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Reaction engineering of emerging oxidation processes

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Abstract

A review of the recent developments in emerging multiphase catalytic oxidation processes for the manufacture of various key chemicals, and an overview of reaction engineering principles needed for reactor design and interpretation of performance are presented. The utility of combining a knowledge of the catalytic chemistry through fundamental mechanisms and kinetics with transport effects and hydrodynamics using recent advances in experimental methods is also discussed and reviewed with reference to liquid phase oxidation. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, there has been an increasing interest in the development of catalytic oxidation processes for the manufacture of commodity and fine chemicals. The application of catalytic oxidation is very vast, so this paper is mainly limited to emerging liquid phase catalytic oxidation processes. Some of the well-known examples of liquid phase oxidation in industry are: oxidation of *p*-xylene to terephthalic acid, cyclohexane to adipic acid, *n*-butane to acetic acid and higher homologues and ethylene to acetaldehyde, oxidation of butadiene to 2,4-diacetoxybutene, epoxidation of propylene to propylene oxide, and hydroxylation of phenol to hydroquinone and catechol using H_2O_2 as oxygen donor. One motivation in developing liquid phase catalytic oxidation processes is also due to increasingly stringent government regulations concerning emission of organic and inorganic wastes and related environmental problems. The older generation of oxidation processes were based on classical stoichiometric oxidants such as dichromate, permanganate, manganese dioxide and nitric acid, which are not accepted from environmental considerations as they produce large quantities of waste materials and employ toxic reagents. Catalytic liquid phase oxidation has played a vital role in providing alternative to these stoichiometric reagent based processes with minimal amount of undesired by-products [1]. As an example, two routes for the synthesis of hydroquinone in the liquid phase using stoichiometric organic reagents to a more recent approach based upon a catalytic oxidation process are compared in Fig. 1. The classical process [1] via nitrobenzene generates more than 10 kg of inorganic salts per kg of hydroquinone. On the contrary, the catalytic route involves the auto-oxidation of *p*-di-isopropylbenzene to bis-hydroperoxide. The latter intermediate is readily converted to hydroquinone by a straightforward

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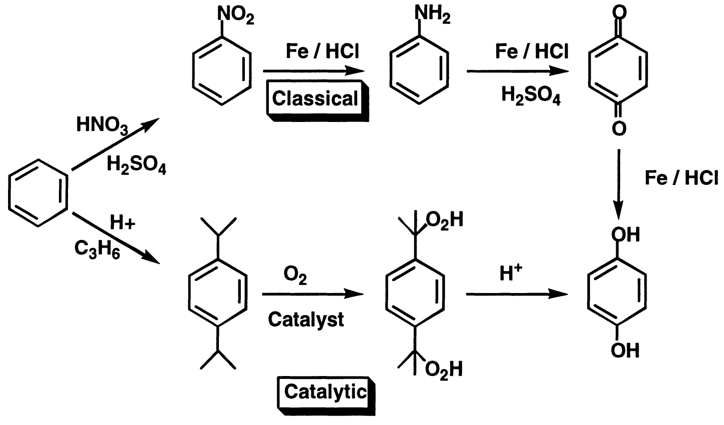

Fig. 1. Comparison between classical and catalytic route to hydroquinone [1].

acid catalyzed reaction, which produces less than 1 kg of inorganic byproduct salts per kg of product.

Liquid phase oxidation processes fall into the categories of gas–liquid, gas–liquid–solid and gas–liquid–liquid reactions depending on the type of catalyst used. The multiphase character of the processes poses several challenges from a reactor engineering viewpoint as the overall performance of the process would depend on interphase and intraparticle (for solid catalysts) heat and mass transfer, mixing of gas and liquid phases, and the complexities of reaction kinetics. A special feature or a constraint on operating ranges in oxidation is also related to safety in handling of oxygen and organic reactants/products in a given reactor. Indeed, it is a challenge to design a suitable reactor configuration to achieve optimum process performance, product selectivity and purity and safety. In this review paper, the reaction engineering aspects of the emerging liquid phase oxidation processes have been discussed including novel and emerging reactor types.

2. Distinguishing features

Liquid phase oxidation processes have many distinguishing features, as briefly summarized here. In developing oxidation processes, safety aspects' demand of the use of critical oxygen concentration may be a constraint on the reaction rates and product selectivity. On the other hand, molecular oxygen, being a cheap feedstock compared to other stoichiometric oxidants, is more economical and environmentally cleaner processes can be achieved via catalytic oxidation. For the production of bulk chemicals, the trend is to replace antiquated stoichiometric processes that require hazardous reagents by catalytic routes.

Another distinguishing feature is that the oxidation reactions are highly exothermic and the non-isothermal conditions in a reactor can lead to lowering of selectivity and product quality besides posing safety problems. This is a key reason why reactor selection and design is particularly critical for industrial oxidation processes. The reactor must be capable of controlling the temperature within safe limits using proper techniques of energy management and distribution. Many of the reaction products of oxidation reactions are highly unstable and can undergo decomposition under particular conditions, since they contain reactive organic functional groups, such as aldehydes, carboxylic acids and ethers. The yield of a desired product can be maximized by selection of a suitable catalyst and reactor concept that would allow simultaneous reaction, product separation and elimination of impurities to occur in a single step.

A final important distinguishing feature of oxidation processes is concerned with process safety. Recently commercialized and newly emerging processes are typically carried out using air, oxygen enriched air, or pure oxygen [4]. No matter the reactor type used, the reaction mixture at a given location in the reactor defines a composition on a flammability map. Depending upon the composition, temperature, and pressure, this mixture can spontaneously ignite.

Hence, it is essential that the reactor startup, shutdown, and normal operating policies avoid the flammability region. In addition, if a process upset or component failure can produce a flammable mixture, this condition must be rapidly detected by an appropriate sensor, and safety interlock procedures initiated to reduce the probability for ignition until the process can be returned to a safe operating mode. A recent review on the explosion limits of hydrocarbons in air [5] indicates that the flammability limits determined under static conditions, which are also used to define the safe operating window for reactor operations, are too conservative, since they do not account for mixing effects. In either case, the issue of safe operations is especially critical in the case of oxidation processes due to the potential hazards and damage that can be inflicted.

3. Process overview

In this section, an overview of key manufacturing processes that are based upon selective catalytic liquid phase oxidation is provided. Table 1 shows characteristics of multiphase gas–liquid and liquid–solid oxidation processes with respect to the conversion and product selectivity [6]. Inspection of this list shows that most catalytic oxidation processes have reactant conversions in excess of 90–95% with product selectivity greater than 80%. In addition, these processes can be conducted in either the vapor or liquid phase, which depends upon factors such as: (i) the reactant and product volatility and thermal stability; (ii) the reaction temperature required to activate the reactants in the presence of the preferred catalyst; (iii) the specific reaction rate; (iv) safety aspects; and (v) overall process economics. In many applications, the products are non-volatile or unstable at higher temperature and hence, liquid phase oxidation involving gas–liquid, liquid–solid, gas–liquid–solid or gas–liquid–liquid reactions is gaining importance. The processes differ depending on the type of oxidant and catalyst used besides details of reactor design and separation technology for a particular process. Primarily, oxygen sources like air, molecular O_2, and H_2O_2 (for high value added fine and specialty chemicals) are commonly used in industry. Some important cases of commercial interest are discussed here [2].

The autoxidation of *p*-xylene is one of the largest industrial scale applications of liquid phase oxidation by homogeneous catalysis to produce terephthalic acid (TPA) or its esters (dimethyl terephthalate, DMT), both of which have wide ranging applications in fibers, films and resins. This is a case of a gas–liquid catalytic reaction and the commercial processes of two types are practiced:

1. The Witten process for dimethyl terephthalate was developed involving air oxidation of *p*-xylene using a soluble Co complex catalyst. In the first step, *p*-xylene is oxidized to *p*-toluic acid as an intermediate, which is esterified to methyl toluate and then oxidized to monomethyl terephthalate. The methyl esters are separated by distillation and DMT purified by recrystallization. The typical reaction conditions for oxidation are: 150–180°C and <8 bar pressure and *p*-xylene conversion of 100% and a selectivity of 85–90% is achieved. The oxidation and esterification steps are carried out simultaneously.
2. The AMOCO process is a single step process to produce fiber-grade terephthalic acid (99.99%) using Co/Mn/Br catalyst for air oxidation of *p*-xylene. The process is carried out at 190–205°C

Table 1
Characteristics of key catalytic oxidation processes [6]

Product/process	Reactants	Reaction class	Conversion (%)	Selectivity (%)
Acetaldehyde	Ethylene/oxygen	Gas–liquid	99+	94
Propylene oxide	Propylene/air	Gas–liquid	–	90+
Terephthalic acid	Para-xylene	Gas–liquid	99+	97+
Adipic acid	Cyclohexane/air	Gas–liquid	6–12	80–85
Hydroquinone and catechol	Phenol/H_2O_2	Liquid–solid	85+ for H_2O_2	>90
Benzoic acid	Toluene	Gas–liquid	99+	96
Cumene hydroperoxide	Cumene/air	Gas–liquid	<30	>90

and 15–30 bar pressure and a conversion of >95% and a selectivity of 90% is achieved.

Besides the overall yield of TPA, the purity of final product and safety aspect of the process are important in this technology. The most important intermediate formed during oxidation of *p*-xylene is 4-carboxybenzaldehyde (4-CBA), the presence of which is undesirable since it acts as a chain terminator in the subsequent polymerization application of TPA. Minimizing the formation of 4-CBA is an important aspect of the process, which is found to vary depending on the reaction conditions as well as the reactor design (affecting the oxidation efficiency of 4-CBA to TPA) [28].

The oxidation of cyclohexane to adipic acid involves two reaction steps. In the first step, cyclohexane is converted to cyclohexanol and cyclohexanone via air oxidation using a soluble Co/Mn catalyst at 150–180°C and <20 bar pressure. The conversion of cyclohexane is <15% with selectivity for the mixture of two products in the range of 80–90%. The low conversion of cyclohexane is required to achieve higher product yield. In a second step, the mixture of cyclohexanol and cyclohexanone is oxidized to adipic acid. The commercially used process involves liquid phase oxidation using VO^{2+} or Cu^{2+} catalyst at 60–80°C and <2 bar pressure. A conversion of 100% with a selectivity of 92–96% is achieved.

A process for the manufacture of propylene oxide (PO) is an example of liquid phase epoxidation in which epoxidation is carried out using alkyl hydroperoxide as the oxygen donor. For example, in the ARCO process, the *t*-butyl hydroperoxide (TBHP) is produced via oxidation of isobutane at 130–160°C and elevated pressures. The epoxidation step is carried out at 100–130°C and <69 bar pressure using 10–300 ppm Mo complex as a catalyst. The conversion of olefin is about 10% but the conversion of TBHP and PO selectivity are in the range >90%. In this process, *t*-butyl alcohol is a by-product. An important feature of this process is that a high propylene to TBHP ratio is used to suppress decomposition of a relatively unstable TBHP. Also, higher propylene concentration demands higher operating pressure and under these conditions, the liquid phase may have non-ideal properties, which influence the solubility and mass transfer characteristics.

Surveys of new catalytic process technology that have been recently commercialized in the United States, China, Japan, and Europe are available in several reviews [3,7–10]. New developments in key areas of selective oxidation catalysis such as the oxidation of C_3–C_4 olefins, light alkanes, alcohols, aromatics, oxidations, and photo oxidations over the past 10 years are covered in several extensive conference proceedings and other dedicated symposia [11,12]. Examples of specific reviews on particular oxidation technologies include the selective oxidation of light hydrocarbons [6], wet air oxidations [13], oxidation of alcohols [14], oxidations in the production of fine chemicals [15–17] and removal of H_2S from refinery gas stream by LO-CAT process [18]. Again, the emphasis in these works and the references cited therein is on chemistry and catalysis with much less focus being given to process and reaction engineering issues.

4. Oxidation reactor types

The reactor types that can be used for oxidation processes generally depend upon the following factors: (i) the number and type of reaction phases that are involved; (ii) the reaction classification or characterization from the perspective of the interaction between intrinsic reaction kinetics and local transport effects; (iii) the catalyst activity and selectivity as a function of time-on-stream; (iv) the expected commercial production rate; and (v) the required temperature, pressure and materials of construction to achieve an economically viable operation. In this section, an overview of reactor types that might be used or have recently gained attention as providing possible operational or other related advantages for oxidation processes is presented.

4.1. *Conventional reactor types*

A detailed description of various conventional reactor types that can be used for multiphase gas–liquid or gas–liquid–solid catalytic reactions is given by Mills et al. [19] and Mills and Chaudhari [20]. These reactors are not specifically designed for oxidation systems, but can, in principle, be used for any multiphase reacting system such as hydrogenations, carbonylations, hydroformylations, and reductive aminations. The catalyst can be either a dissolved homogeneous organometallic complex, or a heterogeneous solid that has the form of either a powder, a regularly shaped particle, or an irregular granule. In some cases, a catalyst may not be used and the reaction occurs through a free-radical mechanism. Particular reactor types that are reviewed in the above-cited references include mechanically agitated reactors, bubble columns, trickle-bed reactors, packed bubble flow reactors, gas-lift and loop reactors, multi-stage trayed column reactors, and special purpose designs. Detailed discussion of the advantages and disadvantages of these reactor types is given in the above references, so they will not be covered again here.

4.2. Safety aspects

One of the key considerations when designing multiphase reactors for hydrocarbon oxidations is that the oxygen concentration in the gas–liquid disengagement zone, or any other open space that exists in the system, must be kept below the flammability limit for the expected hydrocarbon mixture. Typically, the oxygen concentration where autoignition will occur for many typical organics is ca. 8–9 vol%. In practice, online oxygen sensors might have a high alarm set to 4–5% before enforcing safety procedures. If air is used as the oxygen source, the reactor must be designed so that the oxygen composition on a dry basis decreases from 21% to at least 4–5% before reaching a gas–liquid disengagement zone. In the case of reactor types where the air is dispersed into the liquid phase, such as that encountered in the mechanically agitated reactor, bubble column reactor, and loop reactor, the bubbles cannot be allowed to coalesce and form bubbles large enough to create a mixture of hydrocarbon vapors and oxygen such that a local autoignition can occur. This suggests that gas spargers and other reactor internals, such as baffles, cooling coils, or heating coils used for startup, must be designed to promote good gas–liquid mixing and hence prevent this situation from occurring under abnormal process conditions. In addition, packed-bed reactors that utilize air must be designed so that the overall oxygen conversion results in an exit gas composition that satisfies flammability limits. This puts practical constraints on the magnitude of the air mass velocities that can be utilized.

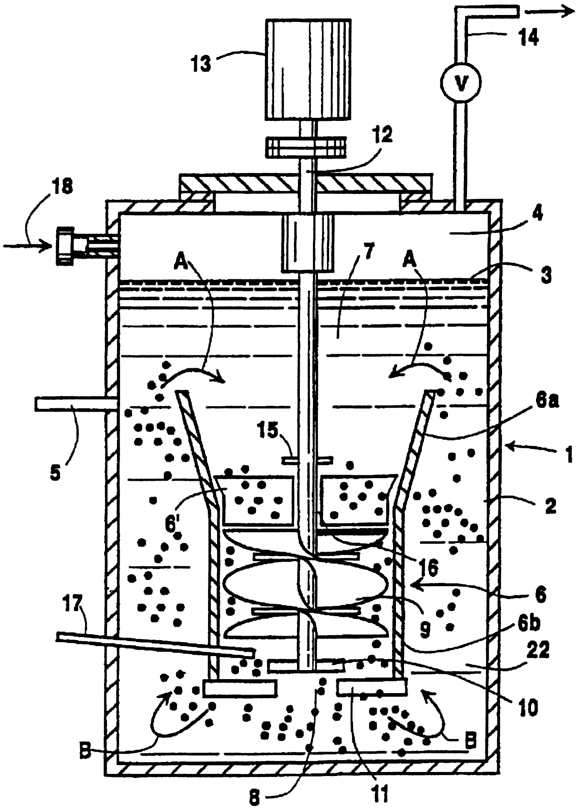

Fig. 2. Praxair liquid oxidation reactor or LOR reactor [21].

4.3. Emerging reactor types

A recent patent issued to Praxair [21] and related open literature [22] claim that the use of pure oxygen for terephthallic acid manufacture from *para*-xylene offers significant process advantages and gives a superior quality product when compared to the conventional air-based process. This is achieved by contacting the liquid reactants and pure oxygen in a mechanically agitated reactor containing an internal draft tube. Fig. 2 shows that the reactor resembles a conventional mechanically agitated reactor, except the internals are quite different. It contains an internal draft tube (6′) whose inside cross-sectional area is larger in the entry region (6a). The draft tube contains a baffle at the top (6) to minimize vortexing caused by the helical stirrer (9) that is powered by the motor (13). The pure oxygen gas is introduced into the bottom of the draft tube through the inlet tube (17). The mixing action results in a net downward flow of the gas bubbles through the draft tube before they contact the agitator (10) and exit the bottom of the draft tube (8). The bottom of the draft tube contains a baffle (11) so that the velocity of the gas–liquid–solid mixture is increased through the exit. The design of the internals is claimed to generate roll cells (region B) that trap oxygen bubbles and hence increase the efficiency of oxygen utilization because of the increased residence time. The bubbles and liquid–solid reaction mixture travel upward in the annular region until they reach the inlet to the draft tube (region A) where they re-enter the inlet of the draft tube. Any bubble that is not recycled may reach the top baffle (3), which separates the gas–liquid–solid reaction mixture from the reactor head space (4). The latter is purged with nitrogen gas through port (18) so that the oxygen concentration in the reactor head space is maintained below the flammability limit.

Some particular claimed advantages of the liquid oxygen reactor (LOR) include: (i) operation at lower reaction temperature when compared to conventional air oxidation; (ii) lower rate of acetic acid burn; (iii) reduced water production rate; (iv) lower concentrations of undesired organic and polynuclear aromatic by-products; (v) higher rate of terephthalic acid production per unit reactor volume; (vi) lower total pressure is required to obtain the equivalent oxygen partial pressure when compared to an air-based reactor system; (vii) reduced flow rate of vent gases, because of the absence of nitrogen in the feed gas; and (viii) more environmentally benign owing to the reduced levels of waste gas components.

Table 2 gives a comparison between the performance of the LOR and a conventional oxidizer [23]. If the optical density is assumed to be an indicator of undesired organic by-products that impart color to the terephthalic acid product, then the LOR produces superior quality TPA. Other notable advantages are the reduced rate of acetic acid losses due to combustion, and the reduced concentration of 4-carboxyaldehyde (4-CBA) in the final product.

The Praxair system appears to be the most recent attempt to conduct liquid-phase oxidation for commercially important reactions using pure oxygen in a novel reaction device. However, to the authors' knowledge, the Praxair technology has not been practiced on a commercial scale, and various technical challenges may occur when the system is scaled-up from the laboratory-scale or pilot-scale to a commercial process.

Table 2
Comparison between the Praxair liquid oxygen reactor (LOR) and a conventional stirred tank oxidizer for terephthalic acid [23]

Parameter	LOR	Conventional
Oxidant	O_2	Air
T (°C)	180	200
P (atm)	9	17
t (h)	1	1
X (%)	100	100
S (%)	98.2	96.2
Acetic acid loss (kg/100 kg TPA)	<3	5–7
4-CBA (ppm)	1500	3000
Optical density at 340 nm	0	1

4.4. Multiphase reactor selection

The choice of multiphase reactor type for a particular application is a key question that arises in the early stages of a process development program. Some reactor types can be given a lower probability of being used simply based upon the required production rate, temperature and pressure required to achieve commercially acceptable reaction rates, and other practical process engineering factors. Once a first pass ranking is established, the next level of screening requires a more detailed understanding of the interaction between kinetics, transport effects, hydrodynamics, energy management, and related issues. Recently, a computer-aided approach for generation and screening of multiphase reactor designs has been proposed [24]. The scheme consists of a two-stage design procedure to screen various design options. In the first stage, elements from stochastic optimization techniques are combined with simulated annealing, which is then followed by a second stage that uses mathematical programming methods. Various combinations of ideal multiphase flow contactors with various feeding, bypassing, and product removal strategies can be generated. In addition, different flow directions for the various phases, different micromixing models, mass transfer effects, hydrodynamics, and kinetics are claimed to be incorporated. It appears that this approach is in an early stage of development and requires additional effort until its utility can be widely accepted. Another approach for reactor screening and selection has been advocated by Krishna [25], which is referred to as a systems approach. In essence, it attempts to identify the preferred reactor by considering all of the various factors that affect performance for a given system. The reader is referred to [25] for details. The details of estimation of the design parameters for multiphase reactors are given in the review by Mills et al. [19].

5. Oxidation reactor modeling and scale-up

5.1. General approach

Development of reliable reaction engineering models for design, scale-up, troubleshooting and optimization of multiphase gas–liquid catalyzed reactors for oxidation processes requires a fundamental understanding of the interplay between reaction kinetics, transport effects and hydrodynamics. A flow path that defines the various tasks involved in the design and modeling of multiphase reactors for a new process is given in Fig. 3. This shows that a variety of interacting tasks must be performed before a final reactor design can be developed. The basis for the design are specifications on the required production rate, yield, and purity of the crude reactor product. Once this is established, a particular reactor retype must be selected. This includes the reactor geometry, reactor internals, and other hardware that is needed to satisfy the process requirements. Next, a mathematical model must be developed that allows prediction of the

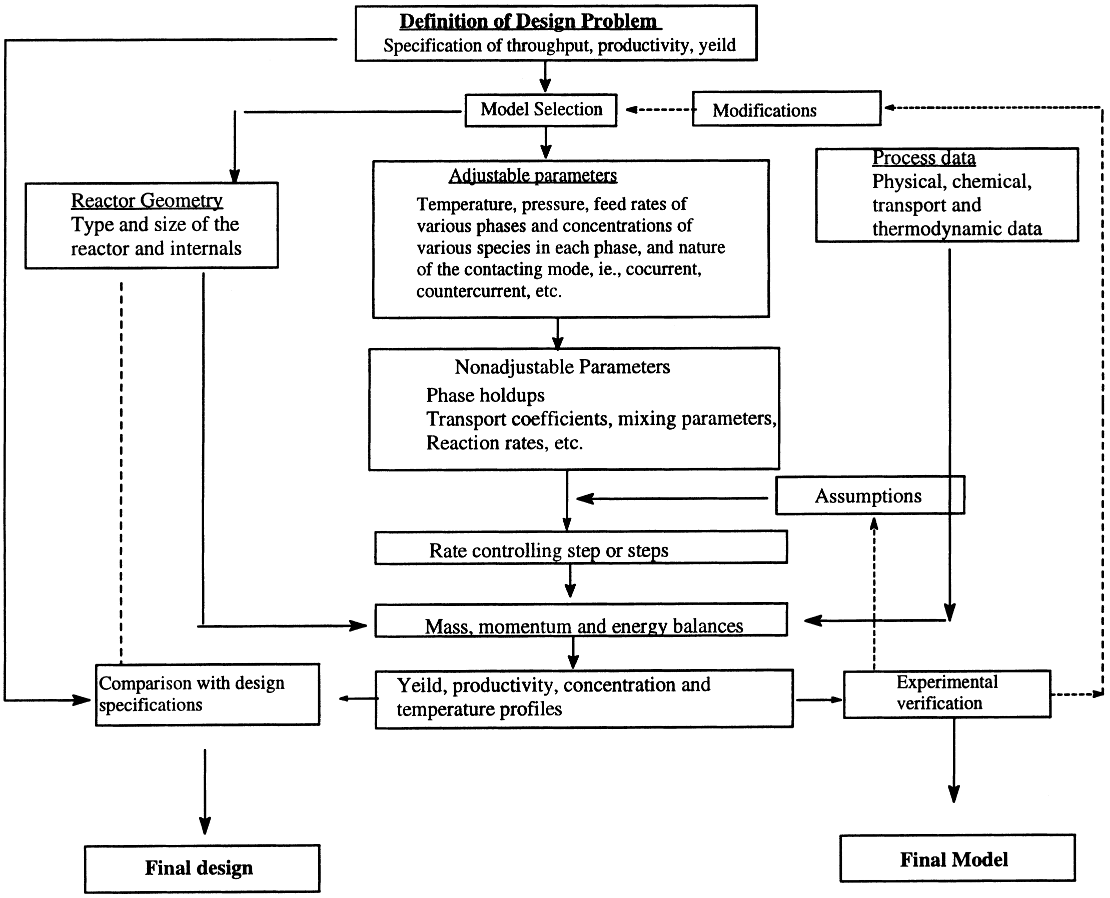

Fig. 3. Flow path of tasks required for design of multiphase reactors.

product rate, product yield, conversion, species concentration and temperature profiles as a function of the adjustable and non-adjustable model parameters. This model requires fundamental physical, chemical, transport, and thermodynamic data, along with the detailed reaction kinetics. Experimental verification of the model predictions using pilot plant data, or data from other existing commercial reactors is necessary for model validation. This latter step may require several iterations until a satisfactory design is developed. If another reactor type is selected for purposes of comparison, the entire process must be repeated. Finally, the design model must be incorporated into a process simulator to obtain predictions of the plant performance. These results are then used as the basis for developing process economics from which decisions where additional research and development can be made.

This approach has limitations in application for multiphase catalytic processes (gas–liquid and gas–liquid–solid) especially when internals are used in reactors and process specific designs are employed. The primary reason is that the local gas, liquid, and or solid phase velocities and hold-up distributions cannot be readily predicted using current state of knowledge of multiphase flow hydrodynamics. Hence, the mathematical operators that describe the temporal and spatial variations are not known. In addition, reactor hydrodynamics for multiphase systems are subject to change as the reactor size is increased and the reactor geometry, which includes various internals, is modified. While characterization of reactor hydrodynamics for laboratory-scale and pilot-scale systems can be performed using available experimental methods, the translation of these hydrodynamics to commercial scale systems is still not well understood and remains one of the outstanding challenges in reaction engineering. Additional details on various aspects of process scale-up are provided in the pioneering monograph of Johnson and Thring [26] and in the more recent edited monograph of Bisio and Kabel [27].

5.2. *Kinetic modeling*

A knowledge of the intrinsic reaction kinetics is essential for analysis of reactor performance and development of robust reaction engineering models. Some illustrations of kinetic modeling for specific types of liquid-phase oxidation are given here.

5.2.1. *Gas–liquid homogeneous catalyzed reactions*

Development of kinetic models for liquid phase oxidation systems using homogeneous catalyst has not received much attention from a reaction engineering perspective. However, reviews on the kinetics and mechanism from a chemical perspective are provided in the monographs of Parshall [28], Kochi [29], Masters [30], Henry [31] and the review of Davidson [32]. Most liquid phase oxidation reactions involve some type of free radical chain mechanism. The mechanism can be divided into four distinct steps: initiation, propagation, branching and termination [1]. For each step, several rate expressions can typically be developed, but one or more of the steps are dominating or rate controlling. One such scheme that has been proposed [1] is given in Fig. 4.

By applying the pseudo-steady-state approximation to the radical concentration and considering reactions (1)–(3), (9a), and (9b), the following reaction rate equation can be developed.

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = r_i^{1/2}\frac{k_{\mathrm{p}2}}{k_{t1}}\frac{k_{\mathrm{p}1}k_{\mathrm{t}1}^{1/2}[\mathrm{O_2}][\mathrm{RH}]}{k_{\mathrm{p}2}k_{\mathrm{t}2}^{1/2}[\mathrm{RH}]+k_{\mathrm{p}2}k_{t2}^{1/2}[\mathrm{O_2}]+k_{\mathrm{t}1}^{1/2}k_{\mathrm{t}2}^{1/2}r_{\mathrm{i}}^{1/2}}. \tag{13}$$

In Eq. (13) $[\mathrm{O_2}]$ is the concentration of dissolved oxygen in the liquid phase, [RH] the concentration of the hydrocarbon, r_{i} the rate of initiation, $k_{\mathrm{t}1}$ and $k_{\mathrm{t}2}$ the termination rate constants, and $k_{\mathrm{p}1}$ and $k_{\mathrm{p}2}$ are the propagation rate constants. When the concentration of dissolved oxygen gas is small relative to the hydrocarbon, the rate is proportional to the dissolved oxygen concentration.

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = r_{\mathrm{i}}^{1/2}\frac{k_{\mathrm{p}2}}{k_{\mathrm{t}1}}\frac{k_{\mathrm{p}1}k_{\mathrm{t}1}^{1/2}[\mathrm{O_2}][\mathrm{RH}]}{k_{\mathrm{p}2}k_{\mathrm{t}2}^{1/2}[\mathrm{RH}]+k_{\mathrm{t}1}^{1/2}k_{\mathrm{t}2}^{1/2}r_{\mathrm{i}}^{1/2}}. \tag{14}$$

When the concentration of dissolved oxygen is large, the rate expression is a function of the hydrocarbon concentration and independent of oxygen.

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = r_{\mathrm{i}}^{1/2}\frac{k_{\mathrm{p}2}[\mathrm{RH}]}{k_{\mathrm{t}1}^{1/2}}. \tag{15}$$

The above arguments can also be applied to the magnitudes of the propagation and termination rate constants. The value for $k_{\mathrm{p}2}$ is usually much greater

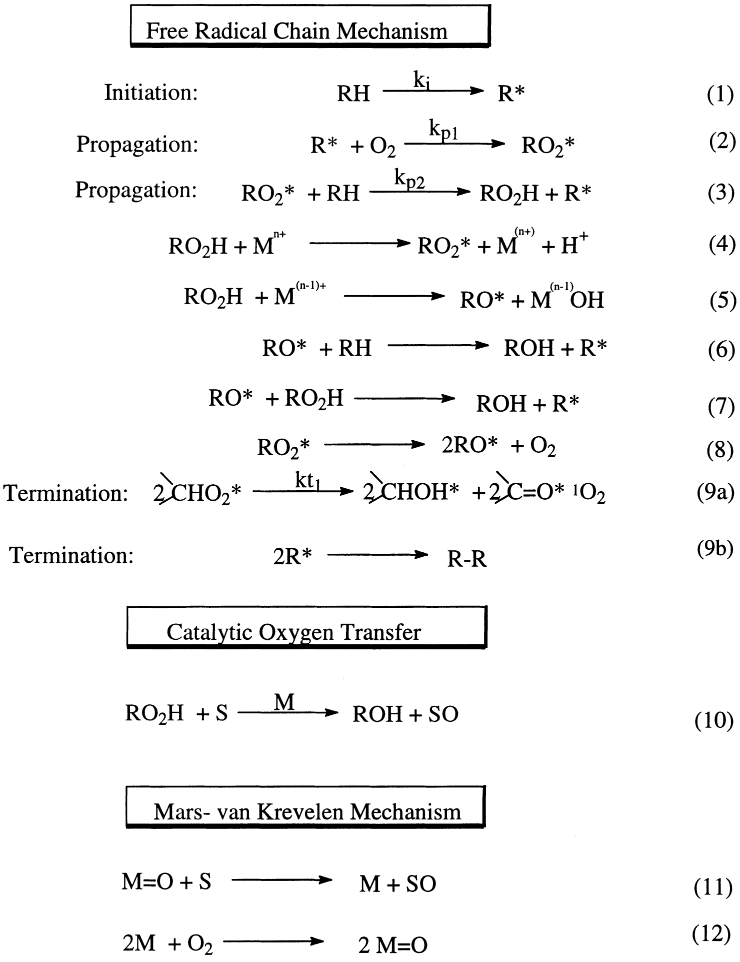

Fig. 4. Reaction mechanism for liquid phase oxidation systems. Adapted from [1].

than k_{t2} [1] so that the first term in the denominator is much greater than the other two. In this case, the rate equation becomes first-order in dissolved oxygen.

$$-\frac{d[O_2]}{dt} = r_i^{1/2}\frac{k_{p1}[O_2]}{k_{t2}^{1/2}}. \tag{16}$$

This analysis shows that the intrinsic rate of reaction can exhibit various types of behavior with respect to the concentrations of dissolved oxygen and hydrocarbon, as well as the propagation and termination rate constants.

For many liquid-phase oxidation processes, detailed kinetic models that account for the formation of the various byproducts are still poorly understood. A particular illustration is the uncatalyzed oxidation of cyclohexane to cyclohexanone, cyclohexanol, and cyclohexylperoxide for the adipic acid process. Recently, the work by Wen et al. [33] describes efforts to develop a kinetic model for this particular system using a laboratory reactor constructed of aluminum, since those constructed of stainless steel catalyzed the decomposition of cyclohexyl hydroperoxide. It was shown that the reaction rate was reduced when an aluminum reactor was used. When the dissolved oxygen concentration was high, the rate of reaction in total products was first-order. This points to the need for more detailed and carefully executed reaction kinetic studies, both on emerging process as well as existing ones where an opportunity for further process optimization exists.

The oxidation of ethylene to acetaldehyde via the Wacker process has been commercially practiced for years, since it was first described in 1959 [32,34]. The key reactions are shown below

$$C_2H_4 + PdCl_4^{2-} + H_2O \rightarrow CH_3CHO + PdO + 2HCl + 2Cl^-$$

$$PdO + 2CuCl_2 \rightarrow PdCl_4^{2-} + 2CuCl$$

$$1/2O_2 + 2CuCl_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$$

$$\text{Net}: \ C_2H_4 + 1/2O_2 \underset{CuCl_2}{\overset{PdCl_4^{2-}}{\rightarrow}} CH_3CHO$$

The details of rate equations for this particular system are given by Gates et al. [34].

5.2.2. *Gas–liquid–solid catalyzed reactions*

Gas–liquid–solid catalyzed reactions are used in selective oxidation processes when the reaction occurs on the surface of a heterogeneous catalyst. Classical Langmuir–Hinshelwood or Eley–Rideal mechanisms are often used to describe the elementary steps from which a reaction rate model can be developed. A good overview of kinetic modeling for heterogeneous catalyzed systems is provided by Froment and Biscoff [35], Froment and Hosten [36] and more recently, by Weller [37].

An illustration of kinetic rate equation for a gas–liquid–solid catalyzed selective oxidation is the oxidative carbonylation of aniline over a palladium-on-carbon catalyst with added NaI promoter [38]. The kinetic rate form that provided a satisfactory fit to the experimental data is given by

$$r = \frac{wk[A][B]^2[E]}{(1 + K_A[A] + K_B[B] + K_E[E])^2}. \tag{17}$$

In Eq. (16), A, B, and E denote the liquid-phase concentration of dissolved dioxygen, aniline, and the product, respectively. The above rate form shows that under certain conditions, the rate can exhibit negative first-order dependence on dissolved dioxygen (species A) and the product (species E), and zero-order dependence on aniline (species B). This rate form is typical of what can be expected for other types of gas–liquid–solid catalyzed selective oxidation reactions.

For reactions involving dissolved dioxygen and liquid phase reactants or products, various complexities, such as competitive adsorption of the components, effect of solvent and ionic media, and changes in the solubility of reacting gas in the liquid phase, should be considered. Generally, the reactants and products in liquid-phase selective oxidations are very complex organic molecules with liquid–solid adsorption characteristics that are also non-linear, which affects the rate of reaction. In addition, the type and concentration of the solvent and reaction impurities often has a notable effect on the intrinsic reaction rate. These features cannot be adequately described by Langmuir–Hinshelwood or Eley–Rideal models, since these are based on the assumption that one of the steps in the catalytic cycle is rate determining. Development of a kinetic model that accounts for these effects and other complexities that occur in a commercially operating process is a significant challenge.

5.2.3. *Summary on kinetic modeling*

One of the common methods used by chemists for discrimination between rate models is based on analysis of initial rate data. While this approach is useful to obtain a preliminary understanding of the kinetic trends with respect to operating parameters, it often fails to explain some important features related to product inhibition and changes in catalyst activity and selectivity with time-on-stream. Therefore, it is suggested that kinetic models should be verified for their applicability using both differential and integral analysis over a wide range of operating conditions, reactant conversions and product selectivity. An alternative approach involves discrimination between various models by direct application of the integral method of analysis. Several examples of this approach have been successfully demonstrated in the literature for gas–liquid–solid catalytic reactions [39–42].

A recent trend in kinetic modeling involves a molecular level approach to the development of rate models. Evidence suggests that there is a close analogy between reaction mechanisms based upon adsorption and those based on molecular species through organometallic intermediate species. This aspect can allow better understanding of the kinetic trends in complex reactions, which are otherwise modeled using empirical approaches. A recent review on this subject is by Waugh [42], though examples of the molecular level approach for industrially important selective oxidation reactions are rare. This approach needs an independent study on the nature of catalytic sites and molecular species formed as intermediates. This might lead to a reaction scheme that can form the basis for deriving rate equations.

5.3. Multicomponent transport and reaction

Multiphase gas–liquid catalyzed reaction for oxidation are often conducted under conditions where heat and mass transfer has an effect on the observed rates of reaction. Before a global reactor model can be developed, an analysis of the overall rates of reaction under differential conditions must be performed. The result of this analysis is a model that can predict the local composition and temperature in terms of the intrinsic reaction rate parameters, heat and mass transfer coefficients, physical and thermodynamic properties of the reaction medium, catalyst properties, and other related parameters. A detailed analysis of coupled reaction-transport processes for gas–liquid and gas–liquid–solid systems is beyond the scope of this work, but this is available in the monographs of Astarita [43], Danckwerts [44], Doraiswamy and Sharma [45] and more recently, Taylor and Krishna [46].

A detailed analysis of mass transfer effects in oxidation of cyclohexane is reported by Suresh et al. [47]. It is shown that the autocatalytic oxidation in liquid phase is zero-order with oxygen. However, at lower O_2 concentration, a first-order behavior was observed, which is due to starvation of dissolved O_2 in liquid phase and mass transfer limitations. The auto-oxidation of cyclohexane also shows oscillations in oxidation rates, as a result of oscillations in dissolved O_2 concentration under certain conditions [48]. These phenomena can lead to multiplicity of rates and temperature profile and need careful consideration in reactor design.

Cao et al. [49] have investigated modeling of a semi-batch gas–liquid reactor for oxidation of *p*-xylene based on a lumped kinetic scheme. Here again, the reaction was found to be zero-order with O_2 and first-order with liquid reactants. A generalized model incorporating mass transfer with reaction has been developed for this system which does not require a prior assumption of the reactor-operating regime. However, this model does not apply to commercial operation since it was not conducted in acetic acid solvent.

The problem of critical oxygen concentration in liquid phase catalytic oxidation following redox mechanism has been analyzed [50] and a method for prediction of critical oxygen concentration has been demonstrated for the Wacker process. It has been shown that, for a given set of conditions, a certain critical O_2 in the reactor inlet is required for the overall catalytic reaction to work with maximum efficiency under steady state. A detailed analysis of a semi-batch bubble column reactor for the Wacker process has also been reported [51] in which plug flow for the gas phase and complete backmixing for the liquid phase has been assumed. The model also incorporated changes in the superficial gas velocities along the height of the reactor and the predictions by this model were shown to be agreeing very well with the experimental data. It has been suggested that a critical ratio of oxygen to ethylene partial pressures exist to obtain optimum performance.

6. Summary and conclusions

An overview of emerging oxidation processes and selected recent developments in reaction engineering that should provide a useful starting basis for the evaluation and scale-up of these process concepts from the laboratory to the next level of development has been given. These newer emerging processes will typically involve multiphase catalytic reactions between gases, liquids, and possibly solid reactants and products, and will operate at high conversion and selectivity with minimal generation of undesired reaction by-products. The use of enriched air or pure oxygen as the oxygen source has a potential advantage for these emerging processes, provided that safe handling and plant operation can be demonstrated.

Scale-up of new oxidation chemistries from invention to commercial operations can be facilitated and proceed with a higher probability of success if reaction engineering principles are incorporated and applied at various stages in process development program. For example, evaluation of new catalyst technology for both activity, selectivity, and other measures of performance requires the use of modern laboratory reactor systems in which transport disguises are negligible so that the true kinetics can be studied as part of the catalyst screening methodology. Identification of the preferred mode of fluid–solid contacting between the catalyst and reactants and other relevant reactor design concepts can be explored and facilitated with new computer automated approaches for screening and ranking of various reactor alternatives. The incorporation of basic and more robust reactor design models that allow the reactor performance to be evaluated in the context of the entire process using modern dynamic and steady-state process stimulation techniques will become more commonplace. This will require a close link between experimental databases for reaction kinetics and thermodynamics with reactor models so that the latest advances in the theory of transport–kinetic interactions and hydrodynamics can be exploited. Hence, reaction engineering of emerging oxidation processes should have an important impact on development of the next generation of commercial processes.

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