Catalytic bi-reforming of methane: From greenhouse gases to Syngas

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1. Introduction

Methane is the main component of natural gas and biogas (80-90% of the total composition). The U.S. Energy Information Administration (EIA) shows that it is an affordable and abundant energy resource and projections show continued growth (Fig. 1a). Shale gas will continue to be the largest source of natural gas and its share of total U.S. natural gas production is expected to increase from 40% in 2012 to 53% in 2040. The overall production of natural gas in the U.S. has been estimated to increase by 56% from 2012 to 2040.

U.S. natural gas production by source in the Reference case, 1990-2040

Figure 1a. Past and projected U.S. natural gas production
(http://www.eia.gov/forecasts/aeo/mt_natural_gas.cfm)

Figure 1b. Projected global CO₂ emission by regions: Baseline scenario 2010-2050.

OECD A1 stands for the group of OECD countries that are also part of Annex I of the Kyoto Protocol.

GtCO₂e = Gigatonnes of CO₂ equivalent

Source: Organization for Economic Co-operation and Development (OECD) Environmental Outlook Baseline

CO₂ is another greenhouse gas and its emission continues to increase globally. A forecast by Organization for Economic Co-operation and Development (OECD) projects that without more ambitious policies than those in force today, the CO₂ emissions will increase by 50% by 2050 (Fig. 1b), primarily due to a projected 80% increase in global energy demand.

In view of the projected increases in CH₄ and CO₂, it is important to find ways to efficiently utilize these two greenhouse gases. In the sections below, options for the conversion of methane and CO₂ are described. Processes based on syngas, a mixture of CO and H₂, are of particular interest here because the conversion of methane via syngas dominates commercial practice.

CH₄ conversion

First, consider the processes in which methane can be converted to higher value products. Generally, the conversion of CH₄ to higher value products can be divided into indirect and direct routes (shown in Fig. 2).

Figure 2. Indirect and direct conversion routes of natural gas

Indirect routes: The indirect conversion of methane into higher value chemical intermediates and liquid fuels is based on reforming, a reaction in which methane reacts with various oxidants to produce syngas:

Regardless of the specific oxidant, the objective of methane reforming is to convert the syngas into desired final products. Steam reforming is the most widely practiced type of reforming:

Like all methane reforming process, this reaction is highly endothermic and temperatures typically above 800-900°C are required. In addition to syngas conversion to methanol, higher carbon-number oxygenates, Fischer-Tropsch products, and other higher value products [1-3], steam reforming is the first step in the production of hydrogen for ammonia and other hydrotreating processes.

Direct routes: Although the direct routes from methane to desired products avoid the formation of syngas, they generally suffer from impractically low net yields of desired products. The high C-H bond dissociation energy (104 kcal/mol) and low polarity of the first C-H bond make it virtually impossible to limit breaking the C-H bonds in methane to the first bond only—because the remaining C-H bonds are weaker than the first one. As a result, all commercial processes based on methane to higher value products are based on syngas [4].

The logical alternative to a syngas-based process would be one in which methane is directly converted to final products, for example, methanol:

Like other direct processes based on partial oxidation of methane to final products, these processes are inevitably accompanied by the undesired complete oxidation of methane to $\text{CO}_2 + \text{H}_2\text{O}$.

Another example of direct conversion of methane is the aromatization of methane to benzene [5]:

Despite interest in this process, formation of undesired solid carbon has limited the commercial application of this process. Like other direct routes for methane conversion to higher value products, further research is needed before they can be scaled-up [3].

CO₂ conversion

Large scale techniques to capture CO₂ from combustion and other processes have provided the incentive to develop methods to convert CO₂ into higher value products. Presently, only a small fraction of CO₂ potentially available for synthesis of higher value products is used for conversion.

Indirect routes: Commercial processes in which methane is reformed with CO₂ to syngas provide a significant opportunity for converting these two gases into higher value/higher carbon-number products. These indirect processes include dry reforming, oxy-CO₂ reforming, and bi-reforming:

Dry reforming is widely studied [6]. Despite significant research, dry reforming is associated with carbon deposition and, in some cases, thermal deactivation. Although carbon is thermodynamically limited at typical reforming temperatures, its formation is inevitable. Another concern is that the 1/1 H₂/CO syngas produced by dry reforming is not directly useful for chemical synthesis, which typically requires 2/1 H₂/CO syngas for most oxygenates, Fischer-Tropsch and other processes.

Oxy- CO₂ reforming has the appeal of autothermal operation, but safety concerns associated with the presence of oxygen has limited its use.

Compared to other CO₂-consuming reforming processes, far less literature has been reported on bi-reforming. However, recent studies have shown the potential for bi-reforming to produce higher value products, particularly methanol [7] and its derivatives.

Direct routes: These processes include the synthesis of urea and its derivatives, salicylic acid, and carbonates. In another process, CO₂ hydrogenation produces chemicals and fuels such as methanol, dimethyl ether (DME), and hydrocarbons. In recent years, the hydrogenation of CO₂ is being intensively studied because of its fundamental and practical applications in catalysis and surface science. For example, the direct conversion of CO₂ via hydrogenation is a straightforward way to produce methanol [8].

Some of the earliest methanol plants in the U.S. in 1920-1930s used this route [8]. A pilot plant built by Mitsui Chemicals, Japan is operational since 2010, which recycles the CO₂ via this route using improved catalysts.

2. Scope of this perspective

The scope of this perspective is to discuss and review bi-reforming of CH₄ to syngas. There are compelling commercial, environmental, and scientific reasons to study bi-reforming:

- (a) far less on bi-reforming has been reported than alternatives for the indirect conversion of CH₄ and CO₂, providing an opportunity for scientific and commercial investigation of bi-reforming
- (b) unlike dry reforming, bi-reforming produces a syngas that is both (i) flexible (by changing CO₂/H₂O ratio) and (ii) matching the 2/1 H₂/CO ratio required by virtually all higher value products, e.g., higher oxygenates and Fischer-Tropsch
- (c) the presence of steam provides a higher oxidant level in bi-reforming that addresses the inevitable and typically intolerable carbon deposition in dry reforming
- (d) a practical limitation of oxy-CO₂ reforming is the danger associated with mixtures of methane and oxygen, which has greatly limited its widespread use.
- (e) a significant proportion of raw natural gas contains CO₂. Reforming using dry or bi-reforming eliminates the need to separate CO₂ and methane, an expensive step.

The next sections will briefly compare bi-reforming with the two alternatives for conversion of CO₂ and CH₄, and discuss the carbon deposition, and the bi-reforming itself.

3. Processes for reforming of CH₄ and CO₂

There are three processes to reform CO₂ and CH₄ into syngas, all of which require temperatures above ~800 °C to reach thermodynamically complete conversions:

3.1 CH₄ Dry Reforming:

Dry reforming of methane is one of the simplest reactions and can be performed at temperature around 800-1000 °C over a variety of catalysts, for instance Ni/MgO [8] or, Rh-substituted pyrochlores [9].

However, the low H₂/CO ratio (1/1) from dry reforming requires the addition of H₂ for reactions such as Fischer-Tropsch or methanol synthesis. The most widely used catalysts for dry reforming are Ni-based catalysts, but they are often plagued with severe deactivation due to carbon deposition. Noble metal catalysts have been found to be more carbon deposition resistant, but their high cost limits their industrial use [6].

3.2 Oxy-CO₂ Reforming:

The oxy-CO₂ reforming of methane has been investigated [10, 11] and found to have improved energy efficiency of the process as compared to dry reforming:

The reaction is autothermal, a clear advantage, as does the fact that the presence of oxygen limits carbon deposition. However, concern of the potent safety of the process, and the less than optimum H₂/CO ratio of oxy-reforming (1.5/1) has greatly limited its industrial use.

3.3 Bi-Reforming:

The reforming of methane with a combination of CO₂ and steam is known as bi-reforming:

Like dry reforming, syngas from bi-reforming can convert CO₂ into higher value products. Also, like dry reforming, bi-reforming can be used to produce syngas from natural gas containing significant amounts of CO₂ and can also be used to react CO₂ separated from flue gases from fossil fuel combustion [7]. Unlike dry reforming, bi-reforming results in a H₂/CO ratio of 2/1, which can be directly coupled with the downstream industrial processes. Several reports also claim that one advantage of bi-reforming is that the H₂/CO ratio can be adjusted by changing the H₂O/(H₂O + CO₂) ratio to meet the downstream requirement [12, 13].

4. Mechanism of Carbon Formation

Carbon formation is inevitable in all methane reforming processes, particularly with the dry reforming of methane. The fundamental steps associated with carbon formation shows that bi-reforming, in particular, addresses this problem.

4.1 Background:

Methane decomposition, the Boudouard reaction, and CO reduction reaction contribute to carbon formation [14] during dry reforming of methane via

All these reactions are reversible, and may remove the $C_{(s)}$ through gasification [footnote (1)]. At temperatures above $\sim 700^\circ\text{C}$, the Boudouard reaction becomes less favored, while methane decomposes on the Ni surface to produce relatively more reactive carbon species (C_α , atomic carbon). Most of them are gasified, but some of them become polymerized and rearranged to less reactive C_β .

Footnote (1): The term $C_{(s)}$ is used herein to designate elemental carbon, as well as generic “coke”, which consists of a wide range of highly dehydrogenated carbonaceous deposits on the catalyst. The terms C_α and C_β refer to various forms of coke, based on their reactivity with oxygen, with C_α being more reactive than C_β , which is more graphitic.

These new particles may be gasified, encapsulate the catalyst surface or may dissolve in the catalyst crystallite [15]. In supported Ni, the electron microscopy investigations have revealed that dissolved carbon can diffuse through the Ni clusters and nucleate at the Ni-support interface, where they form carbon filaments (“whiskers”) that grow, lifting the Ni cluster from the support. Finally, this process results in fragmentation of the catalyst [15, 16]. The buildup of these whiskers plug the channel, and the resulting pressure drop due to the catalyst fragmentation leads to the need to replace the catalyst [15]. Generally, these whiskers are mechanically very strong and accelerate the mechanical deformation of the catalyst [17].

4.2 Thermodynamics:

The equilibrium composition of various species involved in bi-reforming as a function of temperature was calculated at atmospheric pressure by using HSC Chemistry 8 (Outotec, Finland). In Fig. 3, two thermodynamic calculations are shown:

- (a) The equilibrium compositions of CH_4 , CO_2 , CO , H_2 , and $C_{(s)}$ as a function of temperature, 1 atm in the presence of H_2O
- (b) The same calculation as above, but showing the effect of the absence of H_2O on $C_{(s)}$ (dotted line in Fig. 3). The equilibrium compositions of CH_4 , CO_2 , CO , and H_2 in the absence of H_2O is not shown.

Fig. 3 clearly shows the logical equilibrium compositions associated with the conversion of CH_4 , CO_2 , and H_2O to CO and H_2 at higher temperatures. Also as expected, temperatures above $\sim 850^\circ\text{C}$ are required to reach essentially complete equilibrium to CO and H_2 . Another consequence of this analysis is that there is significant thermodynamic driving force for the formation of $C_{(s)}$ at all temperatures below $\sim 800^\circ\text{C}$. Experimental results show that at even higher temperatures, kinetics appear to limit the carbon-removal reactions (reverse of those above), so that $C_{(s)}$ is significant at high temperatures.

Fig. 3 also compares directly two cases: (a) $C_{(s)}$ formed in the presence of steam, and (b) in the absence of steam (dotted curve). Thermodynamic results show that significantly much more $C_{(s)}$ is present in the absence of steam, as anticipated.

Finally, the equilibrium H_2O composition is greater than the initial amount (2 kmol), even at 100°C. This is the net result of the CH_4 decomposition, Boudouard reaction, and CO reduction (reactions 8, 9, and 10 respectively), resulting in more steam than the initial amount (2 kmol).

Figure 3. Equilibrium composition for bi-reforming reaction at different temperatures and atmospheric pressure calculated by HSC Chemistry. The initial amounts of reactants in kmol are $CH_4=3$, $CO_2=1$, $H_2O=2$. Allowed products are CO, H_2 , and $C_{(s)}$. The dotted curve shows $C_{(s)}$ formation under the same conditions, but in the absence of steam.

5. Bi-Reforming reaction and its significance

There are a number of advantages of the bi-reforming reaction over dry reforming and the following section discusses briefly these advantages, catalysts used for bi-reforming, their performance, and reaction mechanism.

5.1 Advantage of bi-reforming over other reactions utilizing both CH₄ and CO₂:

When compared with the dry reforming, one rationale for the use of bi-reforming is to minimize the formation of C_(s), due to the presence of steam (reaction of the reverse CO reduction reaction: $C_{(s)} + H_2O \rightleftharpoons CO + H_2$). A bi-reforming catalyst would be expected to be resistant to deactivation by carbon formation and the catalyst activity should be maintained over practical periods of time.

As discussed above, the carbon deposition is the major issue in converting the greenhouse gases, CO₂ and CH₄ to syngas. In order to reduce the carbon formation on the catalyst surface, adding water and/or O₂ to the feed oxidizes the carbon precursor species (partially CH_x surface species). Furthermore, the methane steam reforming reaction takes place in the presence of steam, resulting in 100% selectivity for both H₂ and CO (based on methane conversion), because the net formation of CO₂ or H₂O becomes zero while the H₂/CO ratio can be controlled [18, 19]. From an energy balance perspective, replacing part of the steam in the inlet with CO₂ reforming consumes the same overall amount of energy while utilizing carbon dioxide [17].

Bi-reforming with a specific ratio of CH₄/H₂O/CO₂ can in practice be easily adjusted to the desired stoichiometric ratio of 3/2/1 by adding steam or CO₂, because typically the sources of natural gas, biogas and coal bed methane are CH₄-rich. This produces the desired 2/1 H₂/CO syngas. Even other components in natural gas such as ethane and propane can also be bi-reformed in accordance to the overall conversion:

5.2 Catalysts used for bi-reforming:

The most widely used catalysts for bi-reforming are Ni-based [20]. Although cobalt-based catalysts have been reported to deactivate rapidly by coke formation and oxidation of the active sites by CO₂, promotion by noble metal has been found to be effective. Catalysts based on noble metals are generally more active and less sensitive to coke formation, but their high cost restricts their use for scale-up of the process. Pt-promoted cobalt catalysts [14] have shown high activity for bi-reforming. The role of Pt is proposed to stabilize the highly dispersed and reduced bimetallic nanoparticles.

The promotion of Ni-based catalysts by lanthanide group metals (La, Ce) has also been investigated. CeO₂ has been found to gasify the deposited coke on the catalyst surface by storing and delivering active oxygen [12, 21, 22].

In one of the few studies of bi-reforming, Olah et al. [7] used NiO deposited on MgO under 7 atm and 830 °C and the catalyst was found to be active and stable. They used a molar ratio 3/2.4/1.2 for CH₄/H₂O/CO₂ and observed stable activity for 320 h with a H₂/CO product ratio of 2/1. The selectivities for CO and H₂ were 100% and 98% respectively and conversions of both CH₄ and CO₂ were in the range

of 70-75%. The undesired formation of carbon was prevented by the presence of steam. As an endothermic reaction, the positive effect of increasing temperature from 830 to 910 °C was that the conversion increased 15%, although the H₂/CO ratio changed little (1.99 to 1.97). An increase of pressure from 7 atm to 28 atm reduced the conversion from 71% to 52%, consistent with thermodynamics, while the H₂/CO ratio increases slightly from 1.99 to 2.02. Moreover, doubling the steam and CO₂ amount at 7 atm enhanced the CH₄ conversion from 71% to 85%.

One of the industrially significant results by Olah et al. [7] was that they were able to adjust the H₂/CO ratio in the product gases by changing the CO₂/H₂O ratio in the feed gas stream. Similar results have been reported by Choudhary's group [10, 11, 18, 23], where they studied the effect of reactant composition on the H₂/CO ratio for the oxy-CO₂ methane reforming process. For bi-reforming reactions carried out by the same group [19, 24], the product H₂/CO ratio was varied from 1.5 to 2.5 by manipulating the relative concentrations of steam and CO₂ in the feed.

5.3 Bi-reforming reaction mechanism:

A reaction mechanism for bi-reforming over MgO-supported catalysts has been proposed by Qin et al. [25]. An in-situ labelled ¹³CO₂ transient experiment showed that carbon formed from CO₂ or CO decomposition was less active than adsorbed CH_x species formed from CH₄ decomposition. Based on the TPR spectra and isotopic transient techniques, they propose that both steam and dry reforming reactions start at the same time. These reactions also share the same intermediate, O_{ad}, which can be produced by both steam and CO₂ dissociation. Moreover, as steam reforming and bi-reforming have the same reaction mechanisms, their reaction kinetics are probably the same. This adsorbed atomic oxygen (O_{ad}) reacts with adsorbed carbon species (CH_x)_{ad} (x=0, 1, 2, and 3) produced by activated CH₄. Therefore, the intermediate is consumed to form CO and decreases the amount of CO₂ and steam. The total bi-reforming process can be explained as follows (M is the active metal site of the catalyst, which is the same for various adsorbing species in the formulas):

Activation of CH₄:

Decomposition of H₂O and CO₂:

Reaction of adsorbed species:

Production of CO and H₂:

The main reaction is that of the adsorbed species, which is the rate determining step, and is proposed to be a Langmuir-Hinshelwood mechanism [25].

6. Outlook

The bi-reforming reaction to produce syngas from CH₄ and CO₂ offers significant advantages over dry reforming and oxy-CO₂ reforming with respect to catalyst deactivation by carbon deposition. This approach has the potential to be a new alternative and is entering the stage of increasing research towards commercialization of the technology. Research is ongoing to develop catalysts that are resistant to high temperatures and the presence of the oxidative environment due to steam. All current research

on bi-reforming catalysis is focused on Ni-based catalysts, which is a logical extension based on commercial materials for steam/methane reforming and dry reforming. However, recent work on thermally stable crystalline oxides have promise, particularly in resisting carbon deposition while remaining stable at the demanding conditions of bi-reforming.

In conclusion, the bi-reforming process has the potential for industrial applications as it can produce the desired H_2/CO ratio by changing the H_2O/CO_2 ratio in the feed stream. The syngas can be produced with near complete selectivity towards CO and H_2 and very high activity. However, bi-reforming is a more oxygen-rich system as compared to dry reforming and the catalyst is vulnerable to oxidation. This could result in the deactivation of the catalyst with time on stream due to the loss of active sites. Therefore, the feed ratio is important and this could be a limiting condition for achieving a higher H_2/CO ratio from the bi-reforming reaction. This also suggests the need for research on catalysts that are stable at the oxidizing conditions of bi-reforming, particularly more practical catalysts based on nickel.

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8. References and recommended reading

Papers of particular interest have been highlighted as:

- Of special interest
- Of outstanding interest

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. Choudhary et al. reported the bi-reforming over Ni-based catalyst in the presence and absence of O₂

. Qin et al. compared various reforming reactions and proposed corresponding mechanisms

Graphical Abstract