

Conceptual Design and Practical Challenges of Gas-Phase Catalytic Reactive Distillation/Absorption

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Reactive distillation/absorption is among multifunctional reactors for process intensification. Conventionally, reactive distillation/absorption is suitable for liquid-phase catalytic reaction, with rare reports for gas-phase catalytic reaction. By reviewing the conventional reactive distillation/absorption concepts, we re-classify RD/A based on the criterion of phase state; and by analyzing the recent advances of column trays and catalyst development etc., we put forward novel conceptual design to conveniently achieve gas-phase catalytic reaction in reactive distillation/absorption process, which is termed as Gas-phase Catalytic Reactive Distillation/Absorption (GC-RD/A). The feasibility of this concept in theory and practice are analyzed from the perspective of catalyst, reactive internals and phase states. Practical challenges are presented comprehensively including equipment design, flow patterns, transport phenomena, reaction selection and operation window, and catalyst design, from fundamentals to industrial implementation.

1. Introduction

Reactive separations integrate the functions of reaction and separation into single spatial domain to achieve the synergistic effect. (Van Gerven and Stankiewicz, 2009) They can achieve better selectivity and high conversion to desired products by removing the products from reaction system. Among reactive separation, reactive distillation/absorption (RD/A) are the most popular. As for RD/A, from fundamental research to industrial applications, several steps are indispensable, i.e. blooming of new concept, feasibility evaluation, conceptual design in equipment and process, bench-scale exploration, observation and modeling of transport phenomena (hydrodynamics, heat transfer, coupled mass transfer and reaction), pilot-scale verification and finally industrial implementation.

Although it's a long-term process to implement RD/A industrially from the beginning, great progress has been made since 1980s. However, recent advances are limited, for example, rare reports for gas-phase catalytic reaction and limited industrial applications.

Gas-phase catalysis accounts for large portion in small-molecule reactions and most of them can be enhanced by removing the products selectively. Therefore, it is imperative to consider reactive separations to enhance these process. Membrane reactor (Gallucci et al., 2013) and reactive adsorption (Sharma et al., 2013) have been widely investigated and regarded as promising methods. However, careful analysis reveals their intrinsic limitations: reactants and products with small molecule or low boiling points are preferred, because all the components must be maintained in gas phase. Therefore, it is not recommended to enhance gas-phase catalysis involving liquid products by membrane reactor or reactive adsorption. For liquid products, although they can be turned into gas-phase by increasing reaction temperature, higher temperature means higher energy consumption, typically Fischer-Tropsch reaction.

Alternatively, RD/A is better for the reactions involving liquid-phase or large molecular products. Generally, when reactants are gas phase with liquid phase products, gas reactants must overcome mass transfer resistance across liquid and reach catalyst surface for catalytic reaction. If there are high mass transfer resistance, RD/A will also not an alternative method. The best way to solve this problem is: direct gas-catalyst contact without liquid covering on catalyst, namely, liquid products detach catalysts once generated.

The above method can be realized by superhydrophobic or superoleophobic surface coming from lotus effect (Su et al., 2016). In last two decades, understanding on surface wettability and functional materials with special wettability flourish. In our group, research are conducted to combine surface wettability and foam column tray and achieve novel flow pattern in foam column tray (Li et al., 2016; Yan et al., 2018); in addition, some research groups prepared catalysts of special wettability (Wang and Xiao, 2014) and improved syngas to methanol process by nonwetted catalyst (Ling et al., 2017).

Here we name this novel idea as Gas-phase Catalytic Reactive Distillation/Absorption (GC-RD/A). In this paper, we first review conventional RD/A and classify them by the criterion of phase state and describe novel concept; then analyze the feasibility of GC-RD/A; finally point out practical challenges and recommendations.

2. Conventional reactive distillation/absorption

Reactive distillation has witnessed great progress since first report of heterogeneous reactive distillation in 1966, for example MTBE production and benzene hydrogenation (Sundmacher and Kienle, 2003). Reactive absorption, as the most important method for gas treatment has also been well developed (Yildirim et al., 2012).

2.1 Categories of reactive distillation

RD are used to enhance reaction conversion, product selectivity or to improve separation efficiency. There are more than one criteria to classify RD. Based on phase state of the reactants, we classify RD into: a) liquid-phase catalytic RD, b) gas-liquid catalytic RD, c) gas-phase catalytic RD.

Liquid-phase catalytic RD: The reactants are in liquid phase and the reaction happens at liquid-catalyst interface. Most of chemical reactions in RD are this type, e.g. the production of MTBE and TAEE. Furthermore, two immiscible liquid phase RD, e.g. synthesis of cyclohexanol, also belongs to this category.

Gas-liquid catalytic RD: The reactants present different phase states, for example, A as gas phase and B as liquid phase. Only both A and B diffuse to catalyst surface, there is possibility for reaction. Reaction rate is generally limited by mass transfer. Hydrogenation reactions are typical examples.

Gas-phase catalytic RD: Different from previous RD concepts, gas-phase catalytic RD means all the reactants are in gas phase. Generally, the reaction is transformation of small molecules to large molecules, such as syngas to methanol (Sundmacher and Kienle, 2003), Fischer-Tropsch reaction (Srinivas et al., 2008).

2.2 Categories of Reactive Absorption

The phase state of RA are simpler compared to RD, part of gas phase are absorbed and reacted with liquid phase. According to the phase state of products, reactive absorption can be classified into: a) gas-phase product oriented RA, and b) liquid-phase product oriented RA.

Gas-phase product oriented RA: This kind of RA is for gas purification or removing harmful substances, and typical examples are CO₂ absorption and H₂S removal. (Yildirim et al., 2012)

Liquid-phase product oriented RA: The typical examples are the production of nitric or sulfuric acid. NH₃ or SO_x gas are first catalyzed on solid catalyst to NO_x or SO₃ and then absorbed, or directly reactively absorbed by solvents to obtain the products. (Yildirim et al., 2012)

3. Novel reactive distillation/absorption

In last section, gas-phase catalytic RD was first presented based on new classification method. If implemented in conventional RD columns, it will show similar characters to gas-liquid catalytic RD due to gas mass transfer across liquid film to catalyst surface. So gas mass transfer resistance is the main obstacle. Here, a new gas-phase catalytic RD concept is presented to achieve direct gas-catalyst contact.

As for reactive absorption, previous research mainly focus on gas-phase products or liquid-phase products. Further attention should be paid on how to assign the sequence of reaction and absorption, in series or simultaneously? In most current RA process, reaction and absorption occur in the solvents simultaneously. However, in some RA cases, it is better to first react on catalyst surface and then absorb the products to liquid solvents. This can eliminate mass transfer limitation to improve reaction rate.

3.1 Gas-phase catalytic reactive distillation

Gas-phase catalytic reactive distillation means that the reactants are in gas-phase, and the products are mainly in liquid-phase under reaction condition. In **Figure. 1a**, liquid film covers the catalyst, which hinders mass transfer of gas reactants to catalyst and also products to outside. To make available catalyst surface larger and mass transfer resistance smaller, the formation of liquid film should be avoided. As the same as Ling et al.'s research for syngas to methanol on nonwetted catalyst, here liquid droplets forming on catalyst

surface are preferred for gas to liquid (GTL) reaction to replace the liquid film forming, seen Figure. 1b. This novel concept is also beneficial for heat transfer by changing heat transfer manner from liquid film to liquid droplet and flowing gas. Moreover, this new concept means reaction and separation are decoupled and occur in series, as shown in Figure. 2b.

Different from conventional RD, decoupled and serial reaction and separation means less interaction between reaction and vapour-liquid equilibrium (VLE). In conventional RD, in situ separation within the reaction zone leads to complex interactions between VLE, vapour-liquid mass transfer, intra-catalyst diffusion and chemical kinetics. Such interactions have formed multiple steady-states and complex dynamics (Xu et al., 2017). Therefore, this novel RD concept not only eliminate liquid film of catalyst surface to improve mass transfer from gas phase to catalyst, but also presents less coupling between reaction and separation.

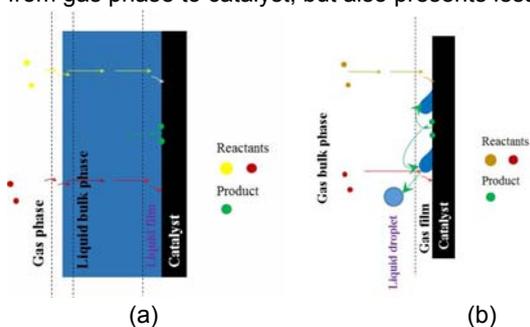


Figure. 1. Mass transfer process of reactants and product molecules on the liquid film covered catalyst (a) and liquid-free catalyst (b). (a) liquid film sticks on the catalyst, (b) droplets form on the catalyst surface and subsequently detached.

3.2 Gas-phase catalytic reactive absorption

This concept applied for reactive absorption means reaction and absorption happen in series. It can be seen as the integration of serial catalytic reaction units and absorption units as shown in Figure. 2. Gas first reacts on catalytic trays, and then part of gas products are absorbed into the liquid above the column trays.

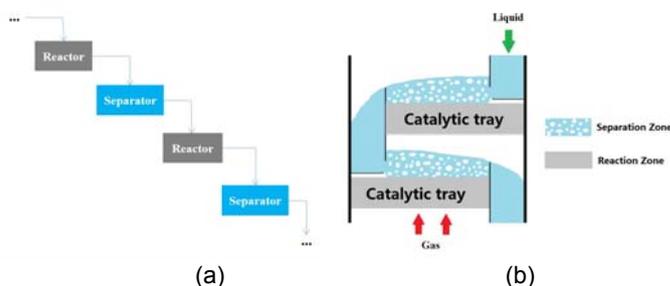


Figure. 2. Comparison between reactor-separator in series and integrated reactor-separator in one column.

4. Feasibility analysis in theory and practice

Feasibility analysis is used to determine the viability of this idea, ensuring the idea is technically feasible and economically justifiable. Here feasibility analysis is conducted only in technical aspect.

4.1 Phase contact state

According to new conceptual design of gas-phase catalytic RD/A, direct contact between gas and solid catalyst are required, which means liquid phase cannot wet the solid surface. Generally, gas-liquid interaction and gas (or liquid) -solid interaction change with fluid physical properties, fluid velocity, column internals' geometry, surface properties of internals' material.

However, previously extensive studies mainly focus on the effect of geometry and operation parameters rather than surface wettability. Internals' materials are normally metal, intrinsically wetted by almost all the liquid; in addition, the thickness of column trays is very small, leading to less importance of gas-solid interaction.

Recently, the research of foam SiC valves (Yan et al., 2018) and metal sieve trays (Yan et al., *submitted*) make us realize that surface wettability presents great influence on hydrodynamics, which originates from special gas-liquid-solid interactions inside the tray. The influence will be more significant when the tray is

thicker. By recovering the mechanism, we found that liquid non-wetting on solid foam, as shown in Figure 3, is the key reason. Coincidentally, it can achieve the absolute gas-solid direct contact, as shown in Figure 4. Briefly, the expected phase contact state can be achieved by tuning surface wettability.

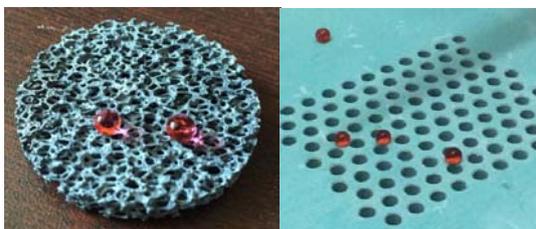


Figure 3 Droplets on the foam SiC valve (Left) and on the metal sieve tray (Right).

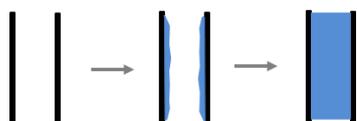


Figure 4 Different gas-liquid-solid interaction states with decreasing surface contact angle and gas velocity. Left: gas-solid direct contact, Middle: Liquid film forms between solid and gas, Right: The space is totally blocked by liquid between gas and solid.

4.2 Catalyst coating

Although preferred phase contact states can be achieved, the coating stability is crucial for long-term operation. Fortunately, catalyst coating on the structured support has highly developed in structured reactors and catalysts. Methods like dip-coating and in situ growth have been well established.

4.3 Catalyst preparation with special wettability

After catalyst coating technology, another consideration will be the preparation of bifunctional catalysts with special wettability and catalytic activity. The surface wettability can be achieved by building microstructure and modifying surface components. As for the catalyst, further focus is to maintain original activity; therefore, the attention is paid to the modification of supports but not active sites.

Follow the design principles shown in **Figure 5**, it is feasible to obtain bifunctional catalysts with the character of, from superhydrophilic (or superoleophilic) to hydrophobic (or oleophobic) and even superhydrophobic (superhydrophobic) (Su et al., 2016).

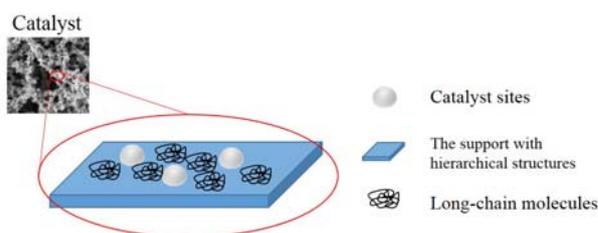


Figure 5. Proposed bifunctional catalyst design. Based on the design principle of superwettability materials, the catalyst support has hierarchical structure and is modified by long-chain organic molecules; the catalyst sites, as the source of catalytic activity, are not changed.

4.4 Phase states of reactants and products

It seems sufficient enough to implement new GC-RD/A concept based on above points, but sadly NO. According to the concept, RD/A reactants must be in gas-phase, and one or all of the products must be in liquid phase. Catalysts development should be paid much attention when considering phase states of reactants and products because of their decisive effect on reaction condition.

The analysis from equipment to catalyst proves its feasibility. In order to further understand the feasibility in practice, there are some research that can be referred: Ling et al. combine the catalyst and surface wettability

to obtain better heat removal, increased reaction rate, larger available specific surface area and less bed pressure drop for syngas to methanol in fixed bed reactor (Ling et al., 2017); Wang and Xiao conducted systematic study and verified that surface wettability of catalyst can improve catalytic activity, product selectivity and catalyst stability (Wang and Xiao, 2014).

5. Practical challenges and recommendations

Although it is feasible to achieve this novel reactive distillation/absorption process, more practical research is necessary to finally realize it industrially.

5.1 Equipment design

Packed bed column and trayed column are available for RD/A. Considering the nature of serial reaction and separation, trayed column is more suitable. For this concept, catalytic trays need special design. To achieve enough reaction space, the tray will be as thick as a small packed bed. Two possible design routes are recommended: structurally packed catalytic tray and randomly packed catalytic tray as shown in **Figure 6**.



Figure.6. Catalytic tray design with multilayers. The main part is (a): straight channels or foam; (b): random packings. The upper and lower layers are used to hold packings and support above liquid layer.

5.2 Flow patterns

Here take the foam column tray as example, the influencing factors consist of pore diameter, foam thickness, surface wettability and gas/liquid velocity.

In our previous study, we have studied the effect of surface wettability on flow pattern inside the foam, and the results shown that gas-liquid-solid interaction can be regulated by changing surface wettability. Although the mechanism and flow pattern map has been presented based on experimental observation and theoretical analysis (Yan et al., 2018), the experimental verification by MRI or X-ray CT is indispensable. Further research experimentally and computationally for integral flow pattern map should be conducted.

5.3 Transport phenomena

Hydrodynamics: In our previous study, preliminary hydrodynamic performance including pressure drop, weeping rate and gas distribution was presented by considering the effect of gas velocity and surface wettability. It give us fundamental understanding on the difference between various surface wettability, but it is not enough and the effect of other operation parameter and structural parameters are still necessary.

Heat transfer: Reaction temperature is extremely important, so the heat transfer control must be carefully considered. Generally, the reactions for RD/A are exothermic, the possible methods for heat removal are: 1) heat transfer between above liquid layer or liquid droplet and catalytic trays, 2) cooling by gas reactants or externally introduced inert gas. More attention should be given to evaluate their pros and cons. Conversely, if the reaction is endothermic, one of the best heat supply methods will be microwave heating.

Mass transfer: With the change of surface wettability of catalytic trays, mass transfer characteristics will differ. For example, the contribution of gas-liquid mass transfer inside foam tray decrease drastically due to non-wetting, and gas distribution in liquid layer and bubbling behavior will change due to the effect of pore wettability on bubble formation (Yang et al., 2016). Therefore, systematic research will be inevitable for all kinds of catalytic trays.

5.4 Reaction selection and operation window

To achieve GC-RD/A concept, selecting suitable reactions is one key steps. The new concept means nothing if there are no suitable reactions. From our perspective, the most promising reactions and their catalysts are shown in Table. 1. However, further reaction screening should be done to dig the full potentials of gas-phase catalytic RD/A.

To implement the GC-RD/A for these promising reactions, the operation window must be located, which is the inevitable step to integrate chemical reaction and distillation/absorption together and make them compatible.

Table 1: Potentially suitable reactions and catalysts for GC-RD/A

	Reactions	Catalysts
GC-RD	Fischer-Tropsch synthesis	Co/Al ₂ O ₃ , Fe/SiO ₂
	Syngas to methanol	Cu/ZnO/Al ₂ O ₃
GC-RA	Nitric acid production (NH ₃ oxidation)	Rh-Pt

5.5 Catalyst design

Catalyst design is always the core for a process. Its importance for GC-RD/A concept is summarized:

- Well developed catalysts make it possible to match reaction condition and separation condition.
- Bifunctional catalyst showing good catalytic activity and surface non-wetting need to be developed.

Although some hydrophobic or superhydrophobic catalysts have been developed, the development of superoleophobic catalysts is imperative because of large portion of organic process .

6. Conclusions and Outlook

In summary, new concept, GC-RD/A, is presented for the first time. Systematic analysis including phase contact state, catalyst coating, catalyst preparation with special wettability and phase states of reactants and products proves its feasibility. GC-RD/A can make up the deficiencies of current RD/A to achieve the intensification of gas-phase catalytic reaction in RD/A columns. However, to implement GC-RD/A industrially, there are still challenges which need more fundamental and practical research, such as, equipment design, flow pattern, transport phenomena at various wettability, reaction selection and operation window, and catalyst design. Guidelines including recommended solutions for these challenges are presented.

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