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Application of the Chemical-Looping Concept for Azeotrope Separation

Xin Gao*, Xueli Geng

School of Chemical Engineering and Technology, Tianjin University & National Engineering Research Center of Distillation Technology & Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300350, China



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ABSTRACT

The need for the separation of azeotropic mixtures for the production of high-end chemicals and resource recovery has spurred significant research into the development of new separation methods in the chemical industry. In this paper, a green and sustainable method for azeotrope separation is proposed based on a chemical-looping concept with the help of reversible-reaction-assisted distillation. The central concept in the chemical-looping separation (CLS) method is the selection of a reactant that can react with the azeotrope components and can also be recycled by the reverse reaction to close the loop and achieve cyclic azeotrope separation. This paper aims to provide an informative perspective on the fundamental theory and applications of the CLS method based on the separation principle, reactant selection, and case analysis, for example, the separation of alkenes, alkane, aromatics, and polyol products. In summary, we provide guidance and references for chemical separation process intensification in product refining and separation from azeotropic systems for the development of a more sustainable chemical industry.

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1. Introduction

In the petroleum and fine chemical industries, the separation of azeotropic mixtures from downstream separation processes is crucial for producing high-purity products or recovering value-added substances [1,2]. However, conventional distillation separation technologies are no longer sufficiently effective, and special separation technologies should be adopted to achieve target azeotrope separation [3,4]. Many special separation technologies have been used and developed, each with its own scope of application, for example, special distillation [5,6], membrane separation [7,8], extraction [9,10], adsorption [11,12], and crystallization [13,14]. Membrane and adsorption methods are mainly used for solvent recovery and the gas separation of low-carbon-number alkene/alkane systems [15,16]. The mechanism of membrane separation has a lot of types, one of which is based on the different particle sizes at molecular level when passing through a semi-permeable membrane. However, it may contain some inevitable limitations for the product separation of alkenes/alkanes due to a similar molecular structure. Nevertheless, its advantages of high efficiency, energy-saving, and environmental protection plays an important role in the separation of special azeotropes.

Crystallization and extraction are mainly used in the fields of medicine and fine chemical industry and are suitable for systems with large differences in the melting point or partition coefficient [17,18].

Compared with other separation methods, special distillation methods, such as azeotropic distillation, extractive distillation, and pressure-swing distillation technology, have been broadly applied for the separation of azeotropic mixtures [19–25]. Azeotropic and extractive distillation can achieve mixture separation using a mass separating agent, but both separation methods have high energy requirements [26]. Pressure-swing distillation is advantageous because the azeotrope composition shows a significant shift with pressure. However, a drawback of this methods is that the azeotropic composition must vary by at least 5% (preferably over 10%) if pressure changes of no more than 1.01×10^6 Pa occur [27]. For decades, the above-mentioned special distillation separation methods have been used to achieve separation by exploiting the special properties of azeotrope mixtures. However, for some special azeotropic systems, such as ethylene glycol (EG) and 1,2-butanediol (1,2-BD) mixtures, these separation methods are not only insufficient effective but also energy intensive [28,29]. A potential special separation method that has drawn attention from academics and engineers is based on the chemical-looping concept. The chemical-looping method is achieved by a reversible reaction with an added reactant to achieve mixture separation.

* Corresponding author.

E-mail address: gaoxin@tju.edu.cn (X. Gao).

The added reactant reacts selectively with one component of the azeotrope to form another substance, breaking the original azeotrope and enabling azeotropic separation.

The concept of chemical-looping was first proposed in the 1950s [30]. In chemical-looping, the reaction and regeneration of a chemical substance occur cyclically to achieve production or separation goals. In more detail, a given process can be divided into multiple sub-reactions using a chemical-looping substance that is reacted and regenerated over the course of the sub-reactions. Early on, chemical-looping concepts were used for the production of hydrogen peroxide from hydrogen and oxygen [31,32]. Recently, Fan and Li [33] reviewed the applications of chemical-looping in fossil fuel energy conversion and proposed that chemical-looping has the potential to become an efficient and environmentally friendly process. The most important role of chemical-looping in oxidation reactions is the inherent safety because oxygen-based or air-based oxidation reactions are often intense and can be explosive [34–37]. Fan et al. [38] also pointed out the prospect and opportunity of chemical-looping processes for CO₂ capture in carbonaceous fuel conversion. In addition, the application of chemical-looping for azeotrope separation processes has also emerged [39–41]. Anastas et al., the father of green chemistry, put forward 12 changes that must be made in the future chemistry field in the *Science* [42]. The first change of future chemistry is mostly from linear processes to circular processes, which means chemical-looping. Although this concept has not been widely applied to azeotrope separation processes, it is based on the difference between the reaction rates of one or two components in an azeotrope with another added reactant, that is, the chemical-looping substance.

In this work, we summarize the fundamental theory and applications of the chemical-looping concept for azeotropic separation. In the second section, we elaborate the fundamental concepts of the chemical-looping separation (CLS) method for azeotropes. In the third section, we analyze the principles necessary for the screening suitable reactants to achieve efficient azeotrope separation. In the fourth section, we use case analysis to illustrate the application of the CLS method for azeotrope separation. This paper aims to provide a systematic overview and analysis of this novel azeotrope separation method based on chemical-looping, as well as point out new research directions aiming to develop this method for the separation of azeotropes.

2. CLS of azeotropes

The CLS utilizes a reactant to perform the cycles of reaction–separation–reverse reaction for separating azeotropes [43]. In this

process, a reactant is reacted and regenerated through the progress of the forward and reverse reaction. This process method of azeotropes separation based on the chemical-looping concept is defined as CLS. The visualization clarification of CLS process can be presented in Fig. 1. Firstly, two components of azeotropes defined as A and B can react with reactant C to form the corresponding products D and E, respectively. Next, the corresponding products can be easily separated from reaction mixtures. Finally, the high-purity A and B can be achieved and reactant C is recycled by the reverse process of corresponding products.

In the process of CLS for azeotrope separation, it is the best situation that only one compound of azeotrope reacts with reactant to form the corresponding product, which have not an azeotropic phenomenon with other components, for example the separation of xylene isomers by crystallization [44]. However, it is difficult to identify the key reactant, which must show different reactivity with the azeotrope components. To a large extent, the reactant can react with the two components of azeotrope in varying degrees, such as polyols separation [28]. Fortunately, the rates of reaction between different substances are generally different, which suggests that the difference in reaction rates could be exploited to achieve azeotrope separation. If one compound of the azeotrope reacts more slowly with the reactant than the other compound, only a small fraction of the undesired product will be formed in the mixture. Thus, the impact on the separation of the target product and its purity is small. The exploitation of reaction rate differences is a second-best situation for azeotrope separation. Furthermore, if such a reactant cannot be obtained for azeotrope separation, both azeotrope components can be reacted with the reactant; this is simpler because reactants for homologous or isomeric azeotropes with similar properties are easier to find. The reaction between azeotrope components and the reactant can be divided into three types based on the above description, and the different types undergo different separation processes.

In Fig. 2, the type-I (single reaction) denotes that the separation process has one reversible reaction, which reactant C only reacts with one component A of the binary azeotrope to form product D. Then the mixture of B and D without azeotropic behavior can be separated, and finally the regeneration of A by the reverse process of corresponding product D via reaction distillation (RD). As shown in Fig. 3, type-II means that the selected reactant C reacts with both components in the azeotrope, but the reaction rates are significantly different. Compared to compound B, the reaction rate of A with C is significant faster. The difference leads to the results that the amount of product D is much larger than E and product D requires further purification. Finally, component A can be recovered by RD. As shown in Fig. 4, type-III (both reactions

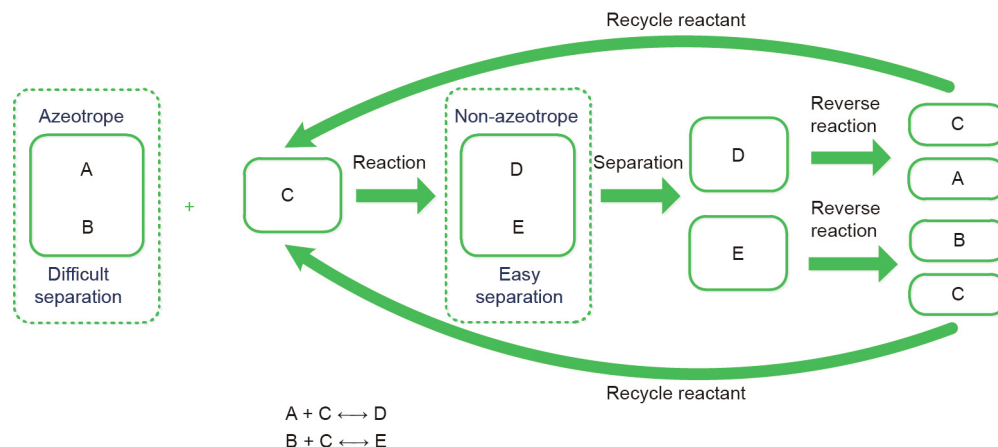


Fig. 1. Visualization clarification of CLS process.

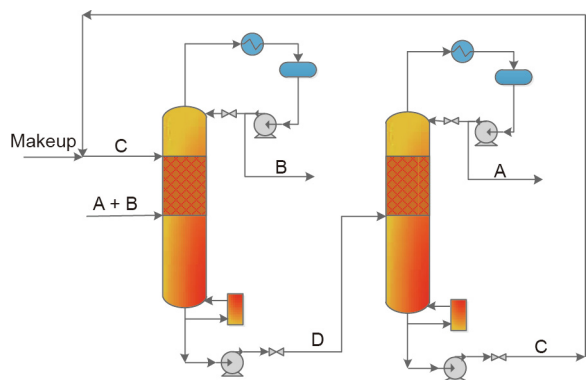


Fig. 2. Type-I CLS method with a single reaction.

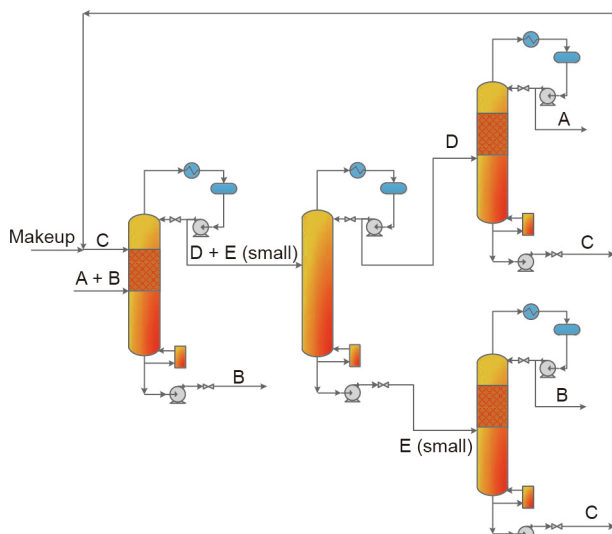


Fig. 3. Type-II CLS method with two reactions and a difference in conversion.

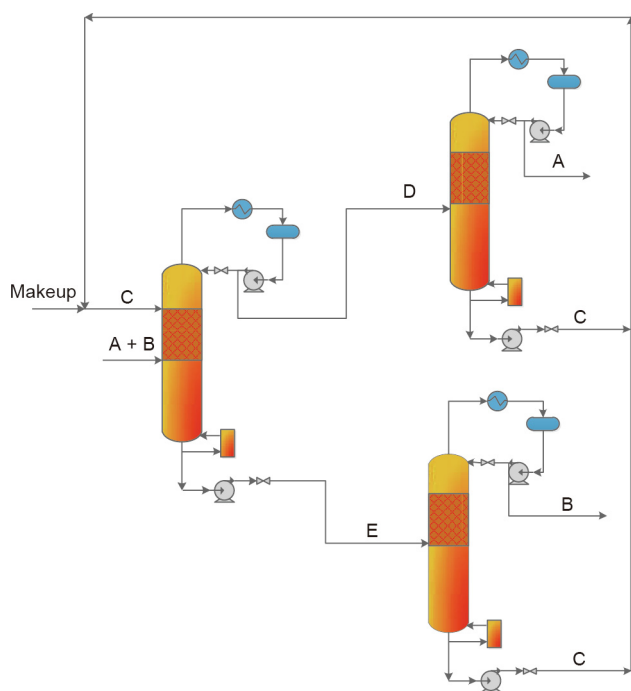


Fig. 4. Type-III CLS method with two reactions with equal conversion.

without conversion difference) means that the selected reactant C reacts with both components of the azeotrope A and B, and the reaction rate of these two reactions is equal. The corresponding products D and E can be separated and decomposed to achieve pure A and B, respectively. Type-I and type-III are special forms of the type II setup, albeit with differences in the reaction rate. Type-I azeotrope separation is expected to be promising from an economic point of view. Therefore, the reactant plays a significance role and reactant screening is crucial for azeotrope separation based on the CLS method. The principle of reactant screening is discussed in detail in the following section.

3. Reactants screening

It is well-known that the key to the effective production of a pure syngas/hydrogen in the chemical-looping combustion process is the selection of oxygen carriers from monometallic oxide systems [45–47]. Likewise, in the reversible-reaction-assisted separation of azeotropes using chemical-looping, reactant selection is also crucial. The azeotrope separation process using CLS consists of reaction, separation, and reverse reaction. Thus, throughout CLS, the reactant plays a major role in separation efficiency and sustainability. A reactant screening method is proposed for azeotropic mixture separation using CLS based on our previous work [48], and the corresponding flowsheet is shown in Fig. 5.

3.1. Pre-screening

First, pre-screening is used to reduce the reactant scope based on some selection principles. The pre-screening step considers the reaction types, material properties, reaction conditions, environmental effect, and material costs as properties of a potential reactant for use as the chemical-looping substance, as shown below.

- Reaction types: reversible, high selectivity (no side reaction), and insignificant reaction heat.
- Material properties: stable and suitable thermodynamic properties.
- Reaction conditions: mild reaction conditions (low temperature and low pressure), and low energy consumption.
- Environmental effect: non-poisonous and green.
- Material costs: easy production and low cost.

If the reaction types are reversible and high selectivity (no side reaction), the extra consumption of azeotropic components and process energy consumption can be reduced to a certain degree [49]. Even though the exothermic and endothermic reactions can affect energy consumption, the influence of reaction heat on the process will be eliminated because of the phase transformation in distillation. If the reaction is an exothermic reaction, it will promote the separation of components in the reaction distillation column (RDC). Although the reverse reaction may be an endothermic reaction and its occurrence requires a higher heat duty of reboiler, the exothermic and endothermic of reaction had no significant effects on the selection of reactants. The stable and suitable thermodynamic properties of the reactant can minimize the introduction of impurities into the mixtures and alleviate the effect of endothermic or exothermic reactions on the process [33]. The mild reactions conditions can decrease energy consumption and total cost. The use of non-poisonous and green reactants not only reduces the impact of human health and the environment but also makes the entire process more economical in view of transportation and storage. Finally, low cost and ease in scale-up of reactant synthesis can promote the industrial application process of CLS method for the separation of azeotropes.

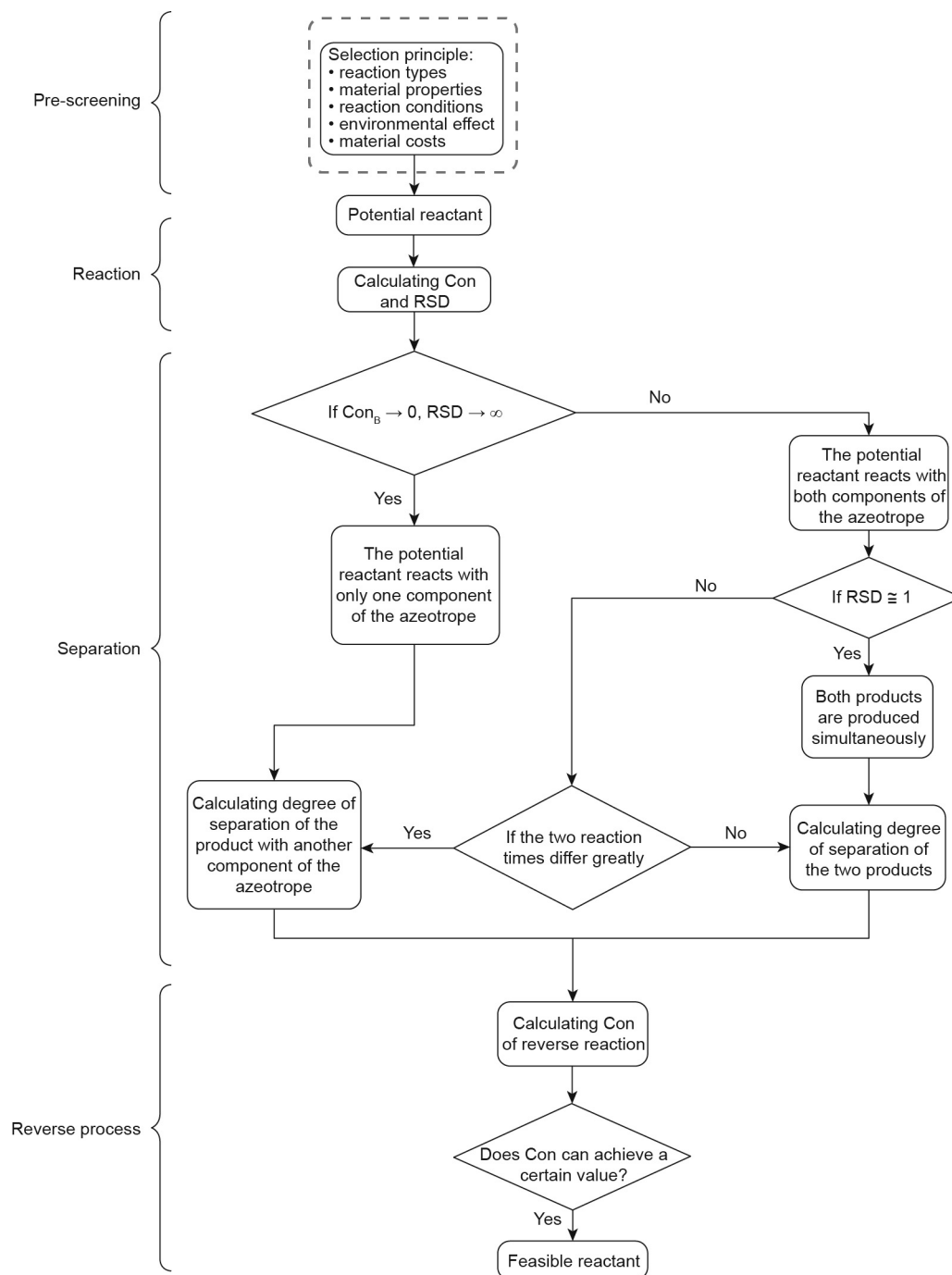


Fig. 5. Reactant screening flowsheet for azeotropes separation via CLS. Con: conversion rate; RSD: reaction selectivity difference.

3.2. Reaction

The reaction conversion rate (Con) and potential reaction selectivity difference (RSD) are calculated for the azeotrope components and the selected reactant (as determined by pre-screening) to determine the reactant suitability. In addition, it is important to determine whether one or both components in the azeotrope will react with the reactants. Con and RSD reflect the degree of reaction and the reaction selectivity difference [46], respectively, as shown in Eqs. (1) and (2).

$$Con_a = 1 - \frac{a}{a_i} \tag{1}$$

$$RSD = \frac{Con_A}{Con_B} \tag{2}$$

where *a* is A or B in the reaction system; *a_i* is initial A or B in the reaction system. A and B are the components of the azeotropic mixture. Here, we assume that the component with a high conversion rate is the numerator and the component with a low conversion rate is the denominator.

There are two kinds of relationships between the potential reactants and the components in azeotropes based on the RSD value and different values of Con. In type-I CLS, the potential reactant mainly reacts with one component of the azeotrope and to a much lesser degree with the other component. In this case, the value of

RSD will tend to infinite because the value of the denominator is close to zero when there is no reaction between the compound and reactant. However, it is usually hard to find a potential reactant for meeting the requirements of type-I because, typically, the chemical components have similar properties. In type-II and type-III, the potential reactant reacts with both components of the azeotrope. In type-III, both products are produced simultaneously, i.e. the Con value of two compounds is not much different and the RSD value is around 1. At this point, the separation process involves the separation of the corresponding products. In type-II, one product is generated much faster than another, i.e. the Con value of one compound is higher than another and the RSD value is a little greater than 1. The selective recycling of the lower-reacting components by changing the reaction conditions not only promotes the conversion of the faster-reacting component but also effectively inhibits component conversion in the azeotrope. Therefore, when selecting the reactants, a larger RSD value indicates a better reaction.

3.3. Separation and reverse process

A higher degree of separation indicates better mixture separation. The degree of separation is affected by the thermodynamic properties of the two components in the mixture, as well as, for example, the relative volatility and distribution coefficient, which must be greater than 1 in distillation and extraction process.

If the potential reactant mainly reacts with one component of the azeotrope and reacts minimally with the other component, the degree of separation of the product and the other component can be calculated to assess the suitability of the potential reactant. If the potential reactant reacts simultaneously with both components of the azeotrope, the degree of separation of both products must be calculated. For degree of separation greater than 1, larger values indicate better separation and lower energy consumption. Finally, the initial component of the reaction with the azeotropic mixture can be obtained through reverse reaction. For this process, it is necessary to calculate the Con of the reverse process. If Con can achieve a set value, the potential reactant can be used in the CLS method. In the next section, specific case studies are used to illustrate these points.

4. Applications of CLS

In this section, chemical-looping for azeotrope separation is describe in detail regarding the separation of alkenes/alkanes, aromatic hydrocarbons, and polyol products.

4.1. Separation of alkenes/alkanes

4.1.1. 1-Alkene separation

1-Alkenes are produced by the Fischer–Tropsch (F–T) process, which has widespread application in the production of oxoalcohols and polymers, such as linear low-density polyethylene [50–53]. In the F–T process, a range of by-products form, and these are typically paraffins, branched alkenes, and linear internal alkenes [54,55]. The recovery and purification of 1-alkenes (e.g. 1-hexene (HE)) from the by-products is challenging because the relative volatility of HE and 2-methyl-1-pentene (2-MP), a typical by-product, is only 1.06 [56,57]. This recovery process is now commercially carried out using cheap raw materials by Sasol (South Africa) [58]. However, 1-alkene recovery is still a difficult and expensive operation because all isomers interact with the solvent in a similar way [59,60]. To improve the recovery of HE, the branched isomer 2-MP is reacted with methanol (MeOH) to form ethers, which have a relatively high boiling point and can be easily separated by distillation [61,62]. However, the number of required columns is large if high-purity HE is required because the undesired by-products must be removed one-by-one. To overcome this uneconomical situation, a novel alternative technology via chemical-looping has been developed using a functional reactant to form π -complexes through reversible-reaction-assisted distillation. This technology was developed based on the study of metal–ligand complexes, phase equilibrium models, and π -complexation effects, and the conceptual design was developed by Kuipers et al. [58] and Wentink et al. [56,57]. The functional solvents are metal–ligand complexes, which not only allow the ligand to retain the metal in solution but also retain its ability to form π -complexes with the desired alkene. For instance, in the separation of HE and 2-MP, the desired 1-alkene (HE) forms a π -metal–ligand complexes faster than 2-MP. This CLS concept for close-boiling alkene isomers using a functional solvent as a reactant is shown in Fig. 6 [56–58]. The reaction separation process is a type-II CLS method.

As shown in Fig. 6, the metal–ligand complexes act as a functional reactant. Both HE and 2-MP react with the metal–ligand complexes via π -complexation. However, the rate of reaction with HE is greater than that with 2-MP. Thus, the difference in reaction rate is exploited to remove the 2-MP continuously to promote the further reaction of HE with the reactant. The HE is regenerated in a decomplexation column and metal–ligand complexes as reactants are recovered into the former RDC. Kuipers et al. [58] used a simplified feed mixture of *n*-hexane (NH), 2-MP, and HE (mole ratio of 1:1:2), and the HE is purified from the simplified mixture by CLS (most experiments have used this feed mixture). Using this method, HE is obtained in 99.5 mol% purity with a minimum recovery of 99% from the top stream.

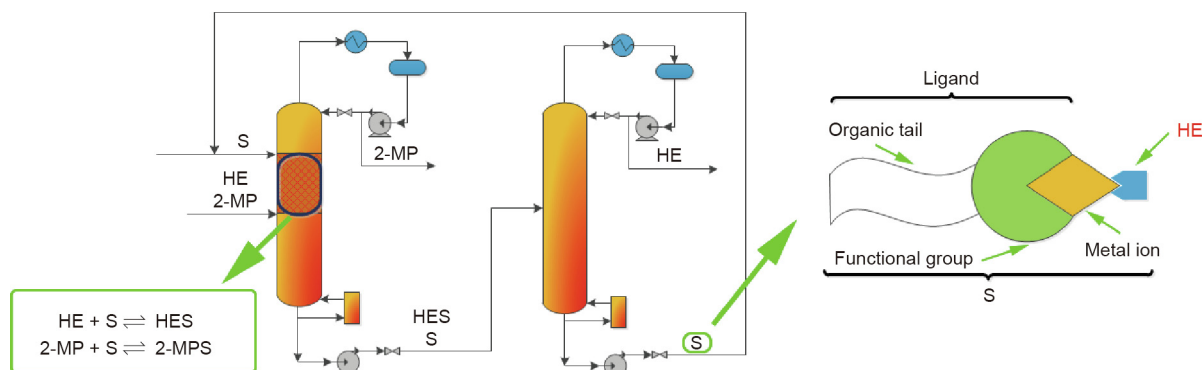


Fig. 6. Conceptual design of the separation of close-boiling HE and 2-MP using a functional solvent (S) as reactant. Reproduced from Refs. [56–58] with permission of American Chemical Society, ©2005, and Elsevier, ©2007.

4.1.2. Production of high-purity isobutene

Isobutene (IB) is found in hydrocarbon mixtures and is used to synthesize additives [63], such as methyl tert-butyl ether (MTBE) for use as an octane booster and clean-air component in gasoline [64–66]. However, MTBE has an adverse effect on the environment and is banned in the United States; thus, alkylates, which have an average octane numbers of 93–96, are considered as the leading candidates to replace MTBE [67,68]. Isooctane, formed by the dimerization of IB, is a potential alkylate source [69]. IB is also valuable starting materials for the polymerization or copolymerization of butyl rubber [70]. Thus, the separation of IB from mixtures of inert C₄ hydrocarbons (represented by 1-butene (nB)) and the efficient separation of its isomers is of significant practical interest [71].

Among the various possible reaction systems, the formation of MTBE by the etherification of IB with MeOH is a particularly useful process [72]. MTBE production has been well investigated and is an industrially established RD process [73–75]. In addition, IB recovery through MTBE decomposition is economical and has been well studied. The whole separation process of IB and nB can be divided into MTBE production by the reaction of IB mixtures with MeOH, the separation of MTBE and nB, and the acquisition of IB via MTBE decomposition. In this process, MTBE is regarded as an intermediate product and MeOH is the chemical-looping substance.

Ideally, two RDCs can achieve the separation of IB and nB mixtures using the chemical-looping/reversible reaction concept. Fig. 7 shows the ideal separation process for IB and nB mixtures in two RDCs. The IB of mixtures and MeOH stream are converted to MTBE in the first RDC where the acidic catalyst is added to upper column part, and IB and MeOH are completely converted to MTBE. The inert component, nB, which does not react with MeOH, is withdrawn as the top product, and high-purity MTBE is obtained in the column bottom. The second RDC, which is fed from the first column bottom product, undergoes the MTBE reverse process. In the second column, the IB is obtained in the column top through MTBE decomposition. The comparatively high-boiling MeOH, i.e. the chemical-looping substance, is withdrawn in the column bottom and recycled to the first column. This separation process is a type-I CLS method.

4.2. Separation of aromatic hydrocarbons

Xylenes are important chemicals which produced from petroleum or coal and mainly used for automobile fuel production in modern industry [76,77]. The separation of xylene isomers (*meta*-xylene (MX) and *para*-xylene (PX)) is not feasible using conventional distillation methods because of the closeness of their boiling points (412.25 and 411.55 K) for MX and PX, respectively

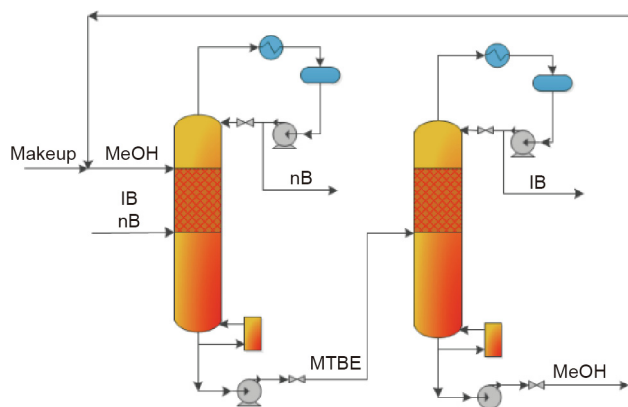


Fig. 7. IB and nB separation using MeOH as the chemical-looping substance via CLS.

[78,79]. As a result, the separation process is very energy intensive. However, the use of chemical-looping can enable the separation of these close-boiling mixtures. It is known that MX can be selectively *ter*-butylated in the presence of a catalyst under mild alkylating conditions to form higher boiling *ter*-butyl *meta*-xylene (TBMX). Clearly, this is a type-I CLS method. Saito et al. [44] investigated the separation of MX and PX mixtures using *ter*-butylbenzene (TB) as a reactant by combining chemical reaction and distillation with the aid of experimental research and theoretical calculations. However, they did not develop a continuous scheme, instead proposing the reaction and separation of MX and PX mixtures through a batch process. Thus, here, we use the chemical-looping concept to analyze the continuous separation of xylene isomers.

Actually, this is an ideal situation for the mixture separation of MX and PX using CLS. The flowsheet for the separation of MX and PX from their mixture with TB as the reactant is shown in Fig. 8.

As shown in Fig. 8, the separation of MX and PX mixtures occurs in three stages: ① TB is added to the MX and PX mixture to form TBMX and benzene (B) because only MX reacts with TB. A mixture of PX, TBMX, and B is then present in the reactor. ② Because of the large differences in the boiling points of PX, TBMX, and B, PX and B are produced in the column top and TBMX is obtained in the column bottom by distillation separation. The PX and B mixture is easily separated again by distillation because of the boiling point difference. PX is obtained for the further production of important chemicals. ③ MX is produced through the reverse process from TBMX by adding B obtained from the previous step. The obtained TB is recycled back to the first step. Therefore, the whole separation process uses B as the chemical-looping substance to separate xylene isomers by a series of forward reaction–separation–reverse reaction reactions. In fact, the forward and reverse reactions can be accomplished by reactive distillation. Thus, the whole process is

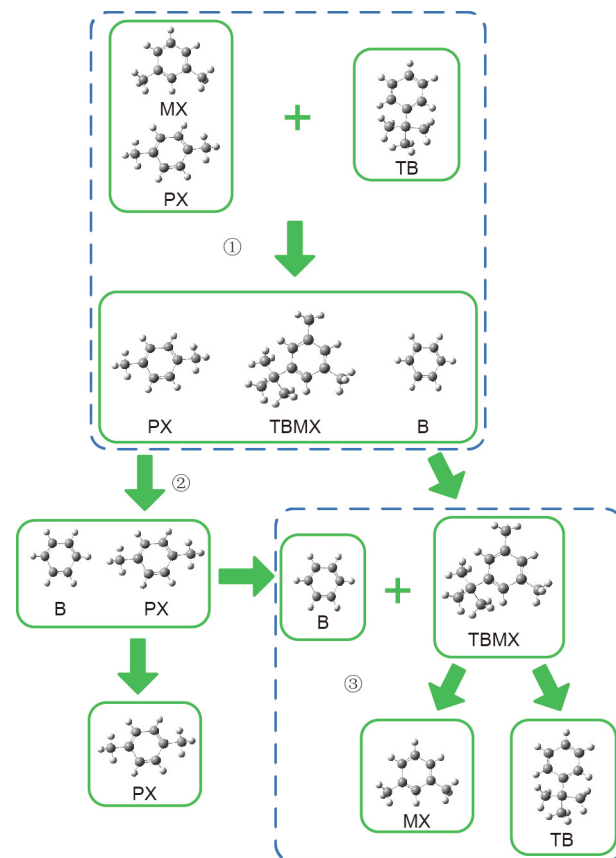


Fig. 8. Chemical-looping flowsheet for the separation of MX and PX mixtures with TB as the reactant. B: benzene.

reversible-reaction-assisted separation with RD based on the CLS method.

4.3. Separation of polyols

Because of advances in C_1 chemistry and the shortage of worldwide oil, EG, which is widely used in the petrochemical industry, is mainly produced from coal syngas [80–82]. However, the separation of EG and 1,2-BD requires an alternative economical and energy-efficient method to the indirect syngas-to-EG reaction, which is drawing increasing environmental concerns [83–85]. The mixture of EG and 1,2-BD is a minimum boiling azeotrope, making their separation difficult [86–88]. Currently, the traditional method of separating this mixture is energy-intensive and costly because of the large reflux ratio and tray number of the conventional distillation column [89,90]. With the aim of enhancing the separation process and improving the competitiveness of EG production based on coal, Li et al. [91] compared conventional distillation, azeotropic distillation, distillation coupled with liquid–liquid extraction, and reaction-assisted distillation using economic evaluation based on the total annual cost (TAC) and annual profit. The CLS method is better than other separation methods because of the comparatively high annual profit, even though the TAC is slightly higher, as shown in Fig. 9. The use of the CLS method for the separation of EG and 1,2-BD mixtures is based on the chemical-looping concept using acetaldehyde (ALE) as a circulation reactant, as shown in Fig. 9. The reaction of EG and 1,2-BD with ALE forms 2-methyl-1,3-dioxane (2-MD) and 2,4-dimethyl-1,3-dioxane (2,4-DMD), respectively, and this reaction separation process is a type-III CLS method. The flowsheet and simulation results of the reaction-assisted distillation process for the separation of EG and 1,2-BD mixtures is given in Fig. 9.

As shown in Fig. 9, in the separation process, the acetals formed using ALE as a reactant are easy to separate, while the acetal hydrolysis can yield high-purity EG and 1,2-BD by additional RDC. The reaction kinetics of EG were studied by Huang et al. [92]. The mole ratio of ALE to glycols was set to 2:1 to ensure the conversion of glycols based on a previous study [28]. Distillation column DC1 is used to recover the unreacted ALE and glycols and DC2 is used to separate the acetals. The hydrolysis of 2-MD and 2,4-DMD occur in RDC1 and RDC2 to regenerate EG and 1,2-BD, respectively, and the recovered ALE is fed back to the reactor. Pure EG and 1,2-BD are obtained by removing water as

by-product in DC3 and DC4, respectively. EG and 1,2-BD separation involves a reactor, and several RDC and distillation column have been designed and simulated using the Rstoic and RadFrac modules in Aspen Plus (Aspen Tech, USA), respectively.

Li et al. [93] investigated reactant screening for the separation of EG and 1,2-BD mixtures and found that propionaldehyde (PLE) is a suitable reactant for the reversible-reaction separation of EG and 1,2-BD mixtures. Using experimentation, Li et al. [48] also investigated the reaction rates between the two components of azeotrope and PLE reactant. The results showed that nearly all of the 1,2-BD is converted to the corresponding product but less than 30% of the EG is converted when mole ratio of 1,2-BD to EG is about 1:2. To promote industrialization, the pilot-scale experiments and process analysis were also researched by Li et al. [93]. Because the reaction rate of PLE with 1,2-BD is faster than EG, 1,2-BD conversion is assumed to be complete. And two conceptual design processes were used to separate 1,2-BD and EG mixtures. One involves the full conversion of 1,2-BD conversion without EG conversion, that is type-II CLS; the other involves the full reaction of both 1,2-BD and EG with PLE, that is type-III CLS. These designs are shown in Figs. 10 and 11, respectively. The key to these two processes is the flow rate of the added PLE reactant. First, 1,2-BD and EG react with PLE to form 2,4-diethyl-1,3-dioxane (2,4-DED) and 2-ethyl-1,3-dioxane (2-ED), respectively.

As shown in Fig. 10, all the 1,2-BD is converted to 2,4-DED by reaction with PLE if the reactant flow is fast. EG is not converted significantly because of the limitations imposed by the reverse reaction with PLE. Therefore, the EG can be obtained in the RDC bottom, and 1,2-BD can be regenerated by the reverse reaction of 2,4-DED, and the PLE is recycled for the RDC for reuse. Thus, in this conceptual process, pure EG and 1,2-BD are obtained based on the reaction rate differences.

As shown in Fig. 11, EG and 1,2-BD are converted to 2-ED and 2,4-DED by reaction with PLE if the reactant flow meets the two components simultaneously. Therefore, pure EG and 1,2-BD can be regenerated separately by the reverse reaction from 2-ED and 2,4-DED through RDCs, and the reactant PLE is recycled. Thus, these conceptual designs based on CLS can produce pure products, but the economy of these separation processes must be compared to evaluate their industrial potential. Recently, Wang et al. [94] reported that the process, which EG and 1,2-BD can be both converted to acetals, has more potential for industrial development from an economic point of view.

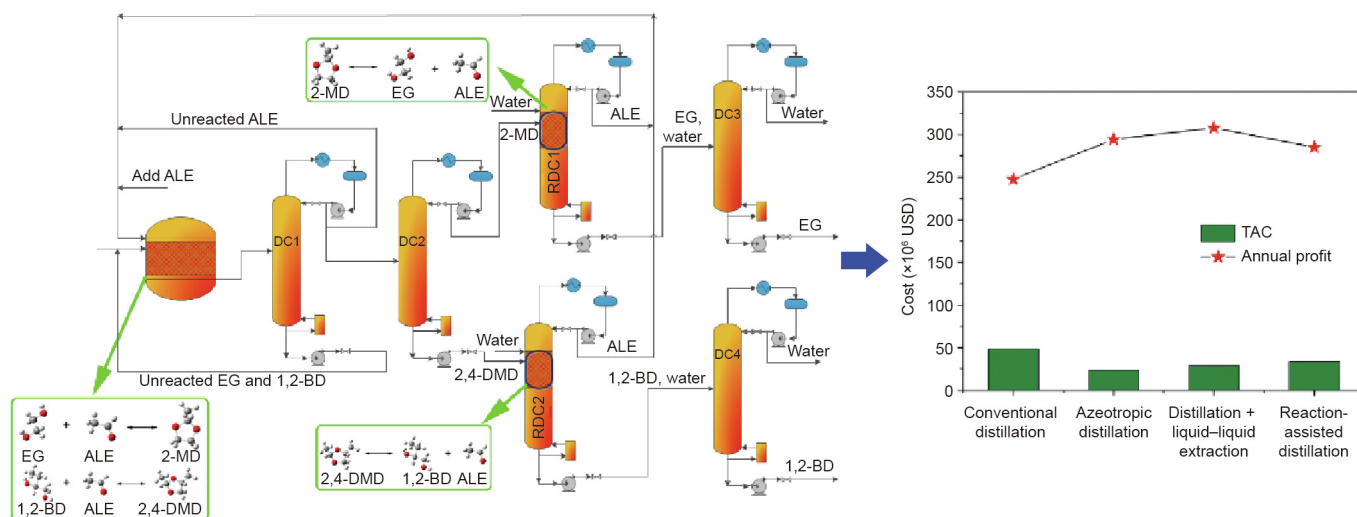


Fig. 9. Separation of EG and 1,2-BD mixtures using ALE as circulation reactant based on CLS. 2-MD: 2-methyl-1,3-dioxane; 2,4-DMD: 2,4-dimethyl-1,3-dioxane. Reproduced from Ref. [91] with permission of American Chemical Society, ©2018.

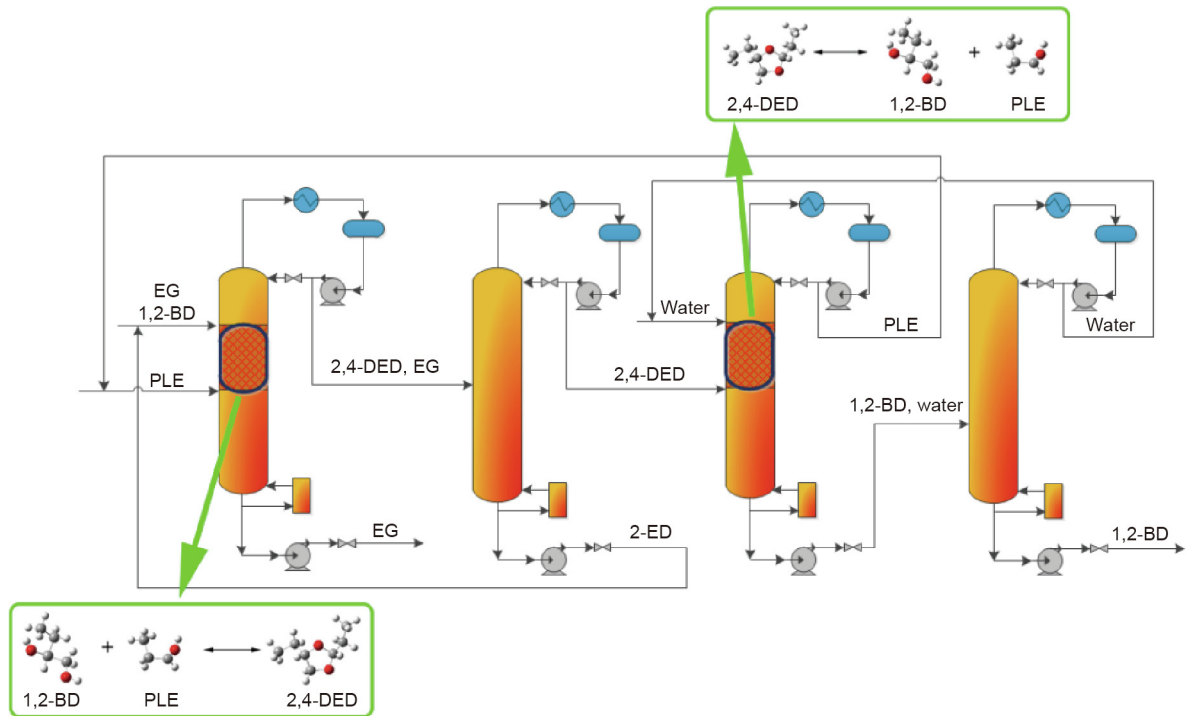


Fig. 10. Process concept using 1,2-BD conversion but no EG conversion using PLE as chemical-looping reactant. 2,4-DED: 2,4-diethyl-1,3-dioxane; 2-ED: 2-ethyl-1,3-dioxane.

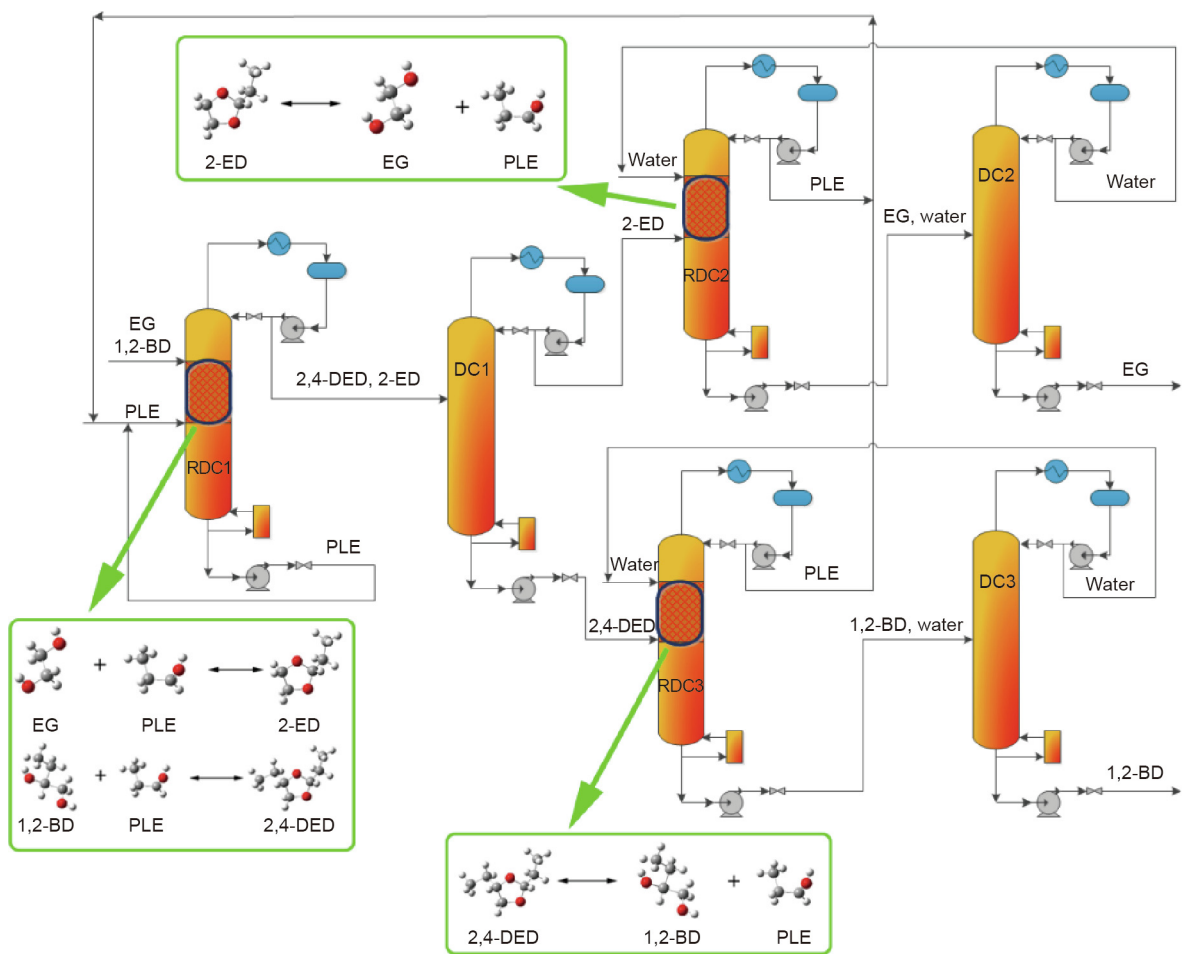


Fig. 11. Process concept using full conversion of both 1,2-BD and EG with PLE as chemical-looping reactant.

5. Conclusions and perspectives

The separation of azeotropic mixture consisted of components with similar properties is difficult and uneconomic using conventional separation technologies. The CLS method, as an emerging and promising technology, is proposed for eco-efficiently and sustainably achieving the azeotrope separation based on the chemical-looping concept. The key of the CLS is that the addition of reactant causes a chemical reaction with azeotropic composition for breaking azeotropic behavior. In this work, the reactant screening principles of CLS for azeotropes separation are systematically summarized for providing some guidance to researchers. Successful case studies based on experiments reveal that the CLS method is feasible and has a huge potential for the separation or purification of azeotrope in the chemical industry. These studies can provide a new method for azeotropes separation based on chemical process intensification, resource utilization, and environmental protection.

Meanwhile, the CLS method can also be considered for purification of drugs, for example, the isomer separation. The CLS method could provide a new idea for the manufacture of high-end chemical products. The different separation methods have their scope of application. For the CLS, the low selectivity of the reaction is bound to increase the cost of the process because of the increasing of separation complexity. For large-scale processes of CLS, the challenge is how to ensure reaction selectivity, and it needs to be further studied by researchers. Therefore, no one method is universal, and the choice of green, economic, and sustainable separation methods is of paramount importance for specific azeotrope systems. Engineers should analyze specific problems, and select and evaluate the appropriate method according to the needs of systems separation target. The CLS method can make up for shortcomings of other separation methods in accordance with the separation characteristics of azeotrope to a certain extent.

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Compliance with ethics guidelines

Xin Gao and Xueli Geng declare that they have no conflict of interest or financial conflicts to disclose.

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