its roots to the first half of the nineteenth century, as ably described by Robertson [2]. On the other hand, chemical reaction engineering (CRE) evolved to become a formal discipline within the field of chemical engineering in the 1940s and 1950s. Early markers of this discipline’s formalization include the inaugural European Symposium on Chemical Reaction Engineering in 1957 (ISCRE History; URL: http://iscre.org/iscre_history.htm) and the publication of Levenspiel’s *Chemical Reaction Engineering* in 1962 [3]. Levenspiel emphasized in the preface of his seminal text that

“the goal is the successful design of chemical reactors...” In spite of the goal stated by Levenspiel and shared by many other CRE textbook authors, the topic of laboratory reactors is inconspicuous in those textbooks. While some CRE textbooks acknowledge the importance of selecting laboratory reactors that will generate accurate data useful for reactor design and provide heuristics to assist in selecting laboratory reactors [4,5], many provide no explicit mention of the importance of or methodology for selecting and designing laboratory reactors.

Earlier Reviews

Many have provided guidance regarding the selection, design, and operation of laboratory reactors. Using a gas-liquid reaction over a powdered catalyst relevant to his work at Mobil, Weekman focused on the decision process for selecting a laboratory reactor, providing heuristics for choosing from a menu of several potential options [6]. When Rase and Perkins [7] introduced their implementation of Høugen’s recirculation reactor concept [8], they emphasized the importance of eliminating temperature and diffusion gradients in order to independently study the effects of each system variable. Smith emphasized the reactor design dilemma caused by non-isothermal heterogeneous catalytic reactors [9]. While these papers focused on concepts rather than quantitative criteria, numerous authors tackled individual components of the macroscopic problem, but, in 1971, Mears provided the first comprehensive review with quantitative guidance for laboratory fixed bed reactor applications [10]. Dommeti et al. later showed the limitations of the Mears criterion for interphase transport [11]. More recent publications have expanded the scope to address additional factors important in trickle bed reactors, such as reviews by Sie [12], Mary et al. [13], Mederos et al. [14], and Bej [15].

Scope of This Review

The 45-year-old paper by Mears provides the launching point for our primer, which will specifically address laboratory scale fixed bed reactors, including both integral reactors and recycle reactors. Analogous concepts and principles apply to other systems, such as stirred tank slurry reactors [16] and single-phase tubular flow reactors [17], but those systems are outside of the scope of our current review.

Common laboratory fixed bed reactors include integral reactors (tubing packed with catalyst) and recycle reactors, which can use an external recycle scheme based on a packed tubular reactor coupled with a recycle pump or compressor or an internal recycle scheme. Internal recycle reactors typically used for gas-solid systems have varied designs and are informally named after their inventors (Berty [18], Caldwell [19], and Carberry [20]), but all have the objective of testing commercial-scale catalyst particles contained in a porous basket. We differentiate these reactors based on the mixing efficiency and the superficial velocities that can be achieved in the catalyst beds, with higher velocities preferred in order to minimize external transport gradients. Users of these reactors must carefully evaluate these reactors to ensure the performance is sufficient to generate data of the required quality for a particular application [19,21-25]. For gas-liquid-solid systems, the Robinson-Mahoney design [26] is the most popular option for testing fixed bed catalysts under well-mixed conditions.

In an effort to miniaturize laboratory fixed bed reactors, one new vista for laboratory fixed bed reactors involves reactors with channel-to-particle diameter ratios approaching unity. Recent publications [27-

29] build on the old idea of a “single pellet string reactor” [30,31] by shrinking the reactor diameter to approach the diameter of the catalyst particles, resulting in so-called packed bed microreactors or microchannel fixed bed reactors. While our present review does not address these cases explicitly, we refer interested readers to these publications. Although the principles in our review equally apply to these cases, the specific correlations for phenomena such as gas-liquid mass transfer or axial dispersion and the evaluation of the importance of wall effects are special cases that must be addressed accordingly.

Next, we will review the guiding principles for laboratory fixed bed reactors and point the reader to useful references while avoiding the reproduction of quantitative expressions previously published in the literature. We close by illustrating the application of these principles to an example system.

Guiding Principles

In this section, we address bed-scale (interparticle) phenomena first, followed by particle-scale (interphase and intraparticle) phenomena.

Bed-Scale Phenomena

Researchers should design and operate their laboratory scale reactors to achieve isothermality, contacting pattern ideality, and isobaricity on the scale of the catalyst bed. The catalyst in gas-liquid-solid systems should be fully wetted.

Isothermality

For integral fixed bed reactors, isothermality is typically the most difficult performance criterion to satisfy. Mears provides a useful criterion, defining isothermality to be achieved when the average reaction rate at the cross-section of the hot spot in an integral reactor is within 5% of the rate at the wall temperature [32]. This criterion applies equally to all possible fluid phase scenarios. The primary challenge to implement this criterion involves choosing appropriate correlations for the wall heat transfer coefficient and the bed effective thermal conductivity that apply for the potentially lower linear velocities and smaller particles used in the laboratory setting. For recycle reactors, isothermality is achieved by attaining a sufficiently high recycle ratio so that the single pass adiabatic temperature rise is negligible [23].

Contacting Pattern Ideality

For integral fixed bed reactors, the ideal contacting pattern is plug flow. Mears provides a conservative criterion for plug flow [33]. In addition to relaxing the Mears plug flow criterion, Gierman observed that, in the limit of low flow rates, the Bodenstein number asymptotically reaches a constant value [34]. Combining those two factors, Sie offers an alternative plug flow criterion based on Gierman’s assumption and observation [12]. Unlike the criterion from Mears, this latter criterion does not require an estimate of the axial dispersion coefficient since that value is implicit in the constant Bodenstein number at low flow rates.

Sie emphasizes that the above criteria assume a randomly packed bed with no variability in the velocity profile as a function of the bed radius [12]. In fact, laboratory scale reactors are very prone to wall

effects because of the greater void fraction near the wall. Sie proceeds to show that, for systems in which the only fluid is a gas, the traditional rule of thumb that the tube to particle diameter exceed 10 is invalid, and ratios as small as 5 or less may still give plug flow performance in spite of wall effects because radial dispersion “erases” the effect of the radial velocity profile. However, because diffusion in liquids is four orders of magnitude slower than in gases, reactors containing liquid should maintain a tube to particle diameter ratio of at least 20.

Another factor often overlooked with respect to the contacting pattern relates to the unintended consequences of inert diluents in a catalyst bed. On occasion, the researcher may choose to dilute the bed with catalytically inert particles in order to reduce the rate of heat generation per bed volume for an exothermic reaction, thereby distributing the heat sources over a larger volume and providing more wall heat transfer area for the heat evolved or consumed by reaction. However, excessive dilution can result in local bypassing that results in deviations from plug flow performance, especially at high conversions [35,36].

For recycle reactors, a sufficiently high recycle ratio ensures a well-mixed system, the appropriate ideal contacting pattern for these reactors.

Isobaricity

For integral fixed bed reactors, isobaricity (negligible pressure drop) is important for systems containing a gas phase. For gas-solid systems, the reactant partial pressures are the driving force terms in the rate expressions. For gas-liquid-solid systems, the partial pressure of a sparingly soluble gas phase reactant, such as hydrogen in a hydrogenation, is directly proportional via Henry’s Law to the concentration of the dissolved gas phase component and, thus, is typically a driving force term in the rate expression. Consequently, achieving negligible pressure drop through the catalyst bed enables the analysis to avoid accounting for or correcting for pressure drop [37], which is not typically measured accurately in small, laboratory-scale reactors. One suggested rule of thumb is that the pressure drop should not exceed 20% of the inlet pressure [38]. For liquid-filled systems, pressure drop is typically negligible and of little importance with respect to reaction kinetics.

For internal recycle reactors, a negligible pressure drop is the necessary corollary of a high recycle ratio. For external recycle reactors, which use a pump or compressor, if a gas phase is present, the previous discussion associated with integral fixed bed reactors applies.

Wetting Efficiency

For gas-liquid-solid integral fixed beds operated as trickle beds, catalyst wetting efficiency is a well-documented but often overlooked performance criterion [39]. We could write an entire review article on this topic alone, which is primarily a concern with small systems, especially laboratory-scale trickle bed reactors. In summary, to achieve the desired state of each catalyst particle engulfed in a continually replenished film of flowing liquid, the researcher has two options: operate at sufficiently high superficial fluid velocities, typically only achievable in a recycle reactor at the laboratory scale [40], or dilute the catalyst bed with inert fine particles [41]. We conclude this brief discussion with four additional comments on this topic. (1) Loading a tube with a mixture of catalyst and inert fines must be executed

carefully [42]. (2) Diluting a catalyst bed with inert fines does not guarantee perfect wetting and decoupling of all hydrodynamic effects [43,44]. (3) Appropriate pre-wetting of a trickle bed is an important precursor to fully wetted, reproducible operation. While this phenomenon has been studied extensively in systems without inert fines [45-52], we are not aware of similar reports for small-scale systems with inert fines, but we are aware of observations of similar effects in diluted beds. (4) While efforts to model the fractional catalyst wetting may lead to a challenging and educational doctoral thesis, we advise against such pursuits if the objective is to evaluate a catalyst or design a larger scale reactor.

Similar wetting concerns apply to external recycle reactors with differential or low conversions, but either dilution with fines or sufficiently high liquid superficial velocities can ensure high wetting efficiencies [40]. On the other hand, for batch or continuous reactors with catalyst contained in a basket and rapid fluid circulation using a gas-dispersing impeller, such as the Robinson-Mahoney design [26], immersion of the catalyst in the liquid ensures complete wetting.

Particle-Scale Phenomena

In addition to eliminating bed-scale (interparticle) gradients, a well-designed laboratory reactor will also minimize external (interphase) gradients and either eliminate or appropriately manage internal (intraparticle) gradients. While we recommended that researchers always strive to eliminate external (interphase) temperature and concentration gradients, we offer two alternatives for managing internal (intraparticle) concentration and thermal gradients: (1) the reactor design can utilize sufficiently small particles to avoid those gradients or (2) the laboratory reactor can use catalyst particles identical to those in the full-scale reactor. Kinetic data generated using the latter option constitute apparent kinetics, where the measured rates are the consequence of the combined effects of intraparticle transport phenomena and intrinsic reaction kinetics. For reactor scaling purposes, measuring apparent kinetics is sufficient as long as the catalyst is not changed, including its size and porosity. The former method is preferred for the early stages catalyst discovery and development, while the latter method is most relevant during later stages of catalyst development as well as for reactor design and optimization.

In designing a new system, we rely on literature correlations to compute external heat and mass transfer gradients, and we employ well-known calculations to estimate internal resistances. These effects are equally important in both integral and recycle fixed bed reactors. We advise researchers to follow their initial calculations with experiments designed to verify those calculations, such as comparing catalyst performance with crushed and whole particles to confirm the absence of intraparticle transport limitations or varying the amount of catalyst with a fixed space velocity to ensure the absence of strong external effects.

External

Dwivedi and Upadhyay offer a mass transfer correlation [53] of the Chilton-Colburn type [54]. Applying the Chilton-Colburn analogy provides an estimate for the heat transfer coefficient as well. Combining these parameters with the measured or estimated local reaction rate per catalyst particle and the bulk fluid concentration of the limiting reactant enables computation of the external concentration and temperature gradients around a single catalyst particle. Reasonable criteria for declaring the system free

of external gradients are a concentration change of less than 5% relative to the bulk concentration and a temperature change of less than 1°C. Alternatively, Mears offers criteria using a constraint based on a maximum deviation of 5% in the rate relative to the intrinsic rate with no transport limitations around the particle [10]. Carberry also defines criteria for evaluating external gradients, where concentration gradients are deemed significant if the observed rate exceeds 1% of the maximum possible mass transfer rate and temperature gradients are deemed significant if the particle surface temperature deviates from the bulk absolute temperature by more than 1% [5].

Internal

Given the observed or estimated reaction rate over a catalyst particle of known physical properties and the assumption of a pseudo-first order reaction in the limiting reactant, we can compute a reasonable estimate of the concentration and temperature gradients within that particle. Satterfield [55] estimates the effective diffusivity from the molecular diffusivity, particle porosity, and tortuosity, as well as a Knudsen diffusivity [56] for gaseous systems with small pores and a pore construction factor for liquid systems [57,58]. Aris identified a useful definition for the characteristic length for diffusion [59], enabling calculation of the isothermal effectiveness factor from the Thiele modulus, which is the square root of the Weisz-Prater modulus [60] divided by the effectiveness factor. Given the Thiele modulus, we can also compute the minimum internal concentration of the limiting reactant [3], and we can compute the corresponding core temperature in the particle by balancing heat generation with removal via conduction [61]. This entire analysis assumes a nearly isothermal particle, which is the most common scenario in practice, but Weisz and Hicks offer a useful check for the possibility of multiple steady-states based on a thermicity factor that is easily calculated using the conditions at the catalyst surface [62].

When screening catalyst materials as small granules, catalyst developers should confirm the absence of intraparticle effects. Reasonable targets are internal and external temperature gradients less than 1°C, an isothermal effectiveness factor that exceeds 95%, and an external concentration gradient that is less than 5% of the bulk concentration of the limiting reactant. Alternatively, Mears provides criteria for achieving an effectiveness factor greater than 95% and sufficiently isothermal performance [10].

Public Domain Tool

The body of this review outlines the methodology for checking a laboratory reactor and catalyst system for undesirable bed-scale and particle-scale gradients. While this procedure is straightforward, collecting the relevant equations and physical properties information is tedious and prone to errors that can easily propagate, resulting in an incorrect analysis. Reaction engineers at The Dow Chemical Company developed a spreadsheet tool in the late 1990s to automate these calculations and eliminate most of the sources of error in these analyses. In order to promote the best practice of routinely performing these simple calculations, the authors of this review have created a similar public domain tool, developed and supported at Purdue University. We have named this tool GradientCheck (www.GradientCheck.com). We encourage the reaction engineering and catalysis community to use this tool to accomplish the important objectives outlined in this article.

Case Studies

We illustrate these principles using two examples from the literature by using our GradientCheck tool. We hope that the availability of this tool will equip our colleagues in the reaction engineering and catalysis community to avoid the design and operation of non-ideal laboratory reactors for heterogeneous catalyst systems.

Example 1

Weisz and Swegler experimentally measured the effect of particle size on the rate and selectivity for a series of cyclohexane dehydrogenation reactions over chromia-alumina catalyst particles with three different sizes [63]. Because the original work did not use a typical continuous fixed bed reactor, we choose arbitrary bed dimensions and assumed differential conversion (1%) to illustrate the importance of bed-scale effects.

With respect to the particle-scale effects, we compare the measured and computed effectiveness factors in Table 1. Given the uncertainties and approximations inherent in this analysis, the agreement between the calculated and measured values is acceptable. The three figures show the complete input table and selected output for the largest particle case. Figure 2 and Figure 3 reveal that intraparticle concentration and external temperature gradients are both significant for this scenario. Furthermore, application of the Mears criterion indicates that the radial bed-scale temperature gradient would be significant, resulting in non-isothermal behavior of our hypothetical 1-cm inner diameter reactor.

This example highlights the most common transport issues in gas-solid fixed bed systems: internal (intraparticle) diffusion, external (interphase) heat transfer, and bed-scale (interparticle) heat transfer often prevent accurate measurement of intrinsic catalyst behavior in laboratory reactor data.

Example 2

Sharma et al. developed a kinetic model and reactor model for fixed bed oxidation of n-butane to maleic anhydride and compared the reactor model predictions with pilot plant reactor performance [64]. We provide the inputs for the experimental conditions in Figure 3 from that reference via the input file linked from the “How to Use” page associated with the GradientCheck tool. Our calculations predict minimal particle-scale gradients but confirm the extreme deviation from isothermality in that reactor. This example illustrates the primary reason that large fixed bed reactors are generally not the appropriate vessels for generating kinetic data. In a non-isothermal reactor like the one in this example, the accuracy of any kinetic parameters fit to pilot data is inextricably linked to the accuracy of the heat transfer model used to simulate the reactor.

Conclusion

In closing, we hope this brief review stimulates our colleagues in the reaction engineering and heterogeneous catalysis community to redouble efforts to exercise discipline in the design and operation of laboratory fixed bed reactors for catalyst screening, catalyst and process development, and measurement of reaction kinetics. This review outlines the key principles and highlights our new public domain tool, which we hope will prove useful for teaching and for guiding experimental activities.

Acknowledgements

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Table and Figures

Table 1. Comparison of measured and computed effectiveness factors for cyclohexane dehydrogenation.

Radius (cm)	Rate (mol/kg/s)	Effectiveness factor	
		Weisz & Swegler (measured)	GradientCheck (calculated)
0.05	1.46×10^{-3}	1.00	0.97
0.184	9.58×10^{-4}	0.66	0.77
0.31	7.03×10^{-4}	0.48	0.58

Gradient✓ (GradientCheck) for Heterogeneous Catalysis:

By using this tool you agree to the terms of the [license](#).

Inputs Section

Open JSON Input File 160122 Weisz and Swegler_big.json

Reaction Phase: / default: Gas Phase

Temperature (T_b & T_w): / K

Pressure (P): / bar

Reactor Radius (R_r): / m -- [Accepts scientific notation e.g. 1e-3]

Bed Length (L_b): / m

Catalyst Particle Shape:

Particle Radius (R_p): / m

Observed Reaction Rate (r_{obs}): / moles of A $\times$ kg-cat $^{-1}$ $\times$ s $^{-1}$

Enthalpy of Reaction (ΔH_{rxn}): / J $\times$ mole $^{-1}$

Reaction Order (n):

Activation Energy (E_{app}): / J $\times$ mole $^{-1}$

Conversion (X_A): / unitless (0 to 1)

Catalyst Bulk Density (ρ_{bulk}): / kg $\times$ m $^{-3}$ [usually 500-1500]

Catalyst Void Fraction (ϵ): / (0 to 1) [often 0.35-0.45 (default 0.4)]

Catalyst Thermal Conductivity (k_p): / W $\times$ m $^{-1}$ $\times$ K $^{-1}$ [often 0.13-0.25]

Catalyst Surface Area (S_{int}): / m 2 $\times$ g $^{-1}$

Catalyst Pore Volume (V_{pore}): / m 3 $\times$ g $^{-1}$

Catalyst Pore Tortuosity (τ): / unitless [often 3-7 for porous catalysts]

Number of Reactants:

Number of Products:

	Main Reactant A	Product B	Diluent C	
Inlet Mole Fractions:	<input type="text" value="0.99"/>	<input type="text" value="0.01"/>	<input type="text" value="0"/>	/ must add to 1
Fluid Viscosity (μ_f):	<input type="text" value="0.000017"/>	<input type="text" value="0.000017"/>	<input type="text" value="0.000017"/>	/ kg $\times$ m $^{-1}$ $\times$ s $^{-1}$
Heat Capacity (C_p):	<input type="text" value="3089.4"/>	<input type="text" value="2407.3"/>	<input type="text" value="2407.3"/>	/ J $\times$ kg $^{-1}$ $\times$ K $^{-1}$
Thermal Conductivity (k_f):	<input type="text" value="0.04782"/>	<input type="text" value="0.108"/>	<input type="text" value="0.108"/>	/ W $\times$ m $^{-1}$ $\times$ K $^{-1}$
Diffusion Volume ($\Sigma_{v,i}$):	<input type="text" value="123"/>	<input type="text" value="90.9"/>	<input type="text" value="90.9"/>	<input type="button" value="Estimate $\Sigma_{v,i}$"/>
Molecular Weight (MW):	<input type="text" value="84.2"/>	<input type="text" value="78.1"/>	<input type="text" value="78.1"/>	/ g $\times$ mol $^{-1}$

Figure 1. Input data for largest particles in last row of Table 1.

	Bed Average	Bed Inlet	Bed Outlet	
Weisz-Prater Modulus (M_{WP}):	0.927	0.927	0.927	/ unitless
Thiele Modulus (M_T):	1.26	1.26	1.26	/ unitless
Effectiveness Factor (η):	0.584	0.584	0.584	/ unitless
External Concentration Gradient:	0.195			/ %
External Temperature Gradient:	-2.23			/ K
Internal Temperature Gradient:	-0.652			/ K
Prater Number (β):	-0.00183			/ unitless
Intrinsic (1 st Order) Rate Constant (k_{int}):	7.62e-5			/ $m^3 \times kg-cat^{-1} \times s^{-1}$
Max Possible Diffusion-Limited Rate (r_{max}):	0.36			/ moles of A $\times kg-cat^{-1} \times s^{-1}$
+Bed Scale Gradients				
Axial Dispersion Coefficient (D_{axial}):	2.49e-4			/ $m^2 \times s^{-1}$
Radial Dispersion Coefficient (D_{rad}):	4.81e-5			/ $m^2 \times s^{-1}$
Pressure Drop Across Bed (ΔP):	1.47e-5			/ bar
Effective Radial Thermal Conductivity (k_{re}):	0.306			/ $W \times m^{-1} \times K^{-1}$
Wall Heat Transfer Coeff (h_w):	85.3			/ $W \times m^{-2} \times K^{-1}$
Internal Heat Transfer Coeff (h_i):	63.3			/ $W \times m^{-2} \times K^{-1}$
Axial Temperature Change (ΔT_{axial}):	-12.1			/ K

Figure 2. Tabulated results for particle-scale (top) and bed-scale (bottom) evaluation of largest particles in last row of Table 1.

Figure 3. Graphical results for particle-scale evaluation of largest particles in last row of Table 1.

Table and Figure Captions

Table 1. Comparison of measured and computed effectiveness factors for cyclohexane dehydrogenation.

Figure 1. Input data for largest particles in last row of Table 1.

Figure 2. Tabulated results for particle-scale (top) and bed-scale (bottom) evaluation of largest particles in last row of Table 1.

Figure 3. Graphical results for particle-scale evaluation of largest particles in last row of Table 1.

Annotations

Special Interest (*)

11. This paper identifies conditions under which the Mears diagnostic test may give misleading results for the interphase transport limitations.

12. Sie shows that radial mixing and diffusion may counteract the axial dispersion resulting from wall flow at low bed-to-particle diameter ratios for gas-solid fixed beds.

34. Gierman provides a global correlation between the Reynolds number and Bodenstein number that gives asymptotic limits at the low flows in small laboratory reactors, simplifying the assessment of axial dispersion.

35. Excessive bed dilution can lead to a non-ideal contacting pattern at high conversions.

41. This paper offers one of the earliest examples that clearly demonstrates the effectiveness of bed dilution with inert fines to enable essentially complete catalyst wetting in a laboratory scale trickle bed reactor.

Outstanding Interest (**)

10. Mears provides an excellent early summary of diagnostic tests for evaluating a fixed bed reactor for intraparticle, interphase, and interparticle transport limitations.

16. Bourne's tutorial on the role of mixing in affecting selectivity in single-phase and two-phase stirred tank reactors is essential reading for anyone using liquid, gas-liquid, and liquid-liquid stirred tank reactors.

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