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Microinterface intensification in hydrogenation and air oxidation processes



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ABSTRACT

Hydrogenations and air oxidations usually have low apparent reaction rate, generally controlled by mass transfer rate, and widely exist in the modern chemical manufacturing process. The key to increase the mass transfer rate is the reduction of the liquid film resistance $1/k_L a$. In this work, the original concept of microinterface intensification for mass transfer and then for these reactions has been proposed. We derived the regulation model and set up the mathematical calculation method of micron-scale gas–liquid interface structure on mass transfer and reaction, designed the mechanical energy exchange device that can produce gas–liquid microinterface system on a large scale, and established the OMIS system which is able on line to measure the diameter and distribution of millions of microbubbles, interface area a and mass transfer film thickness δ_M , as well as developed a series of microinterface intensified reactor systems (MIRs) for the applications of hydrogenation and air oxidation processes. It is believed that this research will provide an up-to-date development for the intensification of hydrogenation and air oxidation reactions.

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1. Introduction

Modern chemical manufacture process such as oil refining, petrochemicals, fine chemicals, pharmaceuticals, material synthesis, wastewater treatment, etc. involves a large number of reactions of hydrogenation and air oxidation, in which the interphase mass transfer of oxygen and hydrogen as the gas phase to the liquid phase is often the limiting step [1]. Therefore, mass transfer intensification of these reaction processes will be greatly beneficial to these processes on energy saving, emission reduction, and intrinsic safety, which will bring significant environmental and economic benefits [2,3].

In these reaction process, the traditional reaction rate refers to the apparent (or macroscopic) reaction rate, rather than the intrinsic reaction rate [4]. The apparent reaction rate of hydrogenations and air oxidations is usually much lower than that of the intrinsic, which means that the intrinsic reaction rate is faster and the interfacial mass transfer rate is slower. The fundamental reason is that

the gas–liquid interfacial area in the traditional bubble reactors is too small to seriously restrict the interphase molecular transfer [5]. For example, the area between the gas and liquid phases is usually $20\text{--}300\text{ m}^2\cdot\text{m}^{-3}$ under normal pressure for the traditional bubbling air oxidation reactor, and in most cases less than $100\text{ m}^2\cdot\text{m}^{-3}$ since the bubble diameter is generally between 5–30 mm [6–8]. Therefore, methods such as increasing the gas circulation or adding reactor internals to enhance mass transfer and improve the mass transfer rate are usually employed in the industrial practice, but their effect is very limited [9,10]. For this reason, researchers have focused on the study of new types of reactors such as microchannel (microfluidics) reactors, hyper-gravity reactors, jet reactors, and microwave reactors, trying to find new modes of interfacial mass transfer and reaction intensification, and have achieved gratifying results in the past decades [11].

For a long time, with regard to the development and design mode of the hydrogenation and air oxidation, one is based on the microscopic diffusion mass transfer (especially eddy diffusion) [12,13] and reaction characteristics on the molecular scale, and the other is based on the macroscale research results of bubbling, stirring and mixing, particle dispersion and agglomeration, flow pattern and particle distribution, equipment structure and

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structure-effect relationship on the millimeter - centimeter scale [14–18]. Both of the models neglect the understanding of the mass transfer and reaction behaviors that occur on the mesoscale between the microscale and the macroscale, so it is difficult to know the controllable influence of the critical parameters on the performance of reactors at the mesoscale. As a result, there are thousands of hydrogenation and oxidation reactors in the industry that are still working under high energy consumption, high mass consumption and high-risk state.

The original work of microinterface intensified reactor/reaction (MIR) and the concept of microinterfacial mass transfer intensification has been proposed since 2001 and 2017 by our team, respectively [19–24], which is to enhance the mass transfer and reaction behaviors occurring on the mesoscale in these reactors. It is different from the above-mentioned gas-liquid mass transfer intensification technologies in at least three points: Firstly, it can still form a complete microinterface system in the reactor under the condition of high gas-liquid ratio, *eg.* more than 10, and the gas-liquid mass transfer interfacial area increases by an order of magnitude, and then the mass transfer rate and reaction efficiency are significantly improved; Secondly, to realize the mass transfer intensification of the existing reactors, it is only necessary to modify the existing various gas-liquid, gas-liquid-solid *etc.* reactors, without the need to manufacture a new reactor, which can minimize the cost of retrofit, while it is impossible to achieve similar results for microchannel (microfluidic) reactors, hyper-gravity reactors, microwave reactors; Thirdly, it is especially suitable for high-capacity reaction devices, such as one hundred thousand tons to one million tons per year.

Different from the traditional reaction intensification technologies that mainly increases the interfacial area a to a certain extent *via* improving stirring, MIR technology not only increases the interfacial area a tens of hundreds of times, but also greatly improves the liquid film mass transfer coefficient k_L . It should be noted that the size and its distribution of microbubbles in the MIR system can be accurately measured based on online measuring and imaging system (OMIS) established by our team. In addition, we derived the structure-regulation model of the liquid film mass transfer coefficient k_L though the mass transfer film thickness (δ_M) of the microbubbles. In the present paper, we focus on the measurement and characterization of the average diameter (d_{32}), liquid film thickness (δ_L) and mass transfer film thickness (δ_M) of the microbubbles. The structure-effect regulation models and some cases of applications in hydrogenation and air oxidation processes were introduced as well.

2. Definition of MIR System

The microinterface assembly (MIA) as the core unit of MIR is a well-designed and elaborately manufactured mechanical structure invented by the authors that allows gas flow or/and liquid flow into the reactors nano-microparticles to form a microinterface reaction system. The advantage and mechanism of MIA, the definition of MIR system were introduced in our previous report [19–24]. Briefly, the MIR system refers to a system dominated by hundreds of millions of microparticles with an average diameter of $1\ \mu\text{m} \leq d_e < 1000\ \mu\text{m}$. The above-mentioned “dominated” indicates that the total number of nano-microparticles accounts for more than 99% of the total number of particles and the sum of the surface area of the particles accounts for more than 99% of the total interfacial area of the reaction system. The morphology comparison of microinterface system in MIR and the macrointerface system in the conventional bubbling reactor (CBR) is shown in Fig. 1.

3. Microinterface Intensification Philosophy

Taking a chemical reaction with an first-order intrinsic reaction as an example [25], the apparent reaction rate expression is shown in Eq. (1), and it can be seen that the apparent reaction rate is affected by mass transfer and intrinsic reaction.

$$-r_A = \frac{1}{\frac{1}{H_A k_G a} + \frac{1}{k_L a} + \frac{1}{k_s a_s} + \frac{1}{(k_A C_B) \chi_A f_s}} \cdot \frac{P_G}{H_A} \quad (1)$$

Eq. (1) shows that the intrinsic reaction rate at this time is determined once the reaction conditions are determined. Then the apparent reaction rate of component A is mainly affected by three mass transfer resistance terms: the gas film mass transfer resistance $1/H_A k_G a$, the liquid film mass transfer resistance $1/k_L a$ and the liquid film mass transfer resistance on the catalyst surface $1/k_s a_s$. According to mathematical analysis, the apparent reaction rate will be infinitely close to its intrinsic reaction rate, indicating that all three mass transfer resistances have been eliminated, as long as the first three terms in the right denominator ($\frac{1}{H_A k_G a} + \frac{1}{k_L a} + \frac{1}{k_s a_s}$) become infinitely small or even zero. Unfortunately, it is so difficult to be achieved on engineering. What we can do is to reduce the mass transfer resistance as much as possible.

For hydrogenation and air oxidation processes, previous studies have shown that the gas film mass transfer resistance is much smaller than the liquid film mass transfer resistance (1–2 orders of magnitude) [26,27]. The specific surface area a_s of the catalyst for certain reaction conditions can be regarded as a fixed value. Therefore, the key problem to intensify the reaction process is how to decrease the liquid film resistance $1/k_L a$. The philosophy of MIR is to make the interfacial area a tens of hundreds of times larger than that of CBR in the same operational conditions even at lower temperature and pressure as well as gas/liquid ratio, by breaking bubbles and/or droplets with a diameter of centimeter/millimeter in the reactors into particles with a diameter of microns and nanometers. Thus it also naturally results in that the mass transfer film thickness δ_M much thinner and the liquid film mass transfer coefficient k_L considerably larger than that of CBR, thus achieving both particularly significant intensifications of the interfacial mass transfer and the reaction [19–24,28].

The structures of the reactor and MIA, the physicochemical properties of the gas and the liquid as reactants, and the operating conditions have an extremely complex effects on $k_L a$, and there are many studies on the correlation between them [9,29–46]. But $k_L a$ is a macroscopic parameter, which cannot reflect the detailed information of gas-liquid mass transfer interface and its two sides. Therefore, more information can be obtained only by separately studying the two parameters k_L and a in $k_L a$. Namely, the liquid film mass transfer coefficient k_L and the gas-liquid interfacial area a are crucial for the precise design and regulation of the reactor [47–49].

3.1. Determination of a

The formula for calculating the interfacial area in the gas-liquid reaction system is:

$$a = \frac{6\phi_G}{d_{32}} \quad (2)$$

The gas holdup can be calculated by the following formula:

$$\phi_G = 1 - \frac{\Delta p}{\rho_L g \Delta h} \quad (3)$$

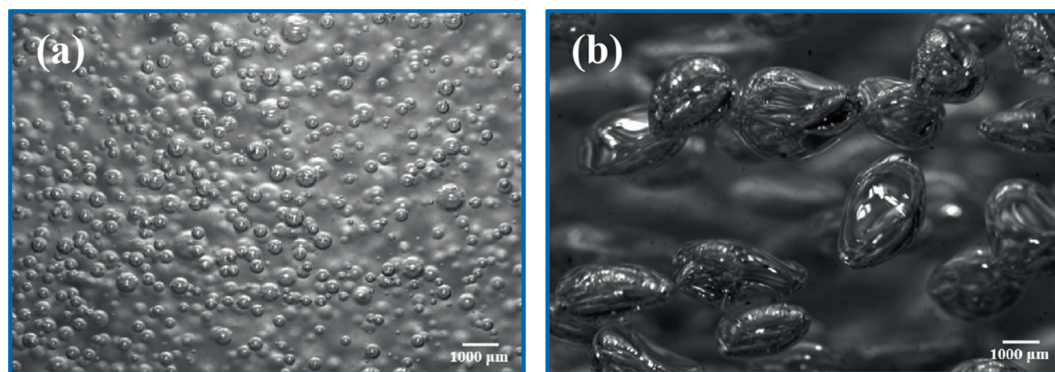


Fig. 1. Comparison of the morphology of microinterface system in MIR and the macrointerface system in the convectional bubbling reactor (CBR) via our online measurement method (OMIS) [24]: (a) microinterface system, (b) macrointerface system.

where Δp is the pressure difference measured during the experiment, Pa; Δh is the height difference between the pressure measurement points, m; and ρ_L is the density of liquid, $\text{kg}\cdot\text{m}^{-3}$.

The Sauter average diameter d_{32} of the microbubbles in the MIRs is defined by Eq. (4):

$$d_{32} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2} \quad (4)$$

Therefore, how to determinate the value of d_{32} is the key to statistically calculate the interfacial area a . The measurement of microbubbles and the determination of d_{32} are described in the section of 4.

3.2. Determination of k_L

Danckwerts *et al.* [50] pointed out that the predicted results of the physicochemical properties of the system by Whitman laminar film theory, Higbie surface renewal theory and Danckwerts stochastic surface renewal theory are very similar for the gas absorption process. Then it should be reasonable to use one of the above three classical theories to establish the mathematical expression of the liquid film mass transfer coefficient of the microparticles in the MIR system.

The liquid film mass transfer coefficient k_L determined by Whitman's theory can be calculated using Eq. (5).

$$k_L = D_L / \delta_M \quad (5)$$

where D_L is diffusion coefficient of gas molecules in the liquid phase, $\text{m}^2\cdot\text{s}^{-1}$, which can be calculated by Wilke's formula.

$$D_L = 7.4 \times 10^{-15} (\Phi M_L)^{1/2} \frac{T}{\mu_L V_{bA}^{0.6}} \quad (6)$$

where Φ is the association factor of liquid components, to be taken as 1 here; M_L is the molar mass of liquid components, $\text{g}\cdot\text{mol}^{-1}$; V_{bA} is the molecular volume of gas at normal boiling point, $\text{cm}^3\cdot\text{mol}^{-1}$.

It is worth noting that δ_M varies with the diameters of the microbubbles, which is different from the macrobubbles. If the relationship between δ_M and their average diameter d_{32} can be established, the mathematical model of the liquid film mass transfer coefficient k_L will be obtained.

Therefore, the key to determine the interfacial area a and the liquid film mass transfer coefficient k_L is to measure the average sizes d_{32} (obtained by size and size distribution of microbubbles) and mass transfer film thickness δ_M of microbubbles in the MIR system.

4. Measurement and Characterization

The measurement and characterization of the characteristics (particle diameter, distribution, number, shape, *etc.*) of the MIR system are the basis for the determination of the interfacial area a and liquid film mass transfer coefficient k_L , as well as the design and structure-effect regulation of the MIR system [21]. As far as an actual MIR is concerned, its particle diameter may range multi-orders of magnitude (from nano to millimeter), and the number of the microparticles may be hundreds of millions or even billions per cubic meter with dynamic changes because of the reaction and the movement. Therefore, there rarely is mature measurement and characterization methods to be employed due to the high complexity of spatio-temporal dynamics and vast quantity.

4.1. Overview of measurement methods for microparticles

To accurately measure and characterize the parameters of bubbles and droplets, researchers have made unremitting efforts to precisely determine the particle characteristics of the multiphase system using a variety of the most advanced instruments and measurement methods worldwide over the past three decades. There are many techniques for measuring the overall average parameters, as well as instruments and equipment for measuring the local parameters of the system. According to whether these instruments are in contact with the object under test, these techniques can be classified into two modes: invasive and non-invasive [51].

Invasive techniques generally use various probes as measuring tools [52–54], whose principle is that the continuous phase and the dispersed phase in multiphase fluid systems have different responses to sound, light, electricity and heat signals, so that the probe can obtain the parameters in the system by the signal transformation of the response difference. At present, optical fiber probe, conductivity probe and ultrasonic probe are the main methods. Among the non-invasive technique with good applicability, the techniques used for global parameter measurement mainly include pressure sensing method [23], bed slump method, acoustic wave technique[54], and the techniques used for local parameter measurement mainly include high-speed photography[24], laser doppler velocimetry (LDA), particle imaging velocimetry (PIV) [55], computer-assisted tomography (CT) [56], capacitance tomography (ECT) [57].

Unfortunately, the above exiting techniques are not suitable for the nano- microparticles in the MIR system. Therefore, developing the measuring and characterizing technique is one of the core important jobs for the study of MIR system.

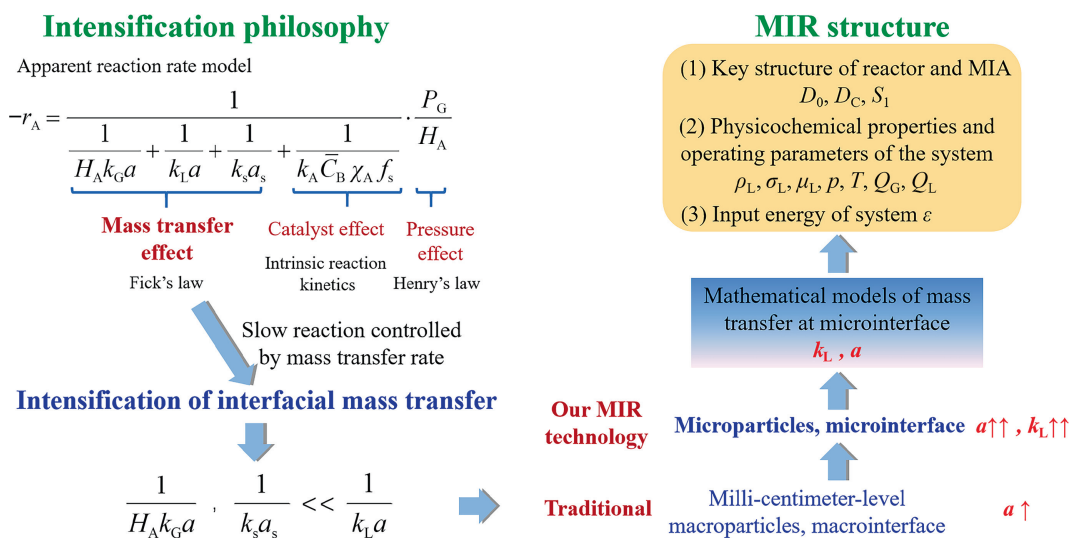


Fig. 2. Schematic diagram of microinterfacial intensification philosophy.

4.2. Online measurement method of microparticles

In view of the vast number of microbubbles and catalyst particles in the MIR system, each individual particle is nano/micron in size and spherical in shape, the deformation is negligible. For the measurement and characterization of such a system, an OMIS was set up consisting of a MIR system, a high-speed camera with a set of macro lens, a set of high-brightness light sources, a locating and adjusting system, and a computer with imaging processing software, as shown in Fig. 3(a).

By the measurement of OMIS, the particle morphology, size, movement, collision, coalescence, crushing and other characteristics of the MIR system can be quickly obtained, as shown Fig. 3 (b). Then, with the particle image recognition software (PIRS) developed by our team, the detailed information such as particle size, distribution, gas holdup, motion trajectory, gas–liquid interfacial area, etc. can be analyzed.

4.3. Determination of d_{32}

Based on the images obtained from OMIS, PIRS can automatically analysis microparticle images to realize automatic identification and statistical calculation of microparticles, as shown in Fig. 4 (a) and (b). Then d_{32} can be calculated according to Eq. (3).

4.4. Determination of δ_L , δ_M and k_L

As shown in Fig. 4(c), the thickness of the liquid film of the microbubbles δ_L can be measured by the OMIS system. Previous studies have shown that there is a linear relationship between the bubble diameter d and the liquid film thickness δ_L for different microbubble systems. By fitting the experimental data, the following approximate relationship exists between δ_L of the microbubbles and their average diameter:

$$\delta_L \approx 0.22d_{32} \quad (7)$$

Based on the experimental data and the formula in the section of 3.1–3.2, k_L can be determined. δ_M can be calculated by Eq. (8).

$$\delta_M = D_L/k_L \quad (8)$$

In-depth analysis of Fig. 4 and other images of microbubbles show that there is an approximate relationship between δ_M and δ_L for the microinterface systems as follows:

$$\delta_M \approx \delta_L/2\pi \quad (9)$$

It indicates that the relationship between δ_M and d_{32} can be obtained as follows:

$$\delta_M \approx 0.22d_{32}/2\pi \quad (10)$$

Then

$$k_L = D_L/\delta_M \approx \pi D_L/(0.11d_{32}) \quad (11)$$

5. The Structure-effect Regulation Models of MIR System

Based on the above measurement and the parameter determination, the mass transfer structure-effect regulation models of the MIR system were established, including four equations of d_{32} , ϕ_G , a and k_L .

5.1. Structure-effect regulation model of d_{32}

Experimental and theoretical studies [58–70] have shown that the size of particles is log-normal distribution and generally exists in the gas–liquid system, and it is no exception for the MIR system. The microbubbles in the MIR system can be considered as ideal spheres according to Young–Laplace equation and the particle size conforms to a single continuous log-normal distribution. The bubble scale model of the MIR system was obtained through the mathematical analysis of the particle size probability density function, as shown in Eq. (12) [19,71].

$$d_{32} = \sqrt{d_{\max} \cdot d_{\min}} \times \exp \left[3.5 \left(8 + \ln \sqrt{d_{\max}/d_{\min}} - 4 \sqrt{4 + \ln \sqrt{d_{\max}/d_{\min}}} \right) \right] \quad (12)$$

Eq. (12) shows that d_{32} is only related to $d_{\max}$ and $d_{\min}$, and they can be determined by Eq. (13) and Eq. (14), respectively.

$$d_{\max} = 0.75(\sigma_L/\rho_L)^{0.6} \varepsilon^{-0.4} \quad (13)$$

$$d_{\min} = 11.4(\mu_L/\rho_L)^{0.75} \varepsilon^{-0.25} \quad (14)$$

where ε is the energy dissipation rate of the MIA of the MIR and it was derived by our previous study shown in Eq. (15) [72].

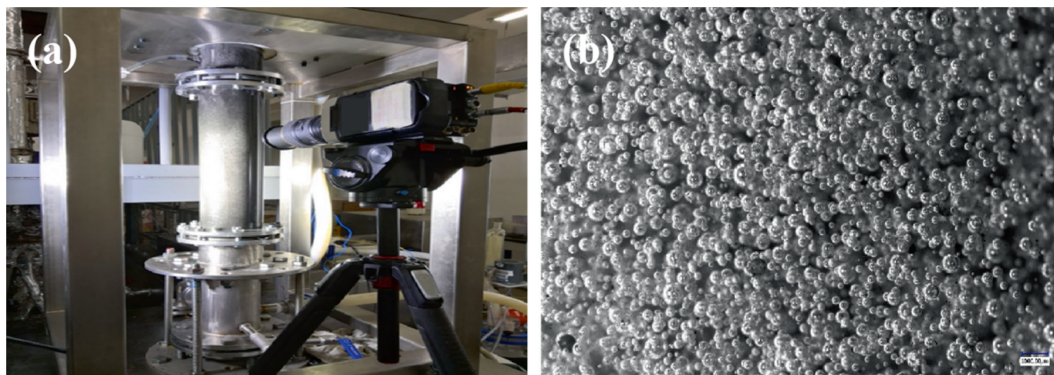


Fig. 3. (a) OMIS system established by our team; (b) The particle morphology in the MIR taken by OMIS system.

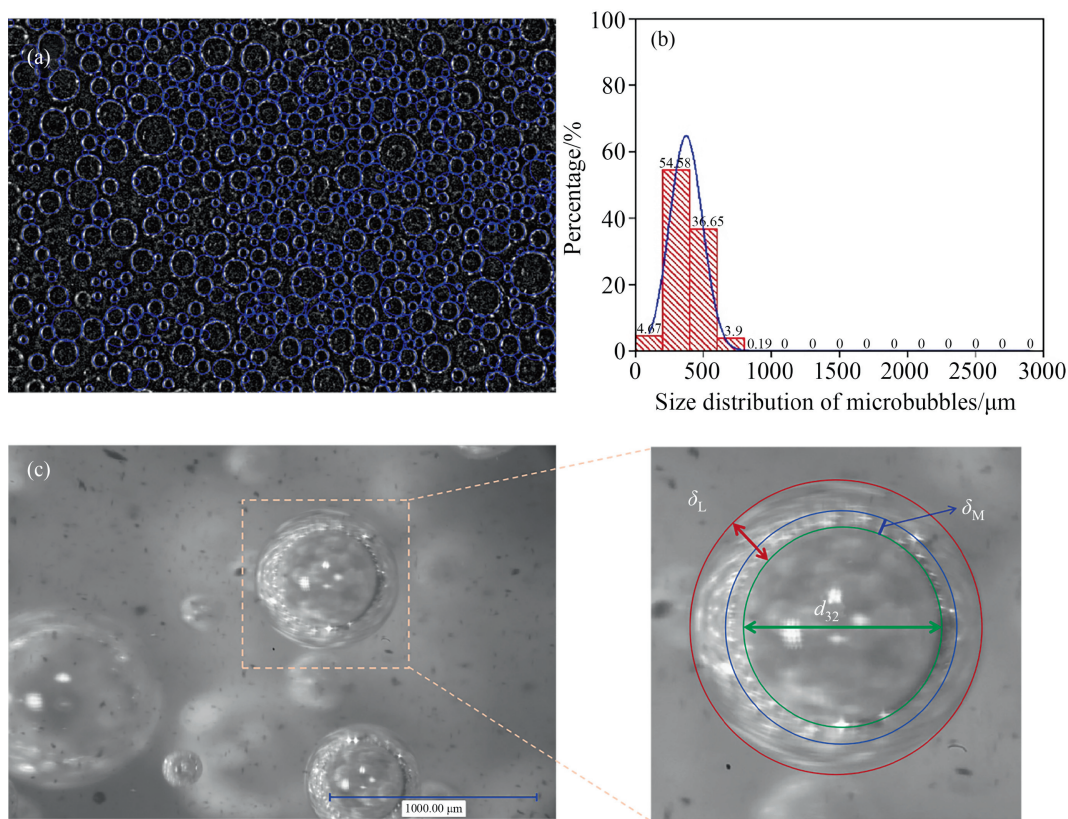


Fig. 4. (a) Particle swarm scale identification by PIRS; (b) The microbubbles distribution of (a); (c) and (d) Magnified the real-time image of microinterface system.

$$\varepsilon = \frac{1+\lambda}{\rho_L V_0} \left\{ \sqrt{2gH_0 / \left(\frac{1}{\lambda^2 S_1^2} - \frac{1}{S_0^2} \right)} P_m \ln \left(\frac{P_m + \Delta P}{P_m} \right) - \rho_L g H_0 Q_{L0} \left(\frac{1}{\lambda^2 S_1^2} - \frac{1}{S_0^2} \right)^{-1} \left(\frac{1+\lambda}{\lambda S_1} \right)^2 \right\} \quad (15)$$

where S_0 and S_1 are the cross-sectional area of the reactor and the bubble breaker, respectively, m^2 ; ρ_L is the density of liquid, $\text{kg}\cdot\text{m}^{-3}$; H_0 is the initial liquid level height in the reactor, m ; V_0 is the initial volume flow, $\text{m}^3\cdot\text{s}^{-1}$; P_m is the mixing pressure, Pa ; Q_{L0} is the initial liquid circulation volume flow of the reactor, $\text{m}^3\cdot\text{s}^{-1}$.

Eq. (15) represents the mathematical relationship between the reactor design parameters and the rate of energy dissipation for bubble collapse. Eqs. (13)–(15) are the structure-effect regulation model of d_{32} in the MIR system.

5.2. Structure-effect regulation model of ϕ_G

Based on the hydrodynamic behavior of the MIR system, the general expression of the gas holdup ϕ_G of the MIR system can be derived.

$$\phi_G = \frac{2v_G}{v_0 + v_G \pm v_L + \sqrt{(v_0 + v_G \pm v_L)^2 - v_G v_0}} \quad (16)$$

where v_G is apparent gas velocity, $\text{m}\cdot\text{s}^{-1}$, v_L is rising speed of the bubble, $\text{m}\cdot\text{s}^{-1}$, v_0 can be calculated by Eq. (17), which is determined by the physicochemical properties of the system and the values of d_{32} .

$$v_0 = \frac{2}{3} \sqrt{g d_{32} (\rho_L - \rho_G) / \rho_L} \quad (17)$$

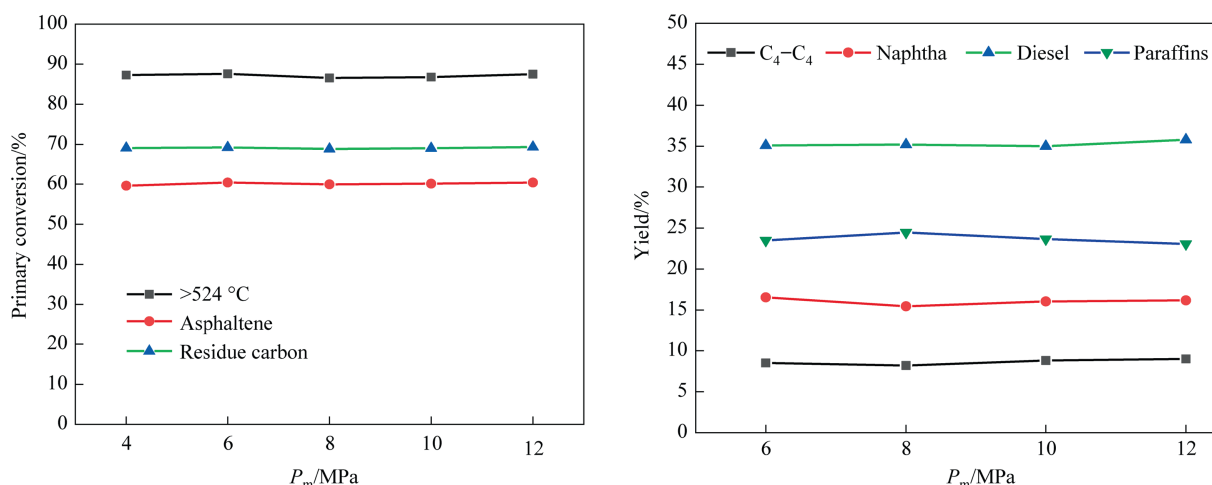


Fig. 5. Operation results of a pilot-scale residue oil hydrogenation on MIR. Material: vacuum residue (VR), $\rho_L = 1010 \text{ kg}\cdot\text{m}^{-3}$ (20 °C), kinematic viscosity $\nu = 1072.33 \text{ mm}^2\cdot\text{s}^{-1}$, $b_p \geq 525 \text{ °C}$ (more than 80% (mass) of the VR), carbon-supported iron catalyst: 6 μm average diameter, operating temperature: 450–455 °C, operating pressure: 4–12 MPa, Q_G/Q_L (normal state) = (1500–2000):1, LHSV: 0.5 h^{-1} .

where ρ_L is density of liquid, $\text{kg}\cdot\text{m}^{-3}$, ρ_G is density of gas, $\text{kg}\cdot\text{m}^{-3}$. Thus, Eqs. (16), (17) and (12) are the structure-effect regulation model of the gas holdup ϕ_G in the MIR system.

5.3. Structure-effect regulation model of a

Based on Eq. (2), combined with the above-mentioned structure-effect regulation models of d_{32} and ϕ_G , the structure-effect regulation model of the gas–liquid interfacial area a in the MIR system can be given as Eq. (18) [73].

$$a = \frac{6v_G}{v_{32}d_{32}} = \frac{12v_G}{\left[v_0 + v_G \pm v_L + \sqrt{(v_0 + v_G \pm v_L)^2 - v_G v_0} \right] d_{32}} \quad (18)$$

where v_{32} is the average rising velocity of microbubbles in the MIR system, and its theoretical model can be derived as Eq. (19).

$$v_{32} = \frac{v_G + v_0 + v_L \pm \sqrt{(v_G + v_0 + v_L)^2 - 4v_G v_0}}{2} \quad (19)$$

5.4. Structure-effect regulation model of k_L

The liquid film thickness δ_L on the surface of the microbubble was measured through the OMIS [74]. Based on Eqs. (6), (11) and (12), the structure-effect regulation model of k_L can also be established, shown in Eq. (20).

$$k_L = \frac{2 \times 7.4 \times 10^{-15} \pi (\phi M_L)^{0.5} T}{0.15 d_{32} \mu_L V_{bA}^{0.6}} \quad (20)$$

6. Application Cases

The above research shows that the MIR system not only improves the interfacial area a , but also increases the liquid film mass transfer coefficient k_L due to the reduction of mass transfer film thickness δ_M . Therefore, the mass transfer resistance of the liquid film $1/k_L a$ is substantially reduced by dual factors k_L and a .

On the basis of above research, a series of hydrogenation and oxidation industrial reactors were designed and applied to practical processes according to the philosophy shown in Fig. 2. Some typical cases are presented as follows.

6.1. Residue oil hydrogenation

The process of residue oil hydrogenation in slurry bed reactor has been studied for more than 100 years. Many typical technologies have been developed, such as VCC [75], HDH/HDHPLUS [76], (CAT/HC)₃ [77], and SOC [78], Uniflex™ [79], ENI [80], etc. However, only a few of them have been implemented actually on a large scale in industry. The actual effect was far from the above-published data in the examples that have been implemented.

High pressure, high energy consumption, high production cost, low liquid hour space velocity (LHSV), and low conversion are their common characteristics. The operating pressure of this process is generally 16–22 MPa in terms of different catalysts. The most-reported operating pressure in slurry bed reactors is 22 MPa and the LHSV is about 0.5 h^{-1} for iron catalysts. The operating pressure disclosed by a few companies is 16–17 MPa for nickel /molybdenum catalysts, but it must be operated at a very low LHSV of 0.08–0.2 h^{-1} .

The MIR employed in a pilot-scale residue oil hydrogenation and the operation results were shown in Fig. 5.

It shows that the residue oil hydrogenation of MIR displays a higher efficiency, higher conversion rate, lower pressure, meaning that MIR can make this process much energy-saving, economic and safe.

6.2. Air oxidation of *m*-xylene to synthesize *m*-toluic acid

M-toluic acid (MTA), a useful organic intermediate, can produce high-efficiency mosquito repellent and is a good developer for color films and artificial preparation of synthetic flavors. It is generally produced by an oxidation of *m*-xylene and air in the presence of organic cobalt as a catalyst. Since the low solubility of oxygen in *m*-xylene, the mass transfer of the oxygen from the air bubble to the liquid phase in the reactor will play a key role.

Due to the low efficiency of the CBR, excess air and pressure must be exerted on the oxidation reactor to improve the gas–liquid mass transfer efficiency, thus increasing the reaction rate. However, this will inevitably lead to an excess energy dissipation and the toxic *m*-xylene outflow along with the tail gas at the top of the reactor. Therefore, it is crucial to find a new way to reduce the operation pressure and the air supply to minimize the *m*-xylene escaping and energy consumption.

Table 1

Comparison of MIR and CBR to produce MTA

Technical parameter	Type of reactor		
	CBR	MIR	MIR/CBR
Product purity/(% (mass))	99.0	99.5	0.5% increase
Residence time of reactants/h	5	2	60% decrease
Reaction temperature/°C	145	135	10 °C decrease
Reaction pressure/MPa	0.5	0.35	0.15 MPa decrease
Unit reactor interfacial area/m ² ·m ⁻³	~500	8000–12000	16–24 times increase
Raw material consumption per product/t·t ⁻¹	1.3	1.1	15.38% decrease
Reactor production intensity/kg·m ⁻³ ·h ⁻¹	18.5	51.2	177% increase
Main product yield/%	59	83.3	41.2% increase
Oxygen utilization in air/%	62.8	91	45% increase
Total energy consumption per product/kW·h·t ⁻¹	2351.3	2085.6	11.3% decrease
Water consumption per product/t·t ⁻¹	3.5	0.25	93% decrease

Table 2

Comparison of M-WAO with WAO for the wet air oxidation of high-salt wastewater

Technical parameter	Type of technology		
	WAO	M-WAO	M-WAO/WAO
Single reactor capacity/t·d ⁻¹	637	936	46.47% increase
Reaction temperature/°C	220	180.9	39.1 decrease
Reactant residence time/min	60	43	28% decrease
Reaction pressure/MPa	8.0	4.15	3.85 decrease
Unit reactor interfacial area/m ² ·m ⁻³	~100	~8000	~80times increase
Air consumption/t·t ⁻¹	0.109	0.063	35% decrease
Reactor productivity/t·m ⁻³ ·h ⁻¹	26.625	39	46.47% increase
specified COD removal rate ^① /%	40	45.7 ^①	14.25% increase
Air oxygen utilization/%	49	>85	30% increase
Overall energy consumption per unit water/kW·h·t ⁻¹	46	39	15.2% decrease

^① Operation data of M-WAO at 8.0 MPa and 220 °C for 60 min showed the COD removal rate of 97%.

The MIR was employed instead of CBR to intensify the mass transfer efficiency. The main technical parameters obtained were listed in Table 1, showing that the air oxidation via the MIR is substantially improved than that of CBR.

6.3. Wet air oxidation of high-salt industrial wastewater

Wet air oxidation (WAO) uses CBR reactor and air as an oxidant under high temperature and high-pressure to oxidize the organic matter into CO₂ and H₂O, or partially oxidized salts into the fully oxidized salts in the industrial wastewater so that the left chemical matters can easily be biochemically degraded. The operating pressure for the reactor of WAO is usually 8–10 MPa, and the temperature is between 210–280 °C in terms of the degradation requirement. Therefore, high equipment investment and high security risks are encountered for this technology.

The M-WAO process using MIR technology was designed and applied in treating the wastewater from a glyphosate and glyphosate production units and accomplished in August 2019 in south-west China. The capacity of this oxidation for the wastewater is 1.2 Mt·a⁻¹ with the salt content of 25.2% (mass), 7902 mg·L⁻¹ of ammonia nitrogen, 26700 mg·L⁻¹ of total COD, and 5028 mg·L⁻¹ of formaldehyde. The results of M-WAO compared with those of WAO were shown in Table 2, indicating that there are dramatic improvements in the reaction temperature, pressure, reaction rate and compressor power consumption, etc. by using MIR technology.

7. Conclusions and Prospects

This study indicates that MIR technology may bring us a new way to solve those universal problems caused by low-efficiency mass transfer in modern chemical manufacture processes, which

are of high operating pressure, high temperature, high unit investment, high production cost and low reaction efficiency of the hydrogenations and air oxidations.

The application cases of residue oil hydrogenation and air oxidation of *m*-xylene and high-salt wastewater displayed that the intensification of mass transfer is very effective for the reaction process controlled by mass transfer.

For the MIR system composed of the nano-micro fluidics (bubbles and liquid drops), it may be different not just from those of the macrointerface systems in CBR on physical level, but also on chemical level, which requires in-depth and more extensive investigations. It is suggested to pay more attentions to theoretical and experimental exploration, especially around the measurement of nano-microbubbles, nano-microdroplets and nano-micro fluidics, as well as innovation of MIR to generate nano-micro fluidics or nano-microinterface system in large-scale. It is believed that this technology will provide a strong technical support for green, low-carbon and sustainable development in the field of chemical industry, and deepen the understanding of nano-micro fluidics (nano-microinterface) and its physicochemical phenomenon from mesoscale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

a	gas–liquid interfacial area, $\text{m}^2\cdot\text{m}^{-3}$
C_B	average concentration of solvent inside the catalyst particles, $\text{mol}\cdot\text{L}^{-1}$
D_L	diffusion coefficient of gas molecules in the liquid phase, $\text{m}^2\cdot\text{s}^{-1}$
$d_{\max}$	maximum diameter of the bubbles, m
$d_{\min}$	minimum diameter of the bubbles, m
d_{32}	Sauter mean diameter of the bubbles, m
f_s	catalyst loading rate, $\text{m}^3\cdot\text{m}^{-3}$
g	gravitational acceleration, $\text{m}\cdot\text{s}^{-2}$
H_A	Henry's constant, $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$
H_0	initial liquid level height in the reactor, m
k_A	first order intrinsic reaction rate constant based on the reaction rate
k_G	gas film mass transfer coefficient, $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
k_L	liquid film mass transfer coefficient, $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
k_S	liquid–solid mass transfer coefficient, $\text{m}^3\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
P_G	partial pressure of component A in the bubble
P_m	mixing pressure, Pa
Q_{L0}	initial liquid circulation volume flow of the reactor, $\text{m}^3\cdot\text{s}^{-1}$
S_0	cross-sectional area of the reactor, m^2
S_1	cross-sectional area of the bubble breaker, m^2
V_0	initial volume flow, $\text{m}^3\cdot\text{s}^{-1}$
u_L	rising speed of the bubble, $\text{m}\cdot\text{s}^{-1}$
u_G	apparent gas velocity, $\text{m}\cdot\text{s}^{-1}$
u_0	rising speed of the bubble in an infinite stationary liquid phase
u_{32}	mean rising speed of bubbles, $\text{m}\cdot\text{s}^{-1}$
δ_L	liquid film thickness of the bubble, m
δ_M	mass transfer film thickness of the bubble, m
ε	energy dissipation rate, $\text{W}\cdot\text{kg}^{-1}$
λ	friction coefficient
ρ	density, $\text{kg}\cdot\text{m}^{-3}$
ρ_L	density of liquid, $\text{kg}\cdot\text{m}^{-3}$
ρ_G	density of gas, $\text{kg}\cdot\text{m}^{-3}$
ϕ_G	gas holdup
χ_A	intrinsic reaction effective factor

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