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Review

Progress in oxygen carrier development of methane-based chemical-looping reforming: A review

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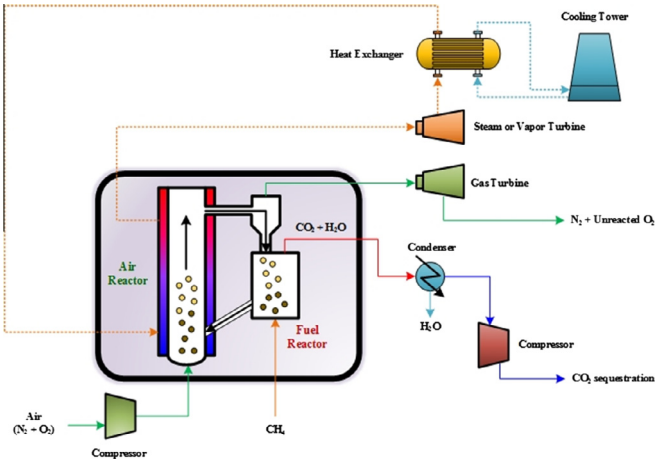
HIGHLIGHTS

- Partial oxidation of CH_4 (POM) possesses advantages over steam reforming of CH_4.
- Applying chemical-looping combustion concept can resolve the drawbacks of POM.
- The appropriate selection of oxygen carrier becomes a critical issue for POM.
- The use of steam or CO_2 to replace air remains to be a great challenge.
- Perovskites using lattice oxygen for syngas production showed prominent results.

GRAPHICAL ABSTRACT



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ABSTRACT

This work comprehensively reviews the recent advances for chemical-looping reforming of CH_4 (CLR) technology, which breaks down the traditional CH_4 reforming process (including steam and dry reforming) into two separate half-steps, namely CH_4 oxidation and replenishment of oxygen carrier (OC) with appropriate oxidizing agents. In order to steer the conversion of CH_4 toward partial oxidation (POM) for synthesis gas (H_2 + CO) production rather than total oxidation for producing CO_2 and H_2O, the appropriate selection of OC becomes a critical issue. Moreover, instead of the commonly used air to re-oxidize the oxygen-depleted OC after reaction with CH_4, steam and CO_2 have been proposed as two alternatives, opening up the opportunities to produce extra H_2 and CO. However, owing to much weaker oxidization ability of steam and CO_2 than air, the low oxidation degree and slow oxidation rate seem to remain as challenges. Furthermore, the resistance of OC to attrition, agglomeration and carbon deposition is also of great importance. In these regards, the latest major milestones are compiled.

Abbreviations: AR, air reactor; CFB, circulating fluidized bed; CLC, chemical-looping combustion; CL-DRM, chemical-looping dry reforming of methane; CLOU, chemical-looping oxygen uncoupling; CL-POM, chemical-looping partial oxidation of methane; CLR, chemical-looping reforming; CL-SRM, chemical-looping steam reforming of methane; COG, coke oven gas; CSR, carbon dioxide splitting reaction; DRM, dry reforming of methane; FR, fuel reactor; GTL, gas-to-liquid; OC, oxygen carrier; OSC, oxygen storage capacity; POM, partial oxidation of methane; SRM, steam reforming of methane; TGA, thermo-gravimetric analyzer; TPR, temperature-programmed reduction; WGS, water–gas shift; WSR, water splitting reaction; YSZ, yttrium-stabilized zirconia.

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Contents

1. Introduction

Sustainable energy supply has become a necessity for the advancement of modern society. Although both renewable energy and nuclear power may lead the growing energy sources globally, each increasing by 2.5% per year, almost 80% supply of world energy consumption through 2040 is projected to strongly depend on fossil fuels (coal, petroleum and natural gas) [1]. However, the combustion of fossil fuels is widely considered as a leading cause for CO_2 emissions, which is the main contributor to global warming effect [2–5]. Among current and emerging technologies for CO_2 capture, chemical-looping combustion (CLC) is a particularly promising approach [6,7]. The first step of CLC involves the reduction of metal oxide (also named as oxygen carrier, OC), MO, in contact with a fuel in one reactor (fuel reactor, FR). The reduced OC, M, is then transferred to the other reactor (air reactor, AR) for replenishment of oxygen with an oxidizing agent which is typically air. Subsequently, the regenerated OC is conveyed back to FR, terminating the chemical loop. After the condensation of steam from the effluent of FR, a high-pressure and high-purity stream of CO_2 can be obtained without further need of expensive gas separation unit. CLC thus offers a uniquely economical and efficient route for clean, NO_x-lean, flameless combustion of fossil or renewable fuels with the efficient production of sequestration-ready CO_2 streams [8].

OC reduction with fuel in FR:

$$(2m+n)\mathrm{MO} + \mathrm{C}_m\mathrm{H}_{2n} \rightarrow (2m+n)\mathrm{M} + m\mathrm{CO}_2 + n\mathrm{H}_2\mathrm{O} \quad (\mathrm{R1})$$

OC oxidization with air in AR:

$$\mathrm{M} + \frac{1}{2}\mathrm{O}_2\ (\mathrm{air}) \rightarrow \mathrm{MO} + \text{depleted air}\ (\mathrm{N}_2 + \text{unreacted}\ \mathrm{O}_2) \quad (\mathrm{R2})$$

Another advantage of CLC lies in its fuel flexibility. CLC can, in principle, work with any fuel as long as OC shows sufficient reactivity toward fuel. Up to date, CLC has been demonstrated with methane (CH_4) [9–15], synthesis gas (syngas, H_2 + CO) [16,17], biofuels [18,19] and even direct coal feeds [20,21].

In this review, we focus on the chemical-looping reforming (CLR) technology, which has been developed in the effort to convert CH_4 to syngas product. In industrial implementation, the syngas product can be further processed to enrich the yield of H_2 via the water–gas shift (WGS) reaction [22].

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CO}_2 + \mathrm{H}_2 \quad \Delta\mathrm{H}^{\circ}_{298\ \mathrm{K}} = -41.2\ \mathrm{kJ\ mol}^{-1} \quad (\mathrm{R3})$$

One of the most important issues in CLC process is the selection of an appropriate OC [22,23]. Typically, OC is composed of a primary metal oxide for active lattice oxygen storage and a ceramic support for enhanced redox stability and activity. Several critical screening criteria for OC have been addressed which include oxygen storage capacity (OSC), reactivity toward both fuel and oxidizing agents, resistance to attrition, agglomeration and carbon deposition, as well as the environmental and economic impacts.

2. Choice of reactor configuration

In general, the CLC concept can be accomplished in different types of reactor configurations, respectively (a) interconnected fluidized-bed reactors (named "move material"); (b) alternating fixed-bed reactors (named "move feed"); (c) rotating reactor (named "move reactor") [1,24]. The schematic representations of the three reactor configurations are shown in Fig. 1.

The most commonly visualized reactor configuration for CLC processes at the moment is composed of two interconnected fluidized-bed reactors, one of them being the FR and the other the AR. The OC particles are transported between the two reactors. In most cases this can be carried out in a circulating fluidized bed (CFB) setup having one riser reactor and one bubbling bed reactor, both of which are connected via the loop-seal devices avoiding the mixing of the feed gases. Although uniform temperature control can be achieved by adopting this configuration, potential fluidization and circulation challenges when using dense transition metal oxides have to be taken into consideration. Particularly, the particle separation is also difficult considering the required, extremely harsh reaction conditions (high pressure and elevated temperature) and the fact that even fines (resulting from inevitable particle attrition) need to be removed to protect the downstream gas turbine [25].

For the fixed-bed reactor configuration, solid OC particles are stationary and alternatively exposed to reducing and oxidizing conditions by periodically switching the feed gases. The main