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Views & Comments

Chemical Looping Clean Energy Technology Toward a Low-Carbon Future

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1. Challenges and opportunities for carbon neutrality

Global carbon emissions, primarily from the use of fossil fuels, have dramatically risen since the industrial revolution, leading to an increase in global temperature and negatively impacting Earth's ecosystems. While the Covid-19 pandemic's economic downturn may have temporarily reduced emissions, the global average atmospheric carbon dioxide (CO_2) level still reached a new record high in 2021 [1]. In response to rising CO_2 levels, achieving carbon neutrality by 2050 is an imperative priority for the world [2]. There is, therefore, an urgent necessity to develop clean energy technologies that enable the use of fossil fuels to produce electricity, heat, or chemicals without generating CO_2 emissions. Chemical looping is an emerging technology for clean energy production with inherent CO_2 capture at a minimal energy penalty. It involves cycling metal oxide-based loop carriers between two reactors to provide lattice oxygen for fuel conversion. This article discusses recent advances in chemical looping, with a focus on its potential for using CO_2 as an alternative to fossil fuels to produce value-added chemicals. It is expected that these new advances will drive the further development of innovative looping carriers and accelerate the large-scale deployment of chemical looping technologies for a sustainable energy future (Fig. 1).

2. Innovations in chemical looping: a path to sustainable energy production

A typical chemical looping system is composed of a fuel reactor, in which the looping material is reduced by carbonaceous fuels,

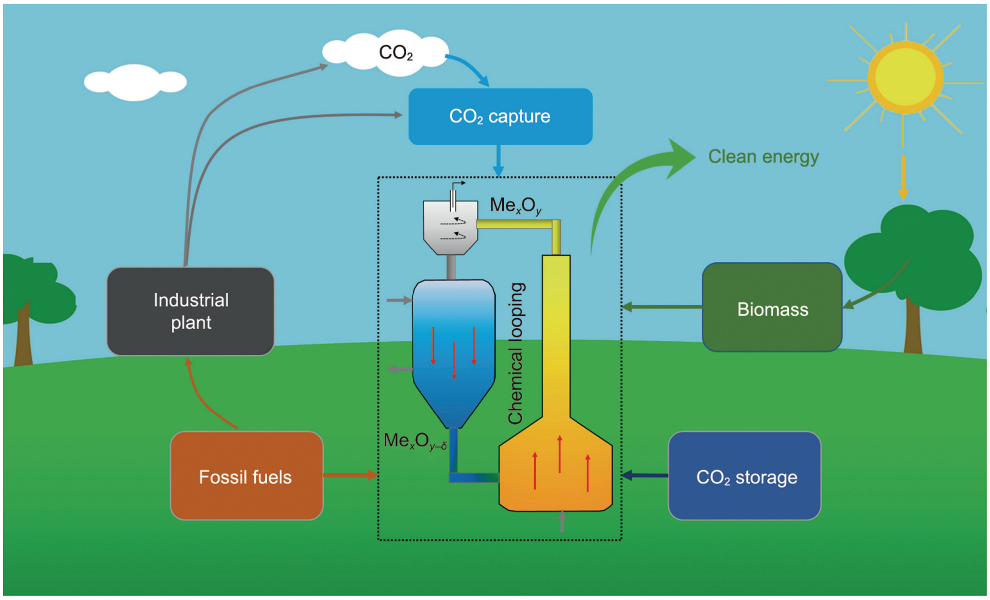

Fig. 1. Chemical looping systems utilize metal oxide-based looping carriers to convert fossil fuels and biomass into clean energy while consuming CO_2. Me_xO_y and $Me_xO_{y-\delta}$ are looping carriers in the oxidized and reduced form, respectively.

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and an oxidation reactor, where the reduced loop carriers are regenerated by the inflow of air. This redox system eliminates conventional energy-consuming air separation units and enables the inherent separation of the CO_2 flue gas generated in the fuel reactor from the air supplied for the regeneration of loop carriers [3]. In recent years, a series of advances have been made in the research of chemical looping that facilitate its integration into a low-carbon energy infrastructure [4,5]. These advances include processes for the complete combustion of fuels such as biomass and other solid wastes, either through chemical looping combustion (CLC) or oxygen carrier-aided combustion (OCAC). Moreover, the CLC of biomass, a carbon-neutral fuel, has the potential to be a carbon-negative source of energy, as a sequestrable-ready CO_2 stream is obtained as a product without the use of any acid gas removal unit. CLC can also be leveraged for energy storage, as the oxidation of carriers, which generates heat, can be delayed with the aid of renewable energy sources until there is a requirement for heat. Apart from combustion, chemical looping is being developed for alkane dehydrogenation, ammonia synthesis, H_2S decomposition, and so forth, due to its numerous advantages. However, the objective of this work is not to present a comprehensive review of chemical looping technologies with inherent CO_2 separation or capture; instead, we aim to present a new prospect of chemical looping for a low-carbon future.

2.1. Chemical looping for CO_2 utilization

By utilizing CO_2 as a feedstock, chemical looping processes have the potential to contribute to both CO_2 reduction and the production of valuable chemicals, aligning with the goal of achieving a sustainable future. Here, we focus on discussing two reforming chemical looping processes that have been demonstrated to be practical and energy-efficient for direct CO_2 utilization.

(1) **Chemical looping partial oxidation (CLPO) with dry reforming.** CLPO involves converting carbonaceous fuels such as methane, biogas, and biomass into syngas [6]. The metal oxide-based looping carriers applied in this process must be tailored to partially oxidize the fuels in order to ensure desirable hydrogen to carbon monoxide (H_2:CO) ratios. The CO_2 can then be used as a soft oxidant for the regeneration of the reduced looping carriers taking place in the oxidation reactor.

(2) **Chemical looping tri-reforming (CLTR).** CLTR can be performed by using CO_2 and water (H_2O) as a partial substitute for methane feedstock, fed with loop carriers in the fuel reactor [7,8]. Methane reforming with CO_2 and H_2O binary mixtures can overcome the limitations of carbon deposition in conventional technologies for the dry reforming of methane and achieve a H_2:CO ratio greater than 1. However, the design of the looping carrier in this process must factor in the extent of oxidation by H_2O and CO_2, as it directly controls the product yield.

2.2. Advances in looping carriers

A high carbon-utilization efficiency could be achieved in the aforementioned processes for the production of value-added chemicals if the CO_2 generated from the conversion of carbonaceous fuels and fresh CO_2 added to the system were to be fully recycled. However, this requires a significant amount of thermal energy input, since CO_2 is a chemically inert and thermodynamically stable molecule. To develop highly active looping carriers and energy-efficient chemical looping systems for CO_2 utilization, it is crucial to understand the underlying mechanism of cyclic redox reactions over looping carriers, which involves the adsorption, activation, and conversion of CO_2, as well as lattice oxygen diffusion in the bulk phase of the loop carriers. The diffusion-induced oxygen vacancy formation on the surface can significantly affect the electronic properties and thus the chemical activity of the looping carrier material. A looping carrier should allow for the proper transportation of lattice oxygen atoms to sustain a sufficient concentration of surface oxygen vacancies, which is critical for CO_2 adsorption and activation [9]. Furthermore, the looping carriers must have appropriate vacancy formation energies so that a suitable amount of lattice oxygen atoms can be released during redox reactions to produce syngas or value-added chemicals such as formic acid and methanol.

The vacancy population of looping carriers can be tuned by adding dopants, supports, or external electric fields to enhance the selective conversion of CO_2 into specific target products. Nanoscale looping carriers with mesoporous supports have also been synthesized to investigate the effects of size and geometry on the conversion of fuels and CO_2 during chemical looping processes [10]. Their high activity over a broad temperature range is attributed to their unique active sites, which significantly promote C–H and C–O cleavage, and their mesoporous supports, which can confine the phase segregation of looping carrier nanoparticles.

To date, it remains challenging to completely understand the relationship between the CO_2 reaction path and the structure of reaction surfaces. *In situ* and *operando* studies that can characterize the structure of local surface oxygen vacancies and reaction intermediates are thus highly desired [11]. In addition, machine learning is a fast-growing trend in fundamental research that has proved to have the attractive ability of reducing experimental trial work [12,13]. Applying this technique coupled with density functional theory calculations can facilitate the study of the redox mechanism and consequently accelerate the design of superior looping carriers that are capable of selectively and economically converting large quantities of CO_2 into a vast array of value-added chemicals.

2.3. Synergistic design of redox reactors and looping carriers

The success of any chemical looping system lies not only in the looping carrier but also in the reactor configuration. The reactor must be designed synergistically with the looping carrier because, even though the reaction kinetics solely depend on the looping carrier, the thermodynamic properties—and, by extension, the CO_2 utilization potential—are determined by the contacting pattern between the carbonaceous fuels and the looping carriers. Moreover, the reactor design must incorporate the intricacies of fluid dynamics, reactor internals, and operating conditions. The regeneration of looping carriers occurs in the oxidation reactor, which is generally designed as a fluidized bed and is coupled with a riser. However, designing the fuel reactor is complicated, as several thermodynamic and kinetics aspects that influence the conversion of fuels and CO_2 need to be accounted for. The fuel reactor is usually designed based on one of the following three modes:

(1) **Packed-bed fuel reactor.** Packed-bed reactors are easy to construct, operate, and scale up, and have relatively low operating and capital costs. Moreover, as there is no carrier movement, a low rate of particle attrition is observed, making this reactor more tolerant toward the mechanical strength of the carrier. However, these reactors have significant heat-transfer limitations, which can result in hotspot formation and the subsequent agglomeration of looping carriers. This can lead to a decrease in CO_2 conversion, diminishing the overall CO_2 utilization prospect. Moreover, packed-bed reactors usually have a high pressure drop and require complex gas-switching mechanisms and multiple reactors for continuous operation.

(2) **Fluidized-bed fuel reactor.** Fluidized-bed reactors in a circulating mode enable continuous operation and have good heat and mass characteristics. Thus, they have a low risk of solid agglomeration and hotspot generation. The designs of most chemical looping sub-pilot and pilot plants are based on circulating

fluidized beds [14]. However, due to the movement of the carriers, a high rate of attrition is observed. Furthermore, for certain oxygen carriers, thermodynamic limitations on gas conversion exist, due to the back-mixing tendency of the reactor. Thus, back mixing must be accounted for during looping carrier selection, as it can lead to low CO_2 conversion in a fluidized-bed reactor, despite exhibiting good CO_2 activity in other bed reactor tests.

(3) **Moving-bed fuel reactor.** Similar to fluidized beds, moving-bed reactor systems allow for continuous operation after being coupled with a fluidized-bed oxidation reactor and riser. They also permit greater control over the residence time of the fuel and looping carriers, and do not present thermodynamic limitations on gas conversions. However, a high rate of attrition is observed, and the moving solid flow restricts the amount of gas flow that can be processed, putting a limitation on the throughput. Moreover, temperature variations can exist across the reactor, possibly hampering the reaction kinetics. This can particularly affect the CO_2 conversion, necessitating detailed reactivity studies prior to designing the system. The moving carrier flow also demands complex solid-flow-control devices, making the operation challenging.

3. Commercialization prospects for chemical looping clean energy technology

Despite these challenges, chemical looping technology that can achieve net-negative CO_2 emissions is getting close to industrial deployment. Several sub-pilot and pilot-scale plant demonstrations of CLC, OCAC, and CLPO have showcased the viability of these technologies. Ongoing research endeavors are dedicated to further enhancing the performance of these plant systems, with a specific focus on developing durable oxygen carriers. Recent progress includes the successful development of aluminum (Al)-supported iron (Fe)-based looping carriers that can endure over 3000 redox cycles and lanthanum–strontium–iron–aluminum (La–Sr–Fe–Al)-based carriers sustaining approximately 4050 redox cycles [5]. These significant advancements further indicate the economic feasibility of chemical looping. We believe that economically viable looping carriers coupled with energy-efficient redox reactor systems and substantiated by pilot-scale operation will bring chemical looping technology to commercial readiness in the near future, for clean energy production and CO_2 utilization toward a low-carbon future.

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