



# Production of inherently separated syngas streams via chemical looping methane cracking



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## ABSTRACT

‘Chemical Looping Combustion’ (CLC) is an emerging clean combustion technology which offers an efficient route for fossil fuel combustion with inherent CO<sub>2</sub> capture. Beyond combustion, chemical looping is also applicable to selective oxidation of fuels to synthesis gas or olefins. In all these applications, the main advantage of chemical looping lies in the inherent air separation, which allows conversion of the fuel without nitrogen dilution. In the present work, we extend this inherent separation principle to separation of the product stream by demonstrating the formation of fully separated syngas streams from methane, i.e. the production of separate, high-purity CO and H<sub>2</sub> streams via (non-oxidative) methane cracking. CH<sub>4</sub> is first cracked catalytically over Ni, producing gaseous H<sub>2</sub> and solid carbon. The carrier is then periodically regenerated by burning off the carbon using CO<sub>2</sub> as oxidant, thus enabling the reduction of CO<sub>2</sub> to CO. Importantly, the Ni carrier is never oxidized during this cycle and hence acts as a “carbon carrier” rather than as an oxygen carrier as typical in chemical looping processes to-date. Autothermal process configurations are discussed, which allow reconciling the use of abundant natural gas reserves with the demand for clean, carbon-free energy production.

## 1. Introduction

The continuing growth in world population along with rapidly rising standard of living in the developing world results in an ever increasing demand for energy and bulk industrial chemicals such as ammonia (fertilizers) and methanol (plastics, textiles). In parallel, concerns over climate change require a transformation in the way that we produce both energy and chemicals in order to reduce the carbon footprint of both industries. While the switch to renewable resources will be a long-term solution, these technologies are still far from the maturity level required for large-scale industrial implementation. Hence, the primary feedstocks for these processes are fossil fuels, and this dependence on fossil fuels is expected to remain largely unchanged over the near future, bolstered further by the recent expansion of economically exploitable natural gas reserves. Consequently, the atmospheric levels of CO<sub>2</sub>, a major by-product of most energy and chemicals producing processes, have increased to historically unprecedented levels and are expected to rise further in the future. With the lack of proven CO<sub>2</sub> sequestration technologies, there is hence a strong motivation to develop chemical processes for CO<sub>2</sub> utilization.

Chemical looping combustion (CLC) is an emerging technology for efficient combustion with inherent CO<sub>2</sub> capture [1–6]. In CLC (Fig. 1a),

an oxide—typically an oxidized transition metal—is used as an oxygen source for fuel combustion in a “reducer” reactor, generating a stream of CO<sub>2</sub> and H<sub>2</sub>O, which can be easily separated via condensation to generate a sequestration-ready CO<sub>2</sub> stream. After combustion, the reduced metal is then regenerated with air in an “oxidizer” reactor and recycled back to the reducer, completing the materials “loop.” Thus, CLC bypasses most of the problems of conventional fuel combustion, including NO<sub>x</sub> formation and CO<sub>2</sub> separation from dilute gaseous streams, and is currently emerging as a favored solution for large-scale clean combustion applications.

More recently, the chemical looping scheme has been applied successfully beyond combustion toward CO<sub>2</sub> utilization and fuel upgrading to value-added chemicals [1,7,8,9]. In the absence of commercial technologies that can economically convert methane directly to chemicals, current methane utilization proceeds via an indirect route, i.e. it requires conversion to syngas (a mixture of CO & H<sub>2</sub>) or pure H<sub>2</sub> as a first step. We have demonstrated in recent years that pure H<sub>2</sub> streams can be produced by replacing air as oxidant with H<sub>2</sub>O, resulting in chemical looping steam reforming of methane (CLSR) [10], or with CO<sub>2</sub>, enabling CO<sub>2</sub> activation via reduction to CO (a useful and highly reactive chemical feedstock) [11,12]. Beyond tailoring operation of the oxidizer reactor, we have also shown that the fuel conversion in the

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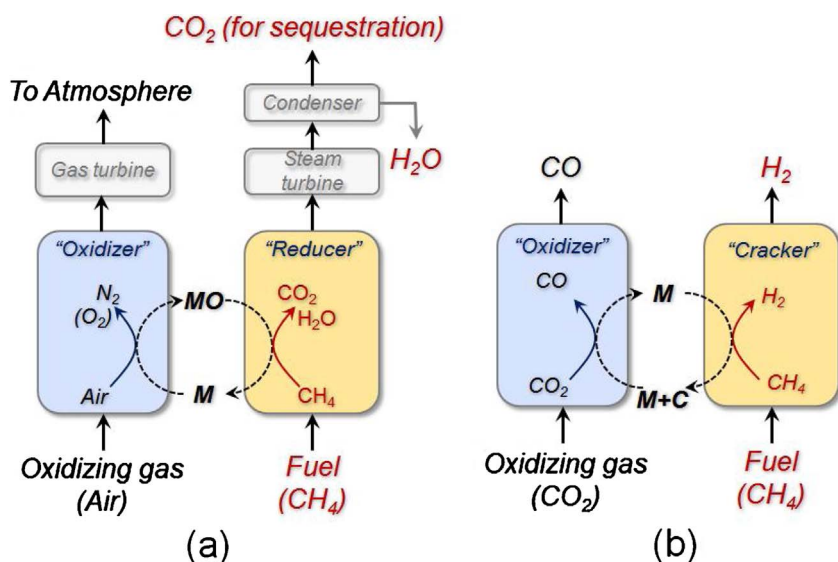


Fig. 1. Chemical looping processes: a) chemical looping combustion and, b) proposed process for inherently separated syngas streams.

“reducer” reactor can be engineered to produce syngas from methane, resulting in chemical looping partial oxidation of methane (CLPOM) [13,14] or chemical looping dry reforming (CLDR) [15], i.e. the chemical looping variants of the conventional methane partial oxidation and dry reforming processes. Several other research groups have since demonstrated further chemical looping configurations for syngas production [16–18] and for CO<sub>2</sub> activation [19–22]. Several recent reviews discuss both materials [23] and reactor aspects of such configurations [7,24,25] in more detail. While syngas produced in both CLDR and CLPOM has the typically desired syngas ratio of 2 (H<sub>2</sub>:CO ~ 2) for direct utilization in Fischer-Tropsch or methanol synthesis processes, it would be further advantageous to add flexibility to the downstream use of the produced syngas—such as high purity H<sub>2</sub> for fuel cells or ammonia production, where high purity H<sub>2</sub> is required, or pure CO streams for carbonylation reactions—by allowing flexible adjustment of this ratio.

Here, we propose a further modification of these methane converting chemical looping processes that will add this flexibility by producing fully separated H<sub>2</sub> and CO effluent streams (Fig. 1b). CH<sub>4</sub> can be converted to a pure hydrogen stream and solid carbon via thermocatalytic cracking over a metal catalyst in a “cracker” reactor. The deposited carbon is selectively oxidized in an oxidizer using CO<sub>2</sub>, thereby producing pure CO streams, and the regenerated metal is recycled back to the cracker reactor. The metal is thus periodically cycled between the two reactors carrying carbon between the two half steps, i.e. the “oxygen carrier” that characterizes chemical looping processes is turned into a “carbon carrier”.

Thermocatalytic cracking of methane for hydrogen production has been studied extensively over the past several decades, typically using transition metal based catalysts [26–30]. Due to the excellent C–H bond cleavage activity of Ni, supported Ni catalysts have widely been reported as the most favorable for this reaction. Typically, Ni dispersed on inert supports such as Al<sub>2</sub>O<sub>3</sub>, MgAl<sub>2</sub>O<sub>4</sub> and SiO<sub>2</sub> have been investigated [31–34]. During the process of methane cracking, extensive carbon filament formation and concomitant H<sub>2</sub> production occurs, which avoids rapid deactivation of the catalyst via coking and hence allows extended operation [35–39]. Eventually, however, the metal particles are encapsulated by carbon which results in deactivation. This deactivation is highly sensitive to the reaction temperature, with higher temperatures resulting in much faster deactivation. Hence, most cracking studies have focused on the temperature range between T = ~550–700 °C to ensure sustained carbon (and hydrogen) formation [33,40–45]. However, in this temperature range methane conversion is typically only ~50%, which is too low for economic implementation of this process (since it requires a large-scale downstream

separation processes). Non-transition metal based catalysts, such as carbon black, have also been studied as a cheaper alternative. However, reported CH<sub>4</sub> conversions (5–30%) are even lower than for metal catalysts [46–50].

Irrespective of temperature, all catalysts undergo eventual deactivation and require regeneration. Air regeneration (at ~600 °C) has most commonly been reported as an effective means to regenerate the catalysts [51–53]. In air regeneration, oxygen reacts with the deposited carbon to produce a mixture of carbon oxides (CO and CO<sub>2</sub>), depending of the amount of excess air used. This process again results in CO/CO<sub>2</sub> emissions since the products cannot be separated easily from the N<sub>2</sub> in the air. Hence, a few studies used CO<sub>2</sub> as an oxidant. Takenaka et al. studied methane cracking over various nickel catalysts at 550 °C and subsequent regeneration of the catalyst using CO<sub>2</sub> at elevated temperatures 650 °C [54]. They reported incomplete removal of carbon possibly due to the weak oxidation capability of CO<sub>2</sub>. Li and Smith also used CO<sub>2</sub> for regeneration of an alumina supported Ni catalyst, and reported extremely slow kinetics; at T ~ 500 °C oxidation with CO<sub>2</sub> was 20-times slower than with O<sub>2</sub>/air [55]. Pinilla et al. used CO<sub>2</sub> to regenerate an activated carbon catalyst at high temperatures, but reported simultaneous burn-off of the catalyst [56]. Recently, Liu et al. utilized H<sub>2</sub>O as for regeneration of activated carbon catalysts used for methane cracking [57]. However, beyond slow reaction kinetics, the activated carbon catalyst was consumed during the stream regeneration and a fresh make-up was required periodically. Most recent work by Antonio et al. furthermore reported the use of Al<sub>2</sub>O<sub>3</sub>-supported Ni-V-Li catalysts, using a mixture of CO<sub>2</sub> and O<sub>2</sub> as oxidants. However, their results were hampered by formation of Ni-aluminates, which resulted in lower catalytic activity and thus reduced methane conversion [58]. Overall, while there have been some reports for cyclic operation of methane cracking processes, all of the reported processes suffer from low CH<sub>4</sub> conversion during catalytic cracking and large periodic temperature excursions during carbon burn-off in the oxidation half cycle.

The use of “active” supports is well established in heterogeneous catalysis, where in particular CeO<sub>2</sub> is in widespread use as a support for metal nanoparticles in oxidation and redox catalysis [59], such as automotive exhaust abatement [60], water gas shift [61,62] and catalytic methane oxidation [63]. Moreover, the strong metal support interactions for CeO<sub>2</sub> are known to help maintain smaller particle sizes, which are critical for most catalytic reactions [64]. However, few studies to-date have used CeO<sub>2</sub> as a support for the thermocatalytic cracking of methane. Li et al. investigated Ni-CeO<sub>2</sub> systems prepared by various methods and reported that interactions between Ni and CeO<sub>2</sub> are critical for carbon formation [65]. Zapata et al. reported that addition of

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