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Microwave-Assisted Direct Fluorination of Polymers in Vibro-Fluidized Beds: From Reaction Kinetics to Reactor Design

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Abstract. Direct fluorination of polymers is a key surface modification technology for producing high-performance fluorinated materials, but conventional batch and screw reactors face long-standing problems such as low heat transfer efficiency, severe particle attrition, and inconsistent product quality in industrial production. This paper reviews the process intensification strategy of polymer direct fluorination based on the combination of vibro-fluidized bed technology and microwave-assisted heating from the perspective of reaction engineering. The radical chain mechanism and kinetic characteristics of direct fluorination are briefly introduced, and the hydrodynamic advantages of vibro-fluidized beds in improving gas-solid contact uniformity and reducing particle attrition are analyzed. The enhancement mechanism of microwave volumetric heating on reaction kinetics and the self-regulating heating effect caused by the evolution of polymer dielectric properties are discussed. On this basis, a conceptual design of a continuous circulating vibro-fluidized bed microwave fluorination reactor with closed-loop gas purification and recycling is proposed, and its process flow, key structural modules and main operating parameters are systematically described. Finally, the main technical challenges in pilot-scale application, including particle attrition control, process safety and scale-up methods, are summarized, and corresponding future research directions are pointed out. The review can provide a reference for the upgrading and optimization of industrial polymer fluorination processes.

Keywords: *Process intensification; Vibro-fluidized bed; Microwave-assisted heating; Direct fluorination; Computational fluid dynamics; Reaction kinetics; Polymer surface modification.*

1. Introduction

Fluorinated polymers, such as fluorinated polyethylene (FPE), polyvinylidene fluoride (PVDF), and perfluoroalkoxy alkanes (PFA), possess unique properties derived from the strong electronegativity and low polarizability of the C–F bond [1,2]. These materials demonstrate remarkable chemical inertness, excellent thermal stability, superior dielectric properties, and extremely low friction coefficients, rendering them critical in harsh-environment applications including chemical containment, semiconductor fabrication, and advanced membrane technologies [1,3]. The global demand for high-performance fluorinated polymers continues to grow, driving the need for more efficient, sustainable, and controllable fluorination processes [4].

The direct fluorination of polymers using elemental fluorine (F_2) represents the most straightforward method for introducing fluorine atoms into polymer backbones or surfaces [5,6]. This gas-solid reaction proceeds via a radical chain mechanism initiated by homolytic cleavage of the C–H bond and subsequent reaction with molecular fluorine. The strong C–F bond (bond dissociation energy ~485 kJ/mol) formed during fluorination confers the exceptional properties characteristic of fluorinated materials. However, the high reactivity of elemental fluorine and the exothermic nature of the fluorination reaction pose significant challenges for reactor design and process control [6,7].

Traditional industrial fluorination methods predominantly rely on direct fluorination using elemental fluorine (F_2) or fluorinating agents in batch autoclaves or continuous screw reactors [6,8]. Using polymer monomers as raw materials and ammonium persulfate as an initiator, polymerization is initiated followed by hydrolysis. Fluorine gas is introduced into a screw reactor under high temperature and high pressure for fluorination end-capping to finally obtain fluorinated polymers (Figure 1). These approaches typically require elevated temperatures (200–400 °C) and elevated pressures to achieve adequate fluorination degrees. Such severe operating conditions lead to several inherent drawbacks: (i) non-uniform temperature distribution resulting in inconsistent product quality; (ii) significant particle attrition and agglomeration due to mechanical shear; (iii) high energy consumption and safety risks associated with handling toxic fluorine gas at high pressure; and (iv) environmental concerns related to waste gas emissions and by-product formation [9,10]. Consequently, the development of novel reactor technologies capable of simultaneously enhancing reaction efficiency, product quality, and operational safety represents an urgent research priority.

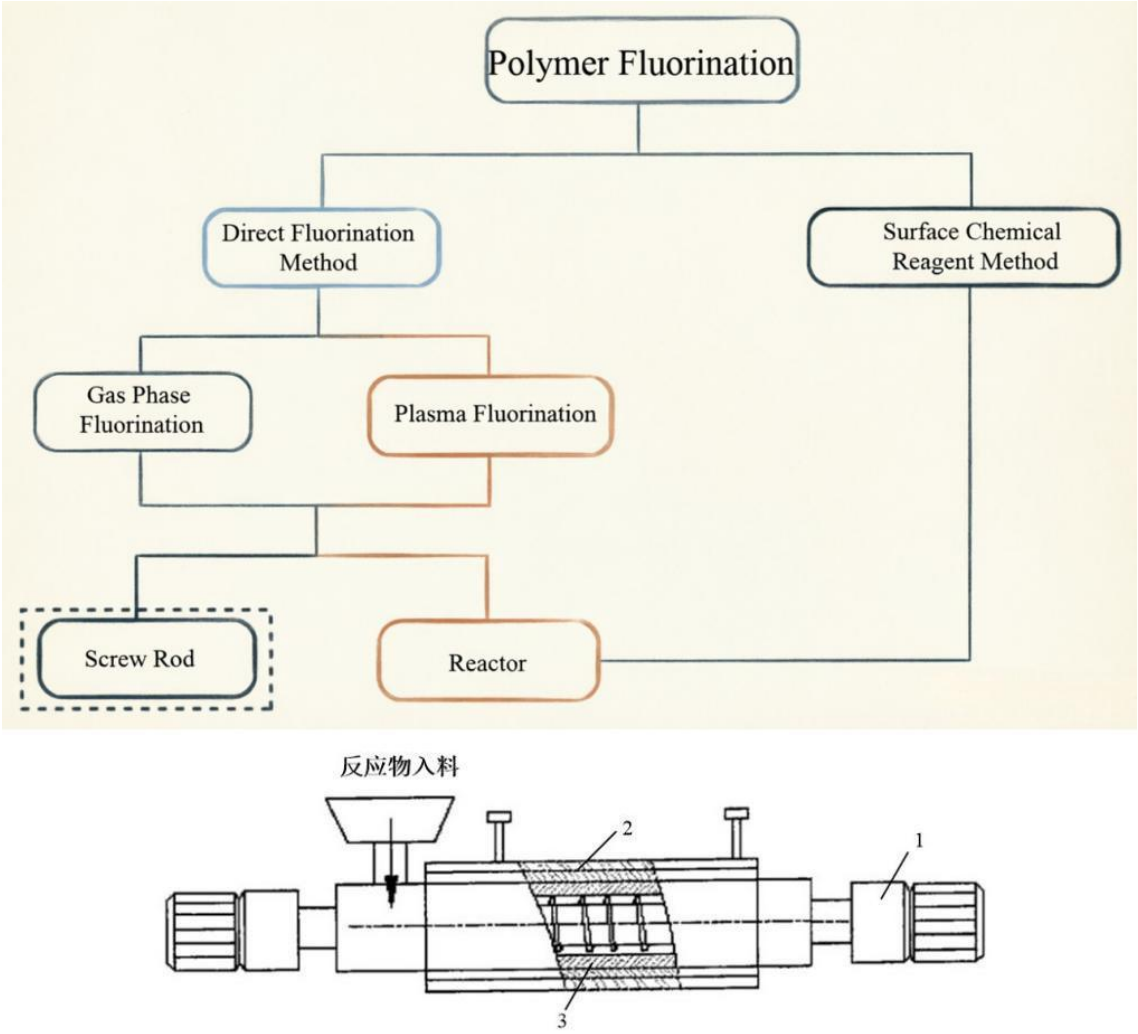


Figure 1. (a) Reactor for the production of fluorinated polymers; (b) Screw reactor (1—Motor; 2—High-temperature heating jacket; 3—Screw shaft).

Fluidized bed reactors have long been recognized as effective gas-solid contacting devices owing to their excellent heat and mass transfer characteristics, uniform temperature distribution, and continuous operation capability [11,12]. Among various fluidization regimes, vibrated fluidized beds (VFBs) offer distinct advantages for processing fine or cohesive particles that are difficult to fluidize conventionally. The application of mechanical vibration reduces the minimum fluidization velocity, suppresses bubble formation, and enhances particle mobility, thereby creating favorable conditions for surface modification reactions [13,14]. More recently, the concept of circulating vibro-fluidized beds, which integrate particle circulation with vibrational energy input, has attracted attention for processes requiring controlled residence times and continuous product removal [15,16].

Concurrently, microwave-assisted chemical processing has revolutionized heterogeneous reaction engineering by enabling rapid, volumetric, and selective heating [17,18]. Unlike

conventional conductive heating, microwave irradiation penetrates particulate materials and generates heat directly within the particles through dielectric loss mechanisms. This characteristic is particularly advantageous for fluorination reactions, where rapid heating can activate the polymer surface, reduce induction periods, and potentially lower the activation energy required for C–H bond substitution by fluorine [18,19]. The combination of microwave heating with fluidized bed technology thus presents a compelling pathway for process intensification in polymer fluorination.

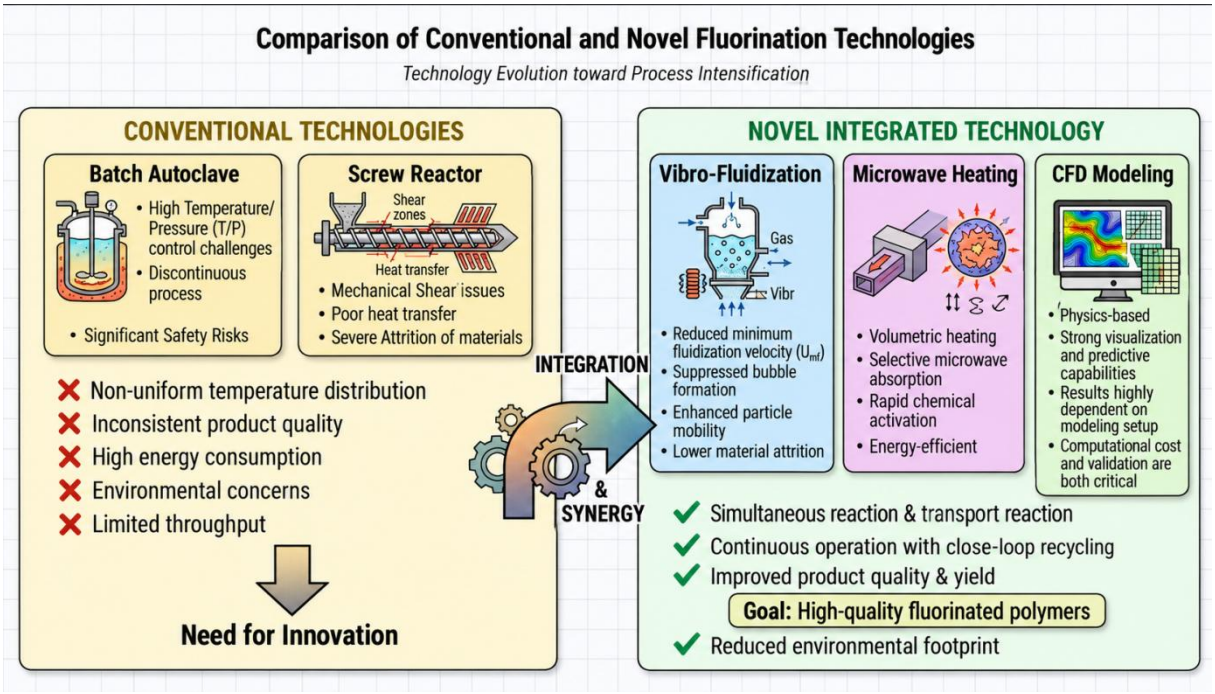


Figure 2. Comparison of conventional fluorination technologies (batch autoclave and screw reactor) and the proposed novel integrated technology.

Despite the promising features of both vibro-fluidization and microwave fluorination, their integration remains largely unexplored, particularly regarding the complex multiphase flow dynamics and reaction-transport coupling phenomena occurring within such hybrid reactors. The mesoscale flow field—characterized by particle clusters, interphase interactions, and localized reaction zones—plays a decisive role in determining reactor performance, product uniformity, and scale-up feasibility [20,21]. Computational fluid dynamics (CFD) modeling, especially coupled Euler-Euler multiphase approaches with surface reaction kinetics, has become an indispensable tool for unraveling these mesoscale phenomena and guiding reactor optimization [21,22]. Figure 2 presents a comparative overview of conventional fluorination technologies versus the proposed novel integrated approach, highlighting the synergistic advantages of combining vibro-fluidization, microwave heating, and CFD modeling. Conventional approaches suffer from non-uniform temperature distribution, inconsistent

product quality, high energy consumption, and environmental concerns. The novel integrated system combines vibro-fluidization (reduced minimum fluidization velocity, suppressed bubbles, enhanced particle mobility), microwave heating (volumetric heating, selective absorption, rapid activation), and CFD modeling (mesoscale prediction, stability analysis, scale-up guidance) to achieve simultaneous reaction and transport intensification, continuous closed-loop operation, improved product quality and yield, and reduced environmental footprint [20,23].

This review aims to provide a comprehensive analysis of the technological convergence between vibro-fluidized beds and microwave-assisted fluorination for polymer surface modification. We examine the fundamental hydrodynamics of vibrated gas-solid systems, the kinetic and thermal characteristics of microwave fluorination, and the current status of multiscale CFD modeling methodologies. Furthermore, we propose a conceptual framework for circulating vibro-fluidized bed microwave fluorination reactors and discuss the critical research needs for establishing operation stability models based on particle attrition theory and for developing coupled CFD-reaction models capable of predicting mesoscale flow fields. This synthesis is intended to guide future experimental and theoretical investigations toward the rational design of next-generation fluorination reactors.

2. Direct Fluorination of Polymers: Reaction Mechanisms and Kinetic Characteristics

2.1. Fundamental Reaction Mechanism

The direct fluorination of hydrocarbon polymers proceeds via a complex radical chain mechanism. The initiation step involves the homolytic cleavage of the C–H bond by elemental fluorine, generating hydrogen fluoride (HF) and a carbon-centered radical [5,6]:

$$R\text{–}CH_2\text{–}R' + F_2 \rightarrow R\text{–}\dot{C}H\text{–}R' + HF + F\cdot (Initiation) \quad (1)$$

The fluorine radical (F·) then propagates the chain reaction by abstracting hydrogen from adjacent carbon atoms:

$$R\text{–}\dot{C}H\text{–}R' + F_2 \rightarrow R\text{–}CHF\text{–}R' + F\cdot\ (Propagation) \quad (2)$$

The fluorine radical can also abstract hydrogen from another polymer chain, propagating the radical chain:

$$F\cdot + R\text{–}CH_2\text{–}R' \rightarrow HF + R\text{–}\dot{C}H\text{–}R' \ (Propagation) \quad (3)$$

The termination step involves radical recombination or disproportionation. The presence of oxygen in the fluorinating mixture can lead to competing oxidation reactions, resulting in the formation of oxygen-containing functional groups such as carbonyl (C=O), carboxyl (–COOH), and hydroxyl (–OH) moieties [6,10].

The fluorination of aromatic polymers, such as polystyrene, involves electrophilic substitution of hydrogen atoms on the benzene ring, as well as addition reactions at the aliphatic backbone. Recent studies have demonstrated that non-destructive hydrogen-substituting fluorination prevails under mild conditions, with fluorination occurring into both the benzene ring and the main carbon chain [7,24].

2.2. Kinetic Characteristics and Activation Energy

The kinetics of polymer direct fluorination are governed by several factors: (i) the concentration of elemental fluorine in the gas mixture; (ii) the reaction temperature; (iii) the polymer crystallinity and morphology; and (iv) the diffusion rate of fluorine through the fluorinated layer. The apparent activation energy for C–H bond fluorination typically ranges from 40–80 kJ/mol, depending on the polymer structure and fluorination conditions [6,9].

The fluorination rate often exhibits an induction period, attributed to the initial formation of fluorine radicals and the establishment of a stable radical chain. Once initiated, the reaction can proceed rapidly, with the fluorination front advancing into the polymer matrix. The thickness of the fluorinated layer (δ) typically follows a parabolic growth law with respect to time (t):

$$\delta = k \cdot t^{(1/2)} \quad (4)$$

where k is the effective rate constant incorporating both reaction and diffusion contributions.

2.3. Effect of Fluorinating Mixture Composition

The composition of the fluorinating gas mixture significantly influences the reaction kinetics and product characteristics. Typical mixtures contain 1–20 vol.% F_2 diluted with inert gases (N_2, He) and may include O_2 for oxyfluorination [25]. Higher fluorine concentrations accelerate the reaction but increase the risk of polymer degradation and thermal runaway. The addition of oxygen promotes the formation of polar functional groups, enhancing surface hydrophilicity and adhesion properties [3,10].

Table 1 summarizes the operating characteristics, product quality, and inherent limitations of conventional fluorination technologies alongside emerging reactor concepts.

Table 1. Comparison of conventional and emerging fluorination technologies.

Technology	Temperature (°C)	Pressure (MPa)	Residence time	Fluorination uniformity	Particle attrition	Energy efficiency	Key limitations
Technology	Temperature (°C)	Pressure (MPa)	Residence time	Fluorination uniformity	Particle attrition	Energy efficiency	Key limitations
Batch autoclave	150–400	0.1–5.0	Batch (hours)	Poor (hot spots)	Low (static bed)	Low (long heat-up)	Discontinuous, safety risks, thermal runaway
Screw reactor	200–350	0.1–0.5	Continuous (min)	Moderate (RTD effects)	High (mechanical shear)	Moderate (wall conduction)	Severe attrition, electrostatic caking
Conventional fluidized bed	150–300	0.1–0.3	Continuous (min)	Moderate (bubble bypassing)	Moderate (bubble eruption)	Moderate (convective)	Elutriation, poor fluidization for fines
Vibro-fluidized bed	100–250	0.1–0.2	Continuous (min)	Good (suppressed bubbles)	Low–Moderate	Improved (lower U)	Limited reactive-system data
Microwave-assisted VFB (projected)	80–200	0.1	Continuous	Excellent (volumetric heating)	Low–Moderate	High (direct heating)	Unvalidated; arcing risks; dielectric data lacking

As evident from Table 1, conventional technologies struggle to simultaneously achieve uniform fluorination, low particle attrition, and high energy efficiency. Fluidized bed reactors, by virtue of their excellent heat and mass transfer characteristics and continuous operation capability, offer a fundamentally different contacting strategy [11,12]. Among fluidization regimes, vibrated fluidized beds (VFBs) are particularly promising for processing fine or cohesive polymer particles that resist conventional fluidization [13,14]. The following section examines the hydrodynamic principles of VFBs and their implications for surface modification reactions.

3. Vibro-Fluidized Bed Technology for Enhanced Gas-Phase Fluorination

3.1. Fundamental Hydrodynamics

Vibro-fluidized beds (VFBs) represent a hybrid gas-solid contacting regime where mechanical vibration is superimposed on conventional gas-fluidization. The vibration is typically imparted to the entire bed or the gas distributor via electromagnetic or eccentric motor drives, with operating frequencies ranging from 5 to 100 Hz and amplitudes from 0.5 to 10 mm [13,26]. The vibrational energy modifies the fluidization behavior of particulate materials by reducing interparticle cohesive forces and lowering the minimum fluidization velocity (U_mf). This enables the fluidization of fine particles (Geldart Groups A and C) that otherwise exhibit channeling, slugging, or defluidization tendencies [14,27].

The hydrodynamic regime in VFBs is governed by the dimensionless vibration acceleration,

$\Gamma=A\omega^2/g$, where A is the amplitude, ω is the angular frequency, and g is the gravitational acceleration. Depending on Γ and the superficial gas velocity (U), VFBs operate in various regimes: fixed bed with vibration, vibrated fluidization, and fully fluidized states. The vibrated fluidization regime, characterized by homogeneous expansion and suppressed bubble formation, is particularly desirable for surface modification reactions requiring uniform gas-solid contact [13,14]. Figure 3 illustrates the hydrodynamic regime map of vibro-fluidized beds, identifying the optimal operating window for polymer fluorination processes. ($\Gamma=A\omega^2/g$) and superficial gas velocity normalized by minimum fluidization velocity (U/U_mf). Four distinct regimes are identified: (i) Fixed Bed with Vibration (low Γ, low U/U_mf), where particles remain essentially static despite vibrational input; (ii) Vibrated Fluidization (intermediate Γ, moderate U/U_mf), characterized by homogeneous expansion and suppressed bubble formation—this is the optimal operating window for surface modification reactions; (iii) Fully Fluidized (high U/U_mf), exhibiting conventional bubbling or turbulent behavior; and (iv) Vibration-Dominated Regime (high Γ), where excessive vibrational energy leads to particle ejection and elevated attrition risk. The optimal operating window is highlighted in green, balancing adequate fluidization quality with minimal particle attrition.

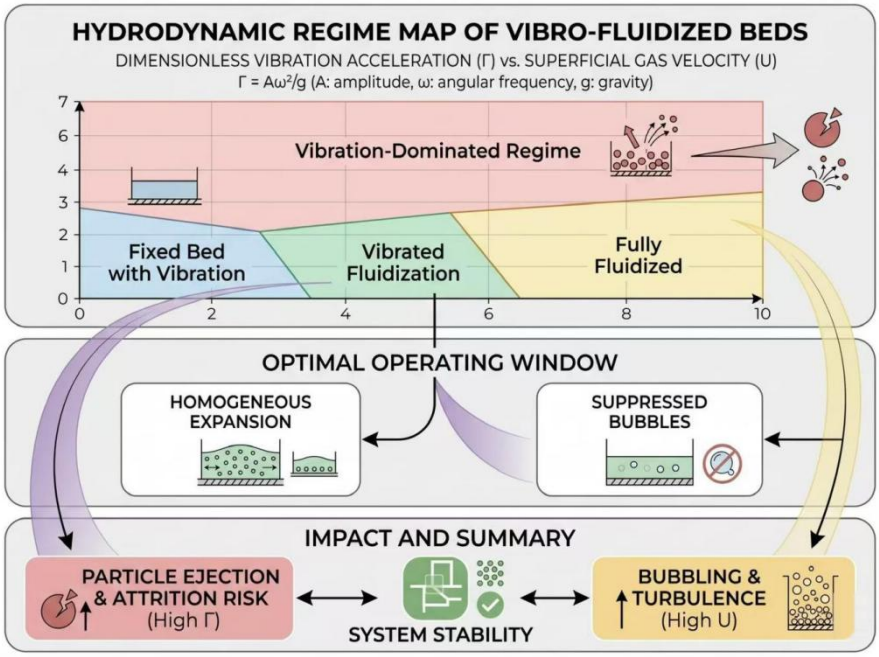


Figure 3. Hydrodynamic regime map of vibro-fluidized beds as a function of dimensionless vibration acceleration.

3.2. Advantages for Surface Modification Processes

For polymer fluorination, VFBs offer several critical advantages over conventional fluidized beds and mechanical reactors. First, the reduced bubble activity and enhanced particle mobility

promote uniform exposure of particle surfaces to the fluorinating gas, minimizing the formation of unreacted cores. Second, the gentle mechanical agitation prevents the severe attrition associated with high-velocity bubbling or turbulent fluidization, thereby preserving particle morphology and reducing fines generation [13,28]. Third, the ability to operate at lower gas velocities decreases the elutriation of fine particles and reduces the gas load on downstream separation and purification equipment.

3.3. Circulating Vibro-Fluidized Bed Concept

The circulating vibro-fluidized bed (CVFB) extends the VFB concept by incorporating a particle circulation loop, wherein particles are continuously fed, processed, and withdrawn while the gas phase undergoes separation, purification, and recycle [15,29]. This configuration decouples the residence time from the gas contact time, allowing independent optimization of reaction duration and gas utilization. For fluorination processes, the circulation loop facilitates temperature control through staged microwave heating, enables continuous product removal, and supports the integration of in-line gas purification systems for fluorine recycling [15,16].

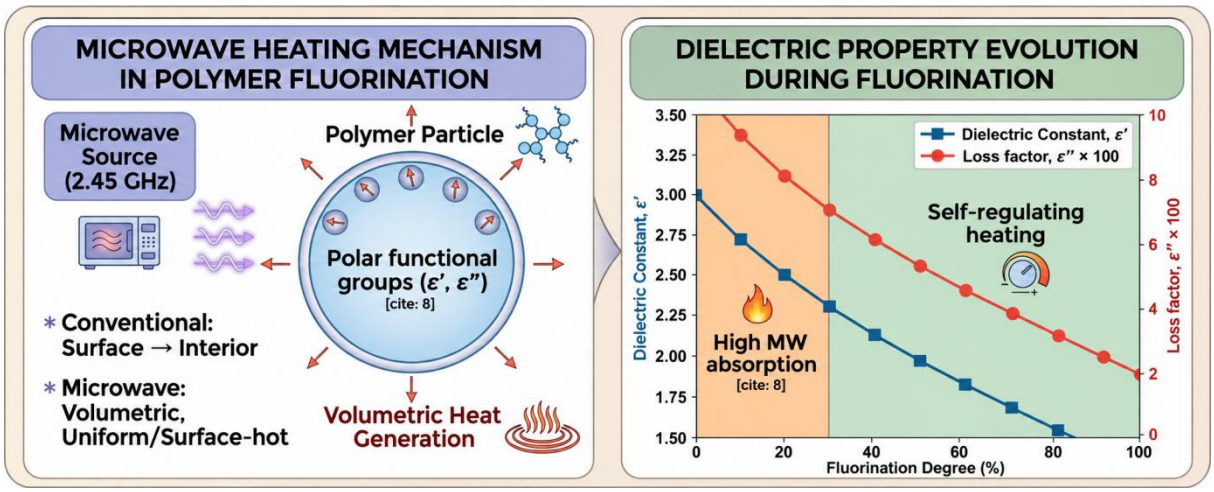
4. Microwave-Assisted Fluorination: Kinetics and Thermal Effects

4.1. Microwave Heating Mechanisms in Polymer Fluorination

Microwave heating relies on the interaction of electromagnetic radiation (typically 2.45 GHz in industrial applications) with polar molecules or conductive materials. In polymer fluorination, microwave energy is absorbed primarily by the polar functional groups on the polymer surface and by any moisture or residual solvents, generating rapid volumetric heating [17,19]. Unlike conventional heating, where thermal gradients develop from the surface inward, microwave heating can establish more uniform temperature profiles or deliberately create surface-hot conditions favorable for initiating fluorination reactions.

The dielectric properties of polymers—specifically the dielectric constant (ε') and loss factor (ε")—determine their microwave absorption efficiency. Most fluorinated polymers exhibit low dielectric loss, meaning that once fluorination begins, the microwave coupling efficiency may decrease, providing a self-regulating heating mechanism that prevents overheating of fully fluorinated regions [17,30]. This selective heating behavior is advantageous for achieving controlled surface fluorination without bulk degradation. Figure 4(a) is the schematic illustration of microwave heating mechanism in polymer fluorination. Microwave irradiation (2.45 GHz) penetrates the polymer particle and generates volumetric heat through interaction

with polar functional groups on the surface (dielectric constant ε', loss factor ε''). Unlike conventional surface-to-interior conductive heating, microwave heating establishes uniform or surface-hot temperature profiles, with heat radiating outward from the particle interior. Figure 4(b) shows the evolution of dielectric properties (ε' and ε'') as a function of fluorination degree. In the initial stage (0–30% fluorination, orange shaded region), high microwave absorption occurs due to abundant polar C–H bonds. As fluorination progresses (30–100%, green shaded region), the decreasing dielectric loss factor provides a self-regulating heating mechanism that prevents overheating of fully fluorinated regions, enabling controlled surface modification without bulk degradation.



(a) (b)

Figure 4. (a) Schematic illustration of microwave heating mechanism in polymer fluorination; (b) Evolution of dielectric properties (ε' and ε'') as a function of fluorination degree.

4.2. Reaction Kinetics Enhancement

Microwave irradiation can influence chemical reaction kinetics through both thermal and non-thermal (specific microwave) effects. In fluorination reactions, the rapid heating rates achievable under microwave conditions (up to 100 °C/min or higher) can significantly reduce the induction period associated with fluorine radical formation and surface activation [18,31]. Studies on microwave-assisted direct fluorination have reported reduced apparent activation energies and enhanced reaction rates compared to conventional isothermal heating, although the extent of non-thermal contributions remains debated in the literature [31,32].

For polymer particles in a fluidized state, microwave heating offers the additional benefit of simultaneous heating of the particle ensemble without relying on gas-phase heat transfer. This is particularly important in vibro-fluidized beds, where the gas flow rates may be insufficient to provide the heat required for endothermic or high-temperature reactions through convective

transfer alone. The coupling of microwave power input with gas flow rate and vibration parameters creates a multi-parameter operating space that can be optimized for simultaneous reaction and transport intensification [18,30].

4.3. Dielectric Property Evolution During Fluorination

A critical aspect of microwave-assisted fluorination is the evolution of polymer dielectric properties as fluorination progresses. In the initial stage (0–30% fluorination), high microwave absorption occurs due to abundant polar C–H bonds. As fluorination progresses (30–100%), the decreasing dielectric loss factor provides a self-regulating heating mechanism that prevents overheating of fully fluorinated regions, enabling controlled surface modification without bulk degradation (Figure 4b). This dielectric evolution has important implications for reactor design and process control, as the microwave power input must be adjusted dynamically to maintain optimal heating rates throughout the fluorination process [17,30].

4.4. Safety and Process Control

Microwave heating in fluorination environments requires careful engineering to prevent arcing, plasma formation, and localized overheating. The presence of fluorine gas, which is highly reactive and can form conductive by-products, necessitates the use of corrosion-resistant microwave window materials (e.g., alumina, quartz) and rigorous gas sealing [30,33]. Additionally, the design of microwave applicators—such as multimode cavities or traveling-wave systems—must account for the load characteristics of fluidized particle beds, which present a dynamically changing dielectric medium. Advanced process control strategies incorporating real-time temperature monitoring (e.g., infrared thermography) and microwave power modulation are essential for safe and reproducible operation [30,33].

5. Multiscale Flow Field Modeling and CFD Approaches

5.1. Overview of Multiphase Modeling Approaches

Two primary CFD approaches are used for modeling gas-solid flows in fluidized beds: Euler-Euler (two-fluid model, TFM) and Euler-Lagrange (discrete element method, DEM). Table 2 compares their key characteristics and applicability to vibro-fluidized bed fluorination reactors.

5.2. Euler-Euler Multiphase Modeling

The computational modeling of gas-solid flows in vibro-fluidized beds presents significant challenges due to the complex interplay between particle-particle, particle-wall, and particle-

gas interactions. The Euler-Euler (two-fluid model, TFM) approach treats both the gas and solid phases as interpenetrating continua, with closure relations derived from kinetic theory of granular flow (KTGF) [21,34]. This framework is computationally efficient for industrial-scale simulations and has been widely applied to conventional fluidized beds.

Table 2. Comparison of Euler-Euler and DEM models for gas-solid flow simulation.

Model Type	Advantages	Disadvantages	Applicability
Euler-Euler (TFM)	Computationally efficient; suitable for industrial-scale simulations; well-established closure models	Cannot directly resolve individual particle collisions; requires empirical drag correlations	Reactor-scale flow field prediction; parametric studies; scale-up analysis
Euler-Lagrange (DEM)	Accurately simulates particle-particle and particle-wall interactions; can model particle attrition and breakage	Computationally expensive; limited to small-scale systems ($\leq 10^6$ particles)	Particle-level mechanism studies; attrition model development; mesoscale structure validation

For VFBs, the TFM must be augmented to account for vibrational effects, typically through modified drag laws, additional body forces representing vibrational acceleration, and enhanced granular temperature dissipation terms [13,35]. The choice of drag model—such as the Gidaspow, Syamlal-O'Brien, or Wen-Yu correlations—significantly influences the predicted bed expansion, pressure drop, and bubble characteristics. Recent studies have emphasized the importance of using drag models that incorporate the effect of heterogeneous structures (clusters) at mesoscales, such as the Energy-Minimization Multi-Scale (EMMS) drag model, as standard homogeneous drag models often overpredict the fluidization quality [36,37].

5.3. Particle Attrition and Stability Modeling

Particle attrition in fluidized beds results from impact, abrasion, and compression forces experienced by particles during bubble eruption, bed expansion, and wall collisions. In vibrated systems, attrition is further influenced by the vibrational intensity and the resulting particle kinematics. Understanding attrition is critical for fluorination processes because excessive fines generation increases the specific surface area uncontrollably, alters the reaction rate, and complicates downstream gas-solid separation [28,38].

Theoretical models for particle attrition in fluidized beds typically combine fracture mechanics principles—such as the indentation fracture theory—with population balance frameworks to predict the evolution of particle size distributions [28,39]. For VFBs, the attrition rate can be correlated with the granular temperature, which quantifies the fluctuating kinetic

energy of particles. By establishing relationships between operating parameters (vibration frequency, amplitude, gas velocity), granular temperature, and attrition rates, it is possible to define "stable operating windows" where attrition is minimized while maintaining adequate fluidization quality [38,40].

5.4. Mesoscale Flow Field Characteristics

The mesoscale in gas-solid fluidization refers to the intermediate scale between individual particle interactions (microscale) and reactor-scale hydrodynamics (macroscale), encompassing structures such as particle clusters, streamers, and bubbles. In VFBs, mechanical vibration suppresses mesoscale heterogeneity by breaking up particle clusters and reducing bubble size, leading to a more homogeneous flow structure [13,41]. This homogenization is beneficial for fluorination reactions, as it reduces gas bypassing and improves interphase contact efficiency.

However, when chemical reactions are introduced, the mesoscale flow field becomes coupled with reaction heat release and species transport. Localized reaction zones may form in regions of high solid concentration or preferential gas flow, creating mesoscale temperature and concentration gradients that are not captured by macroscopic reactor models [20,21]. The prediction of these coupled phenomena requires CFD models that resolve or accurately model mesoscale structures, such as the Energy-Minimization Multi-Scale (EMMS) drag model or filtered TFM approaches [37,42].

5.5. CFD-Chemical Reaction Coupling

The integration of surface reaction models into CFD simulations of fluidized beds enables the prediction of reaction conversion, selectivity, and product distribution alongside hydrodynamic behavior. For fluorination reactions, the surface reaction model must account for the heterogeneous nature of the gas-solid reaction, where fluorine diffuses to the polymer surface and reacts with C–H bonds to form C–F bonds, potentially releasing HF as a by-product [6,7]. In Fluent or similar CFD platforms, surface reactions are typically implemented through user-defined functions (UDFs) that specify the reaction stoichiometry, rate expressions, and Arrhenius parameters [43].

The resulting coupled CFD-reaction model provides detailed spatial distributions of velocity, solid volume fraction, temperature, and species concentrations within the reactor. These distributions constitute the "mesoscale flow field" and are essential for identifying dead zones, short-circuiting paths, and regions of excessive particle heating or attrition. Such insights are invaluable for guiding the geometric design of the reactor, the placement of microwave

applicators, and the selection of operating parameters [21,44].

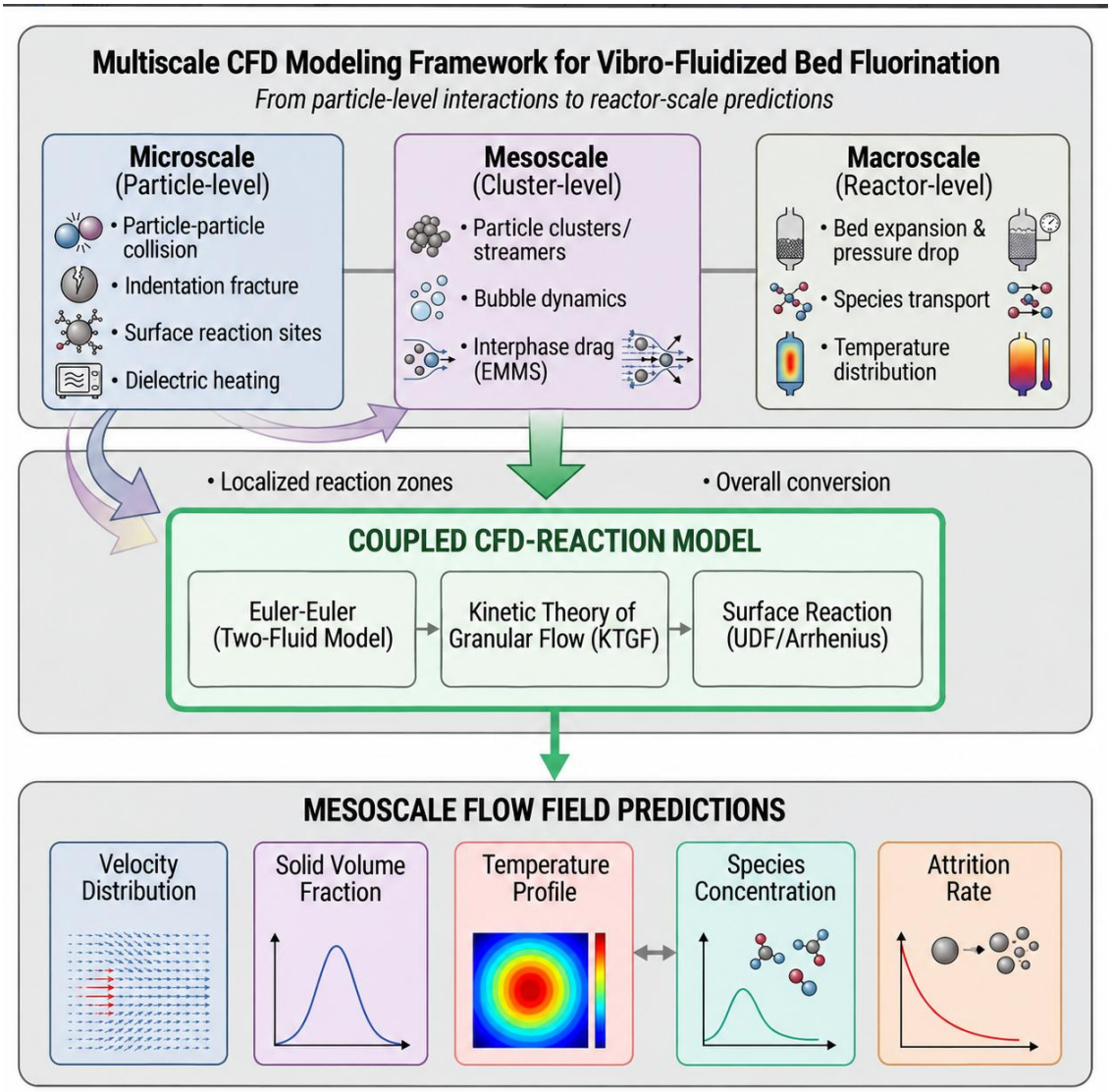


Figure 5. Multiscale CFD modeling framework for vibro-fluidized bed fluorination reactors.

Figure 5 illustrates the multiscale CFD modeling framework that integrates microscale, mesoscale, and macroscale phenomena through coupled Euler-Euler and surface reaction models. The framework spans three hierarchical scales: (i) Microscale (particle-level), encompassing particle-particle collisions, indentation fracture mechanics, surface reaction site distribution, and dielectric heating effects; (ii) Mesoscale (cluster-level), capturing particle clusters and streamers, bubble dynamics, interphase drag via EMMS corrections, and localized reaction zones; and (iii) Macroscale (reactor-level), predicting bed expansion, pressure drop, species transport, temperature distribution, and overall conversion. These scales are coupled through the Euler-Euler two-fluid model (TFM), kinetic theory of granular flow (KTGF) closures, and surface reaction models implemented via user-defined functions (UDFs) with

Arrhenius kinetics. The integrated model outputs critical mesoscale flow field predictions including velocity distribution, solid volume fraction, temperature profile, species concentration, and attrition rate.

6. Integrated Reactor Design: Circulating Vibro-Fluidized Bed with Microwave Fluorination

6.1. Process Flow and System Integration

The proposed integrated reactor system combines the continuous processing capability of circulating fluidized beds with the enhanced fluidization quality of mechanical vibration and the rapid heating benefits of microwave irradiation. The system comprises five integrated modules: (1) Feed System—polymer particles are sized and introduced with inert gas (N_2 or He); (2) Vibro-Fluidization (Pre-treatment Zone)—particles are preheated and homogenized via a vibrated distributor with controlled vibration parameters; (3) Microwave Fluorination (Core Reaction Zone)—fluorine gas is introduced and microwave power (2.45 GHz magnetrons) is applied for surface fluorination with volumetric heating and rapid activation; (4) Separation System (Recovery Zone)—cyclone separator performs gas-solid separation and product cooling; (5) Purification & Recycle (Closed-loop System)—solid scrubbers ($KF/NaF/AlF_3$) remove HF and recover F_2 for recycling [15,45]. Product collection yields high-purity, uniformly fluorinated polymers with preserved morphology. Key operating parameters for optimization include vibration (f: 5–100 Hz, A: 0.5–10 mm, Γ: 1–5), gas flow (U/U_mf: 1.2–3.0, F_2/N_2 ratio), microwave (power: 500–2000 W), and particle properties (d_p: 100–500 μm, residence time).The process flow follows a continuous closed-loop sequence, as illustrated in Figure 6. Polymer particles are first fed into the vibro-fluidization zone where mechanical vibration ensures homogeneous particle distribution and eliminates channeling or slugging. Microwave heating is then activated, and fluorine gas is introduced into the fluidized bed to initiate the surface fluorination reaction. The gas-solid mixture subsequently enters the cyclone separator, where denser fluorinated particles are recovered as product while the lighter gas phase (containing unreacted F_2 and by-product HF) is directed to the purification tower. The solid scrubber mixture ($KF/NaF/AlF_3$) selectively adsorbs HF through chemical reaction, yielding purified fluorine that is recycled back to the reactor via the circulation pump and heat exchanger. This closed-loop design minimizes fresh fluorine consumption and eliminates hazardous waste gas emissions.

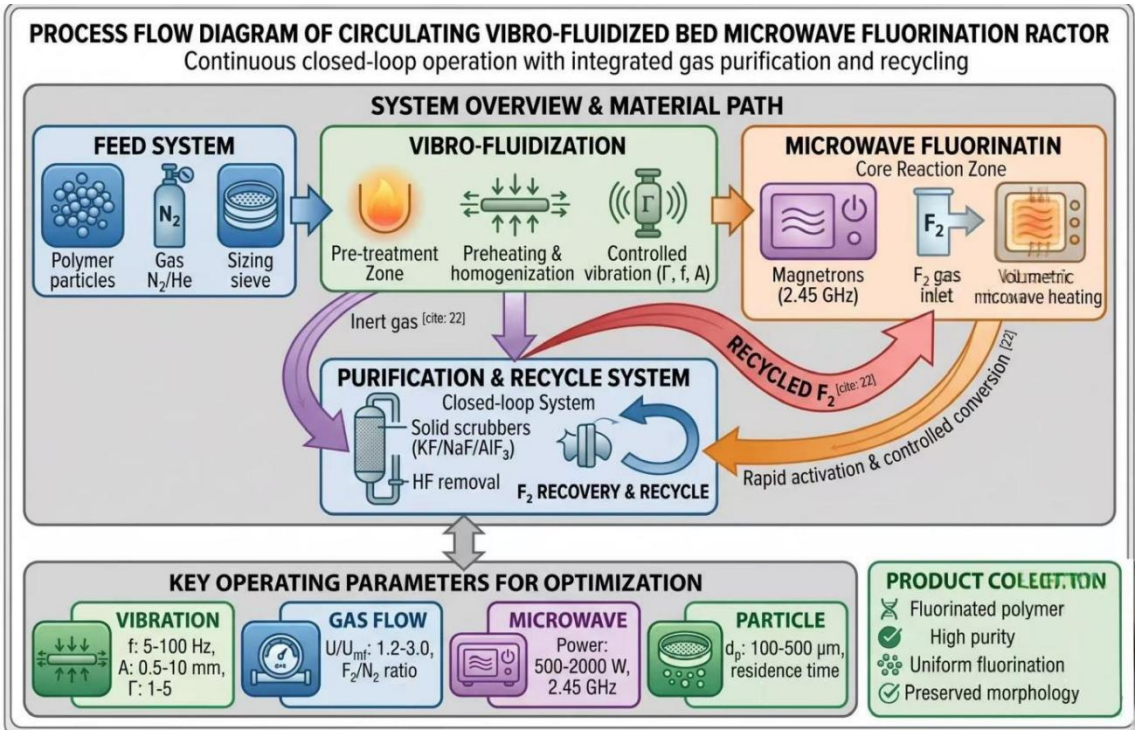


Figure 6. Process flow diagram of the circulating vibro-fluidized bed microwave fluorination reactor.

6.2. Reactor Configuration and Structural Design

Figure 7 presents the detailed structural schematic of the circulating vibro-fluidized bed microwave fluorination reactor, illustrating the spatial arrangement and interconnection of all functional components. As depicted in Figure 7, the reactor system comprises five integrated functional modules that operate in a closed-loop continuous mode. The vibro-fluidization module forms the core reaction environment. Polymer particles are introduced through the feed inlet (1) via the feed pipe (2) into the main reactor body, where they rest on the gas distributor plate (15). The vibration motor (12), mounted beneath the reactor, imparts mechanical oscillation to the entire bed structure, which is supported by spring isolators (13) to minimize vibration transmission to the surrounding infrastructure. This vibration reduces the minimum fluidization velocity and suppresses bubble formation, creating a homogeneous gas-solid contacting regime essential for uniform surface fluorination [13,14].

The microwave heating module is positioned at the top of the reactor. Three microwave generators (3) operating at 2.45 GHz are arranged in series above the quartz window (4), which serves as a critical barrier that allows microwave penetration while preventing the highly corrosive fluorine atmosphere from entering the microwave cavity. The quartz material (typically high-purity fused silica) is selected for its low dielectric loss and excellent chemical resistance to fluorine and hydrogen fluoride at elevated temperatures. Microwave energy

penetrates the particle bed and generates volumetric heat through dielectric loss mechanisms, rapidly activating the polymer surface for fluorination reaction.

The gas distribution and reaction module is integrated within the reactor body. Fluidizing gas (initially inert N_2 or He for preheating, subsequently mixed with F_2 for reaction) enters through the distributor plate (15) and fluidizes the particle bed. The gas outlet (5) at the top collects the reaction gas mixture containing unreacted fluorine and by-product hydrogen fluoride. The observation port (16) allows for visual monitoring of bed behavior and accommodates thermocouples or optical fibers for temperature measurement.

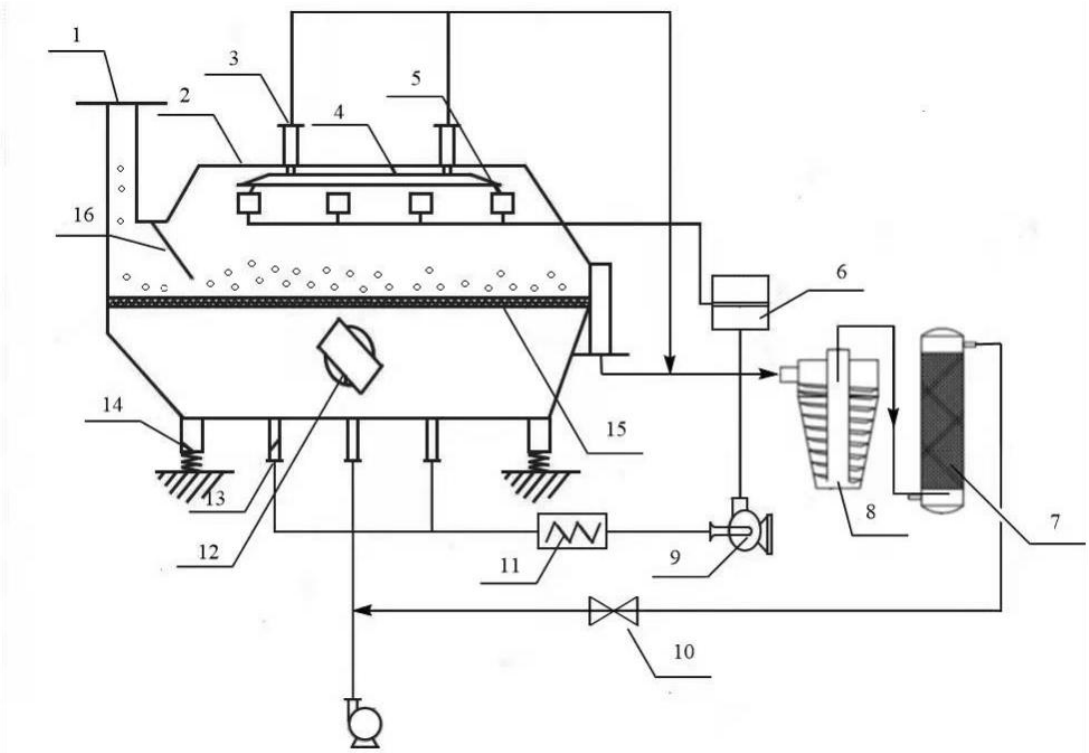


Figure 7. Schematic diagram of the circulating vibro-fluidized bed microwave fluorination reactor. (1) Feed inlet; (2) Gas distributor plate; (3) Microwave generators; (4) Quartz microwave window; (5) Gas outlet; (6) Cyclone separator; (7) Purification tower (packed with $KF/NaF/AlF_3$); (8) Gas recycle pipeline; (9) Circulation pump; (10) Control valve; (11) Heat exchanger; (12) Vibration motor; (13) Spring support; (14) Product discharge; (15) Distributor support; (16) Bed observation port.

The separation and recovery module is located downstream of the reactor. The gas-solid mixture exits the reactor and enters the cyclone separator (6) through the connecting pipeline (8). The cyclone achieves centrifugal separation: denser fluorinated polymer particles are thrown to the wall and collected at the bottom, while the lighter gas phase (containing F_2 and HF) exits through the central vortex finder and proceeds to the purification tower (7). The product discharge (14) enables continuous removal of the fluorinated polymer product, which may be cooled and packaged directly or subjected to further post-treatment.

The purification and recycle module ensures environmental compliance and economic viability. The purification tower (7) is packed with a solid scrubber mixture of potassium fluoride (KF), sodium fluoride (NaF), and aluminum fluoride (AlF_3), which possesses high porosity and specific surface area for efficient HF adsorption. The scrubbing reaction can be represented as:

$$KF + HF \rightarrow KHF_2 \quad (5)$$

The purified fluorine gas, now depleted of HF, is driven by the circulation pump (9) through the heat exchanger (11) and the control valve (10), then returned to the reactor bottom for reuse. The heat exchanger regulates the temperature of the recycled gas, either preheating cold feed gas or cooling hot recycle streams to maintain optimal reaction conditions. The control valve modulates the gas flow rate to maintain the desired superficial velocity relative to the minimum fluidization velocity (typically $U/U_mf = 1.2–3.0$ in the stable operating window) [14,15].

6.3. Multi-Physics Coupling at the Particle Scale

Within the reactor core, three fundamental physical processes occur simultaneously and interactively at the particle scale: microwave heating, gas-solid interphase forces, and particle collision with attrition. Figure 8 presents a local magnification of these coupled mechanisms, which collectively determine the reactor performance, product quality, and operational stability.

Microwave heating (Figure 8a) occurs through the interaction of 2.45 GHz electromagnetic radiation with polar functional groups on the polymer surface. The dielectric loss mechanism converts electromagnetic energy into thermal energy directly within the particle volume, establishing rapid temperature rise rates (up to 100 °C/min) that significantly reduce the induction period for fluorine radical formation. As fluorination progresses, the decreasing dielectric loss factor of the polymer provides a self-regulating heating effect, preventing thermal degradation of the core material while maintaining sufficient surface activation for continued reaction.

Gas-solid interphase forces (Figure 8a) govern the hydrodynamic behavior of the particle bed. The primary forces include: (i) drag force, arising from the relative velocity between gas and particle phases and representing the dominant mechanism for particle suspension and transport; (ii) lift force, generated by velocity gradients and rotation of particles in the shear flow; and (iii) virtual mass force, accounting for the acceleration of surrounding gas as particles accelerate. In vibro-fluidized beds, these forces are superimposed on the vibrational body force, creating complex particle trajectories that enhance mixing and surface renewal while suppressing bubble

coalescence.

Particle collision and attrition (Figure 8b) represent the primary degradation mechanism for polymer particles in the vibrated bed. Three modes of attrition are operative: (i) impact attrition from particle-particle collisions driven by vibrational and fluid dynamic forces; (ii) abrasion

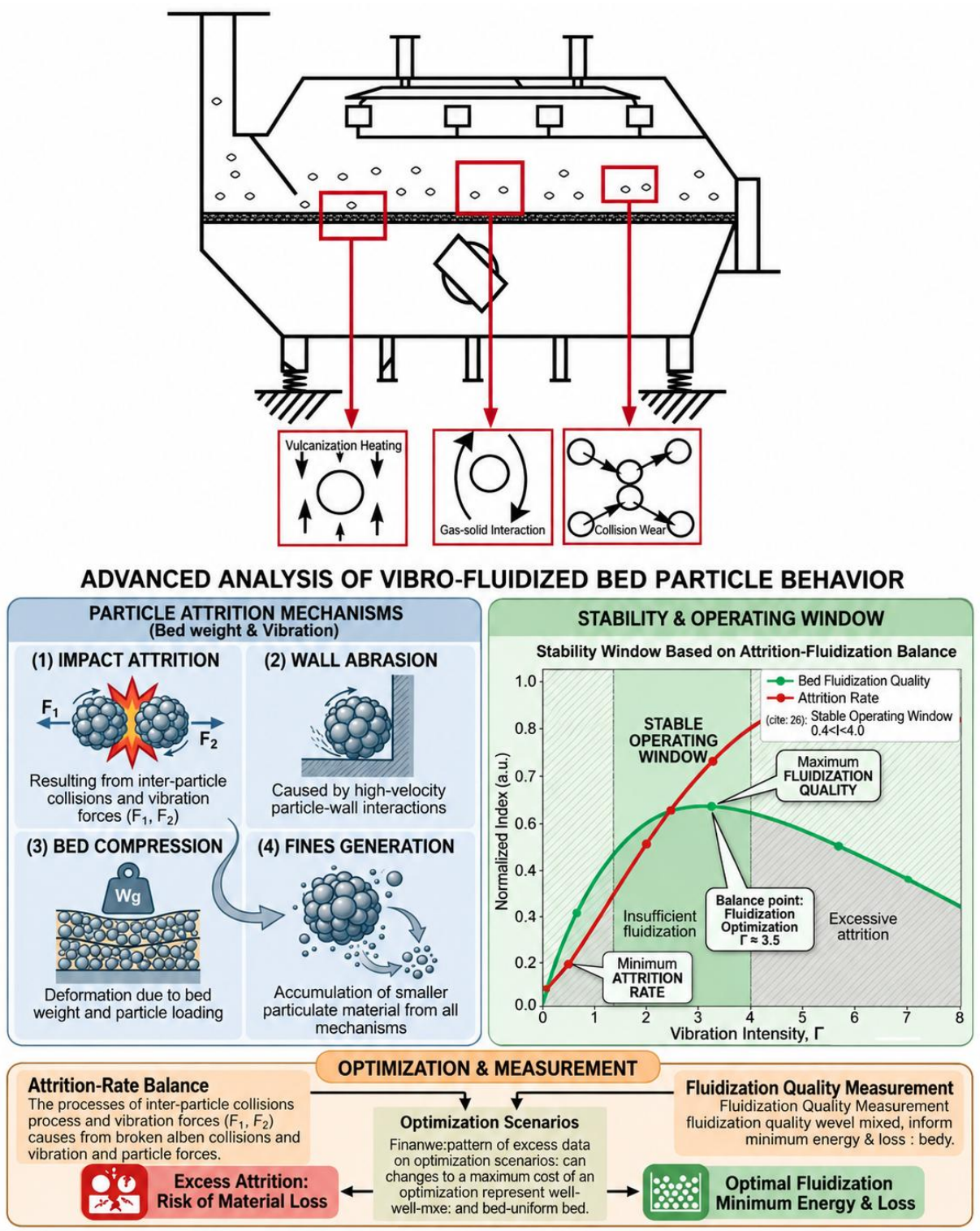


Figure 8. (a) Multi-physics coupling mechanisms at particle scale in microwave fluorination reactors; (b) Attrition modes and stable operating window of vibro-fluidized beds.

from repeated particle-wall contacts at the reactor periphery; and (iii) compression attrition under the static load of the overlying bed. The attrition rate correlates with granular temperature—a measure of particle fluctuating kinetic energy—and must be balanced against fluidization quality to define the stable operating window (see Figure 8).

The coupling among these three mechanisms creates a complex multi-physics environment. Microwave heating rates depend on local particle concentration (affected by fluidization quality), while fluidization quality is influenced by particle size distribution (evolving due to attrition). Meanwhile, attrition rates are temperature-dependent because polymer mechanical properties soften with heating. This three-way coupling necessitates the multiscale CFD modeling framework described in Section 5 for predictive reactor design and optimization [21,40].

6.4. Simultaneous Intensification of Reaction and Transport

The central innovation of this hybrid reactor lies in the simultaneous intensification of reaction and transport (mass, heat, momentum transfer) processes. Vibro-fluidization enhances the external mass transfer coefficient by reducing gas bypassing and improving particle surface renewal. Microwave heating provides rapid, volumetric thermal activation of the polymer surface, reducing the reaction induction time and potentially lowering the overall activation energy. The circulating configuration ensures continuous product removal and fresh surface exposure, preventing over-fluorination and enabling steady-state operation. The synergy between these mechanisms can be quantified through process metrics such as the fluorination rate per unit energy input, the product uniformity index, and the particle attrition rate [7,20].

6.5. Scale-Up Considerations

The scale-up of vibro-fluidized bed reactors from laboratory to industrial scale requires careful consideration of vibration transmission, microwave field uniformity, and gas distribution. Mechanical vibration becomes increasingly difficult to apply uniformly as reactor diameter increases, potentially leading to dead zones or excessive attrition at the walls. Multi-point vibration excitation or segmented vibrator designs may be necessary for large-scale units [12,13]. Microwave scale-up presents analogous challenges, as electromagnetic field uniformity degrades in large multimode cavities. Traveling-wave or slotted-waveguide applicators may offer better scalability than simple cavity designs [30,33].

7. Challenges and Future Research Directions

Despite the promising conceptual and preliminary theoretical framework for circulating vibro-fluidized bed microwave fluorination reactors, several significant challenges remain.

Experimental Validation: The construction and operation of pilot-scale integrated reactors involve substantial engineering complexity, particularly regarding the safe handling of fluorine gas under microwave irradiation and vibrational excitation. Comprehensive experimental campaigns are needed to validate hydrodynamic models, measure reaction kinetics under microwave conditions, and characterize product quality [35,46].

Particle Attrition and Stability: While theoretical attrition models based on granular temperature and indentation fracture theory provide a foundation, the specific attrition behavior of polymer particles under combined vibrational and chemical stress is poorly understood. In-situ particle size and morphology monitoring techniques are needed to develop robust stability models [28,40].

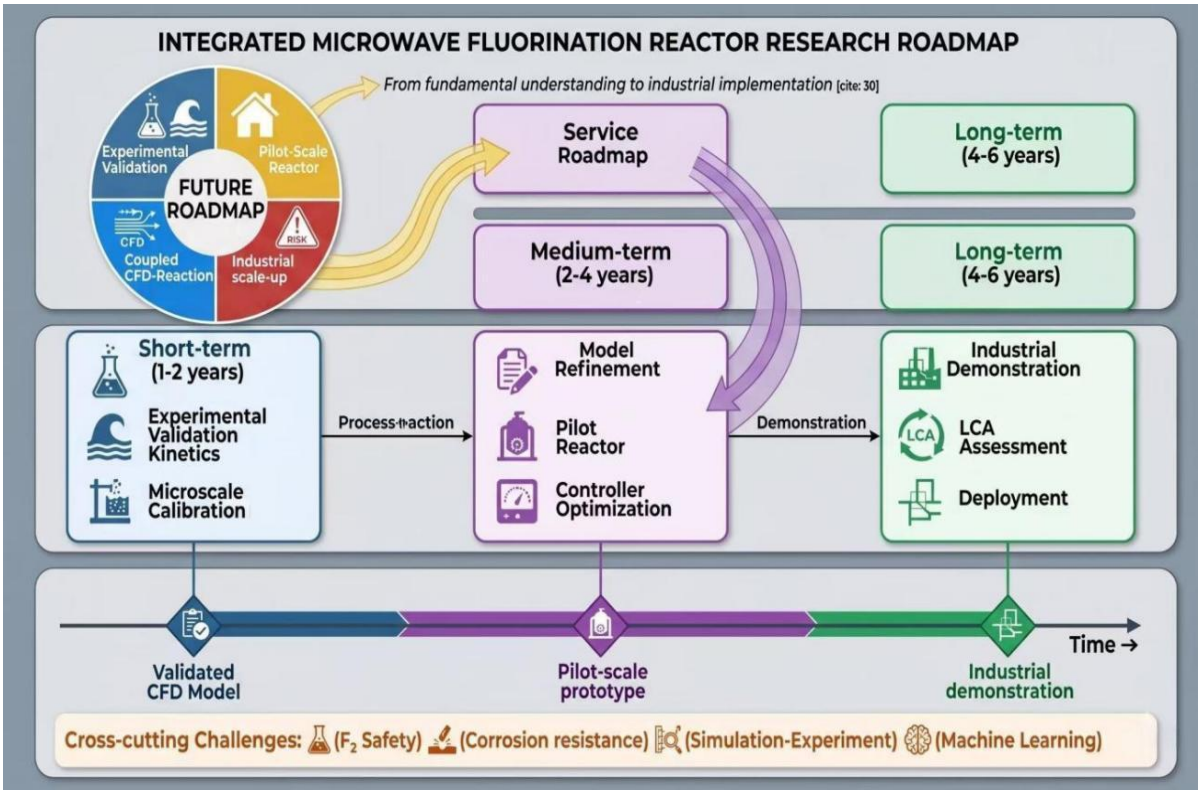


Figure 9. Future research roadmap for integrated microwave fluorination reactors, progressing from fundamental understanding to industrial implementation across three time horizons.

Coupled Model Refinement: Current CFD-reaction coupling approaches rely on simplified global kinetics and homogeneous surface assumptions. Future models should incorporate distributed surface reactivity, multistep reaction mechanisms, and the evolution of polymer

dielectric properties during fluorination. The incorporation of machine learning algorithms for real-time model adaptation based on sensor data represents an emerging opportunity [37,47,48].

Dielectric Property Characterization: Systematic measurement of dielectric constant (ε') and loss factor (ε'') as functions of fluorination degree, temperature, and frequency is essential for optimizing microwave power input and predicting heating behavior. Such data are currently scarce for partially fluorinated polymers [17,30].

Environmental and Economic Optimization: The closed-loop gas purification and recycle system must be optimized for energy efficiency and scrubber regeneration cycles. Life-cycle assessment (LCA) studies comparing the integrated reactor with conventional technologies are needed to quantify environmental benefits and guide industrial adoption [45,47]. Figure 9 outlines the proposed future research roadmap.

8. Conclusion

The development of next-generation fluorination reactors capable of producing high-quality fluorinated polymers with improved efficiency and reduced environmental impact requires the convergence of advanced reactor engineering, novel heating technologies, and multiscale computational modeling. The circulating vibro-fluidized bed microwave fluorination reactor represents a promising paradigm that simultaneously addresses the limitations of conventional batch and screw reactors by enhancing gas-solid contact, enabling rapid volumetric heating, and supporting continuous closed-loop operation.

This review has highlighted the fundamental principles and recent advances in the constituent technologies: direct fluorination reaction kinetics and mechanisms, vibro-fluidized bed hydrodynamics, microwave-assisted reaction kinetics with dielectric property evolution, and Euler-Euler CFD modeling with surface reaction coupling. The integration of these elements into a unified reactor system, supported by particle attrition-based stability models and mesoscale flow field analysis, provides a rational pathway for process intensification in polymer fluorination.

Future research should focus on experimental validation of integrated reactor concepts, refinement of multiscale CFD-chemical reaction models incorporating dielectric property evolution, and the development of scale-up strategies that preserve the mesoscale homogeneity and reaction uniformity achieved at laboratory scale. This review provides a systematic framework for the design of circulating vibro-fluidized bed microwave fluorination reactors from the perspective of fluorine chemistry and reaction engineering.

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